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DISTRIBUTION AND FATE OF BIOGENIC AND PETROLEUM-DERIVED SUBSTANCES IN MARINE SEDIMENTS

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DISTRIBUTION AND FATE OF BIOGENIC AND PETROLEUM-DERIVED SUBSTANCES IN MARINE SEDIMENTS

from

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11. INTRODUCTION

by

I.R. Kaplan

As part of the overall interest in the outer continental shelf, DOE and BLM funded a joint project at UCLA to investigate the distribution and stability of pollutants on the California Borderland. Among the aims to accomplish in this program were the following:

1. To collect and compare samples from unpolluted areas (such as Walvis Bay, S.W. Africa or Guaymas Basin, Gulf of California) with those from marine areas adjacent to high population densities, such as Santa Monica Basin or San Pedro Basin.

2. To compare the distribution pattern of hydrocarbons in continental shelf sediment with those on the continental slope and rise, or even further seaward. Here it was hoped to determine the mechanism by which hydrocarbons may be transported from the OCS to deep water.

3. To search for means to characterize and relate hydrocarbons and other organic markers to their source of origin.

4. To assess the budget of organic matter entering the OCS from both natural and anthropogenic sources.

5. To investigate the relationship of hydrocarbon transfer and isotopic content in different members of the food web.

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In order to satisfy the above goals, several research projects were investigated over the past four years. During the 1980-1981 interval, the following tasks were specifically attempted:

1. Nature and distribution of polynuclear aromatic hydrocarbons PAH) in marine sediments.

2. Quantification of mass of dissolved and particulate organic matter' washed into the ocean during storm runoff from the Los Angeles Basin.

3. Character of the lipid material washed into the ocean from storm runoff from the Los Angeles Basin.

4. Evaluation of the distribution and transport mechanisms for trace elements in the Southern California OCS.

5. The use of stable isotopes to trace food sources in various trophic levels of the Southern California OCS food web.

6. Differentiating carbon sources in the biota associated with submarine fumarolic vents from the East Pacific Rise.

During the past four years, the focus was on understanding the carbon budget in the ocean and the control processes. The immediate aim was to obtain information on environmental problems relating to pollution of the coastal zone. The long range aim was to understand the fluxes of carbon, nitrogen and sulfur compounds between ocean, continents and atmosphere. Some highlights of the research endeavors are summarized below:

By use of GC-mass spectroscopy, the nature of the saturated and aromatic fractions of sediment has been characterized in detail. It has been shown that in unpolluted areas, straight-chain paraffins predominate. Where the input is primarily from plankton, the lower molecular weight saturated and unsaturated hydrocarbons around C_{24}-C_{33} dominate and appear to be related to the lipid content of the algae. Closer to shore, an odd-even relationship develops among the saturated straight-chain alkanes in the C_{27}-C_{33} range. These compounds appear to originate from plant waxes. In polluted sediments, most of the resolvable straight-chain hydrocarbons have disappeared, leaving behind complex cyclic, aromatic and heteroatomic compounds, displaying themselves as a large unresolvable "hump" in the chromatograms.

These humps are not always good indicators of petroleum contamination, as it appears from studies of sediment in the Bering Sea and other clean environments, that biological decay processes of organic-rich sediment might also result in such a qualitative appearance.

Therefore, to assure an accurate interpretation, it is necessary to determine the presence or absence of specific compounds. This has been accomplished in OCS sediments from Southern California by showing that a series of extended triterpanes-hopanes, contain a racemic mixture of different structural entities. This same mixture of hopanes is present in California oils and presumably the source rocks or shales. In unpolluted areas (eg., Walvis Bay), only one isomer of the particular hopane was detected. It therefore signifies that the Southern California OCS sediments have had petroleum-derived hydrocarbons added to them, historically.

By contrast, these hopane hydrocarbons are also present in the continental rise sediments, but only as minor components. Small amounts of aromatic hydrocarbons have also been detected in the deep-sea sediments. These appear to be largely unsubstituted polycyclic aromatic hydrocarbons and their most probable source is from the atmosphere. The major hydrocarbon soruce in the continental rise and marginal deep sea sediments is biogenic, but both higher plant hydrocarbons, as well as planktonic hydrocarbons have been detected. Conspicuously absent, or present in trace amounts only, is DDE and PCB, derived from insecticides.

These compounds have been detected in almost all the surface sediments on the continental shelf and in several cores from basins and were found to be present in traces at depths of up to 30 cm. It is not clear whether their widespread presence in OCS surface sediment indicates introduction from isolated sources, i.e., sewage outfalls, or from a greater variety of sources, such as storm runoff.

To test this, studies have been initiated to capture storm runoff water and sediment in Los Angeles and to characterize the organic matter being washed into the sea. One very specific marker of domestic sewage, is a mammalian degradation product of cholesterol, known as coprostanol. This has been successfully characterized in sewage by GC-mass spectroscopy and is being traced in marine sediments. In addition to organic markers, several trace metals have been successfully used to determine the history of sedimentation of effluent debris adjacent to the Whites Point sewage outfall plant on the San Pedro Shelf.

In a study conducted at the beginning of the winter storms in November, 1978, an estimate was made of the total lipid material washed out of the Los

Angeles Basin. It was estimated that the total annual transport of hydrocarbons from land to ocean by such storm runoff from Southern California is 9.7×10^3 metric tons. By contrast, the mass of hydrocarbons released via municipal and industrial treatment plants (sewage system) is 1.7×10^4 metric tons.

An effort has been made to evaluate all the trace metal studies which have been performed in the Southern California OCS. It was concluded that few of the metals settle near the outfalls. Most are rapidly transported in association with fine particulate to the outer basins. There is a great need for reliable studies to be performed on the solution mechanism of trace metals. At the present time, the importance of solution transport is poorly understood. Many problems in interpretation arise because of the lack of uniformity in methodology. The general conclusion reached in this evaluation, is that petroleum exploration and production probably have little influence on the contribution of trace elements to the ocean in comparison with that which enters from the local sewage systems.

Because weathered hydrocarbons frequently cannot be easily described and traced to a source, we have developed in our laboratory, methods based on the distribution of sulfur and nitrogen and the isotopic ratio of carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$) and particularly sulfur ($^{34}S/^{32}S$). The distribution characteristics of these parameters have proven particularly useful as diagnostic markers for describing tar.

An attempt has been made to understand the transfer of metabolites in a food web and to evaluate how organisms alter the lipid fraction of sediments when they ingest them. In the first case, organisms from various environments have been analyzed for their ^{13}C, ^{15}N and D/H ratios. It appears that the isotopic content of an organism is in part due to its geographic location and in part a function of its place in the food web.

A most interesting opportunity was afforded to test the conclusions reached in studies off California by measuring animal tissues from the Galapagos and 21°N hydrothermal vents. Bivalves (clams) showed an unusual enrichment in ^{12}C, indicating that they were not primarily feeding on detrital plankton remains. Most probably their food source appears to be chemoautotrophic bacteria. By contrast, the tissue of a vestimentiferan worm, had an unusually high enrichment of ^{13}C. The explanation for this is not yet known, but it may be caused by a metabolic pathway related to autotrophic carbon fixation. More recently, it has been shown by G. Rau (1981) that these worms isolated from normal reducing marine environments are capable of enrichments of ^{12}C larger than ever observed in metazoans. Again, this either points to a direct symbiosis between the vestimentiferan worms and bacteria or the capability of the worms to synthesize carbon autotrophically.

From some initial studies with holothurians, it appears that during injestion of sedimentary organic matter, fatty acids and hydrocarbons undergo some changes. In particular, it appears that preferential degradation of C_{22} and C_{24} fatty acids occurs. Straight-chain paraffins are used, leaving the feces relatively enriched in branched and cyclic hydrocarbons. There is some preliminary evidence that triterpenes may be synthesized by the gut microflora.

The studies conducted at UCLA under support of this contract and previously ERDA and AEC, have allowed for a systematic understanding to be developed on the chemistry of carbon compounds in the coastal environment off Southern California. We believe we have obtained among the best estimates available for the rate and quantity of introduced organic matter for world oceans. The studies have further characterized in detail many of the organic substances present in sediments. Rates of breakdown have been investigated and sources characterized by molecular or isotopic methods. In addition, the present state of knowledge of trace element distributions on the shelf has also been evaluated.

III. MANUSCRIPTS SUBMITTED OR ACCEPTED FOR PUBLICATION DURING REPORTING PERIOD

1. Organic geochemistry of sediments from the Southern California borderland. DSDP/IPOD - Leg 63. B.R.T. Simoneit and M.A. Mazurek, In: *Initial Reports of the DSDP, Vol. 63* (in press).

2. Utility of molecular markers and stable isotope composition in the evaluation of sources and diagenesis of organic matter in the geosphere. B.R.T. Simoniet, Alfred Treibs Symposium, (A. Prashnowsky, Ed.), in press.

3. The composition, sources and transport of organic matter to marine sediments--The organic geochemical approach, B.R.T. Simoneit, *Proceedings Symposium: Marine Chemistry Into the Eighties*, (J.A.J. Thoompson, Ed.), National Research Board of Canada (in press).

4. Organic geochemistry of lipids in kerogen and effects of basalt intrusions on unconsolidated oceanic sediments in sites 477, 478 and 481 in Guaymas Basin, Gulf of California, B.R.T. Simoneit and R.P. Philp, In: *Initial Reports of the Deep Sea Drilling Project, Vol. 64* (in press).

5. Extractable organic matter in municipal wastewaters: 1. Petroleum hydrocarbons-temporal varations and mass emission rates to the ocean. R.P. Eganhouse and I.R. Kaplan (Submitted to *Environmental Science and Technology*).

6. Heavy metals behavior in coastal sediments of Southern California: A critical review and synthesis, A. Katz and I.R. Kaplan, (in press: *Marine Chemistry 10*; 261 -299).

7. Thermal alteration of Cretaceus black shale by diabase intrusions in the Eastern Atlantic--II. Effects on bitumen and kerogen, B.R.T. Simoniet, S. Brenner, K.E. Peters and I.R. Kaplan (in press, *Geochimica et Cosmochimica Acts*).

8. Differences in animal ^{13}C, ^{15}N and D natural abundance between a polluted and an unpolluted coastal site: Indicators of sewage incorporation into a marine food web, G.H. Rau, R.E. Sweeney, I.R. Kaplan, D. Young and A. Mearns, (in press *Estuarine and Coastal Shelf Science*).

9. Plankton $^{13}C/^{12}C$ changes with latitude: Differences between northern and southern oceans. G.Ii. Rau, R.E. Sweeney and I.R. Kaplan (in review: *Deep-Sea Research*).

10. Determination of petroleum contamination in marine sediments by organic geochemical and stable sulfur isotope analyses, M.I. Venkatesan, P. Mankiewicz, W.K. Ho, R.E. Sweeney and I.R. Kaplan, (in press: *The Environment of the Deep Sea, Vol. No. 2*, Prentice-Hall, Inc.).

Organic Geochemistry of Sediments from the Southern California Borderland, DSDP/IPOD Leg 63[1]

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ABSTRACT

Selected core samples from the California continental borderland (Sites 467-469) were analyzed to evaluate the nature and composition of the lipids and kerogens in terms of their genetic origin and geological maturity.

The lipids were of a multiple origin. They were derived from primary autochthonous marine (microbial), from allochthonous terrigenous (higher plant wax) and recycled (geologically mature organic matter) sources. This is based on the homolog distributions of the _n_-alkanes and _n_-fatty acids, with the shape and magnitude of the unresolved branched and cyclic hydrocarbons, and the structural and stereochemical compositions of the molecular markers.

The kerogens were comprised of principally marine microbial detritus with a minor input of allochthonous terrestrial material. For the most part, the samples had experienced a thermal maturation according to a normal geothermal gradient, except in the proximity of intrusive. Such additional thermal stress was evident. for the samples from Site 469 and to some extent for Site 467 at about 700-800 m subbottom.

INTRODUCTION

The California continental borderland is an area of great geological complexity and the clues to its Neogene history are to be found in the deep-sea sediments of this area. Recent, near surface sediments from the California Bight and borderland contain organic matter derived from autochthonous production and from allochthonous sources such as natural petroleum seepage and influx of terrestrial detritus (Simoneit and Kaplan, 1980; Venkatesan et al., 1980). Thus, it was of interest to follow these trends versus depth in the sedimentary record. Sites 467-469 (Fig. 1) drilled in the California continental borderland, contain relatively thick sequences of nannofossil chalk, silty and dolomitic claystones, tuff, porcellanite and thin sequences of clay and ooze with glauconite and vitric ash (Haq et al., 1979).

The outer Southern California Borderland may be another natural example of distinct regimes of thermal stress upon organic material (kerogen) within a. localized marine setting, analogous to the case o-F the observed thermal alteration of Cretaceus black shale by basaltic intrusions in the Eastern Atlantic (Simoneit et al., 1978).

Sites 468 and 469 are located on the Patton Ridge along the western edge of the borderland arid are within fifteen kilometers of the inferred paleotrench of Southern California (Table 1). Site 467 is situated at the base of the continental slope at the San Miguel Gap and is on the Pacific Plate, just west of the postulated paleotrench (Haq et al., 1979, Table 1). All three sites have high heat flow values and the respective core lithologies show varying degrees of volcanic influence. Sites 467 and 468 contain locally-derived, Middle Miocene (10-15 Ma) andesitic and dacitic tuffs and breccias, presumably formed after cessation of plate subduction (Haq *et al.*, 1979). Hole 469 overlies a pillow basalt and contains zones of pumiceous tuff and diabasic lithologies (Haq *et al.*, 1979).

Thus, we further characterized the organic matter (i.e., lipids and kerogen) by its chemical, elemental and stable isotope (C and H) compositions to evaluate the effects of differential heating or anomalous maturation as a result of high heat flow or of localized volcanic emanations.

EXPERIMENTAL METHODS

Lipids:

Lipids were removed from subsamples of the freeze-dried sediments by multiple mechanical extractions using shaker table agitation with an extraction medium of 150 ml chloroform and methanol in a 1:1 ratio. The extracts were concentrated on a rotary evaporator and treated with BF_3 in methanol to esterify free fatty acids. The extract was then subjected to thin-layer' chromatography (TLC) using hexane and diethyl ether (9:1) as eluent. The bands corresponding to hydrocarbons, esters and ketones were scraped off the TLC plate after development with iodine vapor, and eluted with methylene chloride. The hydrocarbon and combined ester and ketone fractions were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS).

The GC analyses were carried out on a Hewlett-Packard Model 5830 gas chromatograph using a 25m x 0.20 mm fused silica capillary column coated with SP-2100, programmed from 35-280°C at 4°C per minute and using lie carrier gas.

The GC/MS analyses were carried out on a Finnigan Model 4000 quadruple mass spectrometer interfaced directly to a Finnigan Model 9610 gas chromatography equipped with a 30m x 0.25 mm fused silica capillary column coated with SE-54. The GC conditions for the GC/MS analyses were as those for the analytical GC system. The mass spectrometric data was acquired and processed using a Finnigan-

Incos Model 2300 data system.

Kerogen:

The extracted residue was acidified at room temperature with 25 ml of 2N HCl (organically purified) to dissolve carbonates and labile sulfur compounds. All samples showed considerable effervescence and therefore, two additional 2N HCl treatments were necessary for a. period of two days to ensure complete removal. Samples were then washed repeatedly (10X) with 200 ml additions of double-distilled water to remove extraneous ions. Silver nitrate solution was used to test for the presence of chloride ion.

Silicate dissolution was carried out by the addition of 200 ml concentrated hydrofluoric acid (60%). This step was repeated twice in order to exhaustively saturate with HF and thus, completely decompose all silicate minerals. The nonsilicate residues were washed (7X) with 150 ml of doubly-distilled water.

Residual humates were removed by the addition of 150 ml of organically purified 0.2N NaOH. Only samples 1-3 and 7 showed observable humates and they were extracted another three times with 0.2N NaOH. After base extraction, all remaining kerogen samples were washed by (6X) 200 ml additions of doubly-distilled water and then freeze dried. Aliquots (6-10 mg) of the isolated kerogens were placed in preweighed, organically cleaned and annealed porcelain boats for ash determinations. They were inserted into a muffle furnace and very slowly brought up to 1000°C (time interval 5 hours); they were then held isothermally for three hours. Ash contents were determined by a final weighing and after the samples had completely cooled.

Combustion for the stable isotope analyses were carried out as follows. Kerogen aliquots (6-11 mg) were placed into annealed quartz tubes containing organically cleaned silver envelopes and fired CuO wire. Silver combines with pyrolyzed sulfides and CuO provides. the oxygen source during combustion in the -

evacuated and sealed quartz reaction vessels. Reaction mixtures were combusted at 880°C for two hours. Replicate samples were prepared in order to provide a duplicate in the event of tube explosion during the combustion.

The quartz reaction vessels containing CO_2, N_2 and H_2O combustion products were opened under "vacuum. The three gases were then separated in a CHN vacuum line by sequential freezing followed by revolatilization. Cold traps in thermal equilibrium with liquid nitrogen (-196°C), dry ice with acetone (-73°C) and lastly, with hot water (70°C), were used to retain the desired gaseous product in a condensed state. As CO_2 and H_2O were frozen within the liquid nitrogen cold trap, the sample N_2 gas was isolated by passing it through a Toepler pump and into a calibrated volume manometer where the pressure of the N_2 gas was measured (and later converted to µmol). It was then transferred to a pyrex tube, in which it was sealed for subsequent mass spectrometric analysis. Gaseous CO_2 was similarly isolated, measured and stored after the cold trap temperature was raised to -73°C. The remaining H_2O gas was warmed to ∿ 70°C and then reduced to H_2 gas by passing it through a uranium furnace maintained at 780°C and under vacuum. The Hz gas was. then measured volumetrically and sealed into a pyrex tube.

Stable isotope mass spectrometry of the isolated C02, N_2 and H_2 gases Was performed on a Varian MAT Model 250 triple-collecting mass spectrometer. Correction factors established by Craig (1957) were applied to the directly measured CO_2 mass numbers. The CO_2 gas was measured relative to the Pee Dee Belemnite (PDB) standard, the H_2 gas was compared to Standard Mean Ocean Water (SMOW), and the N_2 gas was referenced to atmospheric. nitrogen. Isotopic deviation from the relative values established by these reference compounds was expressed in the conventional "δ" notation in parts-per-roil, where:

$$\delta\ (‰) = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] \times 1000$$

and

$R = {}^{13}C/{}^{12}C$ for carbon,

$R = D/H$ for hydrogen, and

$R = {}^{15}N/{}^{14}N$ for nitrogen.

RESULTS AND DISCUSSION

Lipids:

The lipid yields were high and the concentrations of the hydrocarbons were generally in excess of the fatty acids (Table 1). Ketones were present as minor components only, with 6,10,14-trimethylpentadecan-2-one as the major analog.

The distribution diagrams for the n-alkanes and n-fatty acids of the samples from Site 467 are found in Fig. 2. The n-alkanes of the samples back to the early Pliocene exhibit an essentially trimodal distribution, with maxima at C_{17}, C_{23} and C_{29}, no carbon number predominance < C_{26}, a strong odd carbon number predominance > C_{26} and a range from C_{10}-C_{33} (Fig. 2a-d). The sources of the homologs < C_{26} are from primarily degraded microbial detritus of an autochthonous origin and the homologs > C_{26} are derived from allochthonous terrigenous plant waxes (Simoneit, 1978; 1979a). The n-alkanes of the lithic tuff (467-85-4, Fig. 2e) exhibit a bimodal distribution, ranging from C_{11}-C_{31}, with no carbon number predominance and maxima at C_{17} and C_{23}. This distribution is indicative of a partially degraded lipid residue from microorganisms (Simoneit 1978; 1979a). The bottom sample in the diatom-nanno ooze (Fig. 2f) exhibits n-alkanes derived from microbial residues (< C_{26}) and higher plant waxes (> C_{26}) The pristane-to-phytane ratios of the upper samples (Fig. 2a-d) are approximately 1.0 (cf., Table 1), indicating incomplete euxinic conditions (Didyk et al., 1978) where the rate of influx of organic detritus did not fully deplete the oxygen in the sedimentary environment. However, this interpretation must be considered with caution since a significant portion of the lipids is interpreted to be not syngenetic but was derived from geologically older material. Thus, the Pr/Ph may not reflect the true sedimentary conditions. The Pr/Ph of the two lowest samples (Fig. 2e,f) are about 2.0, indicating oxic sedimentary conditions (Didyk et al., 1978). The dominance of pristane in these two samples may indicate the major contribution of diatoms to the lipids. Perylene, another indicator of anoxic conditions of sedimentation (Simoneit, 1979b; Didyk et al., 1978), was detected as a major lipid component in samples 467-8-5, 18-5, 41-4, 85-4and 110-3 (Table 2).

The n-fatty acids of the upper samples (Fig. 2g-j) exhibit bimodal distributions, with a strong even-to-odd carbon number predominance, ranges from C_{10}-C_{32} and maxima at C_{16} and C_{26} or C_{28}. The homologs < C_{22} are primarily of an autochthonous microbial origin (Simoneit, 1975) and the homologs > C_{22} when considered in conjunction with the respective n-alkane distributions. , are further markers of allochthonous higher plant lipids (Simoneit, 1975; : The n-fatty acids of sample 467-85-4 (Fig. 2K) exhibit an essentially unimodal distribution, with strong even-to-odd carbon number predominance, range from C_{10}-C_{24} and the major maximum at C_{16}. This distribution is typical of microbial residues (Simoneit 1975; 1978). The n-fatty acids of sample 467-110-T (Fig. 2l) exhibit a bimodal distribution, with a even-to-odd carbon number predominance, range from C_{10}-C_{32} and maxima at C_{16} and C_{24}. This distribution is of a mixed origin from microbial residues and to a lesser extent from terrestrial higher plant wax (Simoneit, 1975; 1978). A minor amount of dehydroabietic acid was detected in some of the samples (Fig. 2), indicating some allochthonous influx of resinous plant detritus (Simoneit, 1977).

The distribution diagrams for the n-alkanes and n-fatty acids of the samples from Sites 468 and 469 are found in Fig. 3. The n-alkanes of sample 468-2-3, 100-120 cm exhibit a polymodal distribution, with maxima at C_{12}, C_{17}, C_{23} and C_{29}, range from C_{10}-C_{33} and a strong odd carbon number Predominance above C_{26} (Fig. 3a). The homologs < C_{26} are of a primarily autochthonous microbial origin and those > C_{26} are derived from allochthonous vascular plant waxes (Simoneit, 1978; 1979a)". In the case of sample 468-18-3, 100-119 cm the" distribution is bimodal, ranging from C_{11}-C_{31}, with maxima at C_{17} and C_{23} and essentially no carbon number predominance (Fig. 3b). This distribution is indicative of a partially degraded microbial lipid residue. and it is the same as for sample 467-85-4, 105-116 cm in the lithic tuff section.

The n-alkanes of sample 469-2-2, 150 cm reflect a primarily allochthonous terrigenous origin from plant waxes by the dominance of the odd carbon number homologs > C_{26} and maximum at C_{29} (Fig. 3c). The minor maximum at C_{23} and homologs from C_{10}-C_{26} are derived from degraded microbial lipids. In the case of sample 469-43-1, 131-150 cm, located in the proximity of the diabase sill, the distribution of the n-alkanes is polymodal, with maxima at C_{13}, C_{17} and C_{29},' ranging from C_{10}-C_{33}, with a strong odd-to-even carbon number predominance> C_{26} (Fig. 3d). The major homologs < C_{26} are derived from partially degraded autochthonous microbial detritus, where the cluster at C_{13} may also be contamination from diesel oil used on the core catcher. The homologs > C_{26} are derived from allochthonous higher plant waxes.

The Pr/Ph of the samples from Sites 468 and 469 are about 1.2 or greater (Table 1), indicating oxic sedimentary environments (Didyk et al., 1978). Perylene was detectable as a minor component in samples 468-2-3, 469-2-2 and 469-43-1 only (Table 2). It is another indicator of anaerobic conditions of sedimentation (Simoneit, 1979b; Didyk et al. 1978).

The n-fatty acids of sample 468-18-3, 100-119 cm range from C_{10}-C_{24}, with a strong even-to-odd carbon number predominance and maximum at C_{16} (Fig. 3f). This is typical of a microbial origin. The n-fatty acids of the other three samples (Fig. 3e,g,h) range from C_{10}-C_{34}, with a strong even-to-odd carbon number predominance and bimodal distributions, with maxima at C_{16} and C_{28}. The homologs $< C_{22}$ are of an autochthonous microbial origin and those $> C_{22}$, when considered with the n-alkanes $> C_{26}$, are of an allochthonous origin from higher plant wax. A trace amount of dehydroabietic acid was detected in the surface sediments only, indicating a very minor influx of allochtonous detritus from resinous plants (Simoneit, 1977).

Molecular Markers:

The concentrations of the n-alkylcyclohexanes, the extended diterpanes, the triterpenoids and the steranes with sterenes are given in Table 2. Major sterane and triterpane concentrations were encountered in samples 467-8-5, 467-18-5, 467-41-4 and 467-110-3.

Microbial markers in the form of n-alkylcyclohexanes were present and their distributions are found in Fig. 4. All samples, except 467-85-4, 105-116 cm, have similar distributions with maxima at C_{21}, no carbon number predominance and an approximate range from C_{13} to C_{25}. The exception (467-85-4) has a maximum at C_{18} and narrower range from C_{14} to C_{23}. These compounds are general indicators of microbial detrital lipids (Simoneit, 1978, 1980).

The relative distributions based on the m/z 191 mass chromatograms of the extended diterpanes and triterpenoids are found in Fig. 5. The extended diterpanes (Structure I) range from $C_{20}H_{36}$ (I, $R=C_2H_5$) to $C_{26}H_{48}$ (I, $R=C_8H_{17}$) with a maximum at $C_{23}H_{42}$. In some samples, the range extends to $C_{29}H_{54}$ and the homologs $> C_{26}H_{48}$ are resolved into two diastereomers. The distribution patterns of the extended diterpanes, when considered with the triterpane distributions, are similar as those of shallow sediment samples from the Southern California Bight (Simoneit and Kaplan, 1980).

The triterpenoids (Fig. 5) consisted of primarily the geologically mature hydrocarbons of the 17α(H)-hopane series (II), with minor amounts of 17β(H)-hopanes and 17β(H)-moretanes. The extended 17α(H)-hopanes ranged from C_{31} to C_{35} and were resolved into two diasteromers at the C-22 position. The 22S to 22R ratios were variable and approach unity for some samples, analogous to the samples from the Southern California Bight (Simoneit and Kaplan, 1980; Venkatesan et al., 1980). The C_{28} triterpane was identified from its retention index and mass spectrum (Fig. 6A) as 17α(H),18α(H),21β(H)-28,30-bisnorhopane (III, Simoneit and Kaplan, 1980; Seifert et al., 1978). It was present in all samples and was the dominant analog in samples 467-3-3, 467-8-5 and 469-2-2. The similarity of the extended diterpane and triterpane distributions of the shallower samples (467-3-3, 467-8-5, 467-18-5, 468-2-3 and 469-2-2) with some of those of the samples from the Southern California Bight (e.g., Fig. 5 I, Simoneit and Kaplan, 1980) lend support to paleoseepage or erosive recycling of more mature bitumen to these sediments. This is further supported by the presence of a broad envelope of unresolved branched and cyclic hydrocarbons in these samples. The triterpenoid distributions of these samples are completely different from the uncontaminated distribution; for example, from the Guaymas Basin in the Gulf of California (Fig. 5J Simoneit et al., 1979).

Indicators of an additional syngenetic component of triterpenoids were the unsaturated hydrocarbons and acids. Triterpenoid ketones were only trace constituents. The major unsaturated triterpenoid was identified as iso-hop-13(18)-ene (IV) from its retention index and mass spectrum (Fig. 6B) (Ageta et al., 1968). It is the major triterpenoid of sample 467-18-5 and occurs in excess of hop-17(21)-ene (V) in all the other samples. Iso-hop-13(18)-ene was not detected in the shallower sediment samples of the Southern California Sight (Simoneit and Kaplan, 1980), where the major unsaturated triterpenes consisted of primarily diploptene and lesser amounts of 17β(H)-hop-21 (22)-ene and hop-17(21)-ene. Diploptene and 17β(H)-hop-21 (22)-ene were not present in these samples. Minor amounts of iso-trisnorhopane (VI) were present in all samples. "This compound may represent a degradation product of iso-hop-13(18)-ene. Ageta et al. (1968) reported iso-hop-13(18)-ene present in ferns. Such a source seems unlikely for these samples, especially when considered with the presence of the other major non-hopanoid structures (cf., III, VI and VII). These compounds are probably derived from microorganisms in the autochthonous environment.

The fatty acid fractions contained varying amounts of extended triterpenoidal acids and samples 467-85-4, 467-110-3 and 468-18-3 contained no detectable amounts of these cyclic acids. The extended 17β(H)-hopanoic acids, ranging from C_{31} to C_{33}, with 17β(H) -bishomohopanoic acid as the major homolog were present in samples 467-41-4, 468-2-3, 469-2-2 and 469-43-1. The predominant stereochemistry was 17β(H) with only one diasteromer and traces of the 17α(H) epimers. Samples 467-3-3, 467-8-5 and 467-18-5 contained a series of extended 28-norhopanoic acids, ranging from C_{30} to C_{33} with the C_{31} homolog as the major compound. The structure of the C_{31} homolog was deduced from its mass spectrum (Fig. 6C) to be 28-norbishomohopanoic acid (VII). The biogenic source of these compounds is unknown, but may be analogous to that of the other extended hopanoic acids from bacteriohopanepolyols of a microbial origin (Ourisson et al., 1979). The biogenic precursors of the extended 28-norhopanoic acids may also be the source of dominant 17α(H),18α(H),21β(H)-28,30-bisnorhopane (III)."

The steranes present in these samples consisted primarily of the 5α and 5β(H),8β(H),14α(H) homologs (VIII , Fig. 7), ranging from C_{26} to C_{29}, with lesser amounts of 4-methylsitostane (VIII, $R'=CH_3$). Samples 467-3-3, 467-8-5, 467-18-5, 467-41-4, 467-85-4, and 467-110-3 contained varying amounts of norcholestane (IX). Pregnane ($C_{21}H_{36}$) was also identified in "these samples (Fig. 7). The presence of norcholestane may indicate an origin from marine biogenic sources (eg., Djerassi et al., 1979). The dominance of the C_{27} sterane in all samples is more characteristic of an origin from marine planktonic detritus (Huang and Meinschein, 1979). However, the high concentrations of the $5\beta(H)$-steranes in the shallower samples (eg., 467-3-3, 467-8-5 and 469-2-2) indicate an admixture of geologically mature bitumen from recycled or paleoseep material (Simoneit and Kaplan, 1980). This can be compared with the example of a sample from the Southern California Bight (Fig. 7h). The isomeric 5α or $5\beta(H)$, $8\beta(H)$, $14\beta(H)$-steranes (X) were present in most of the samples as the second most abundant steranes and occurred in essentially a 1:1 ratio of diastereomers. The 4-methylsitostane is a further indicator of an autochthonous marine component (Simoneit, 1978). Rearranged steranes and their monoaromatic analogs were present as trace constituents only. Pregnane was detected as a significant component of all samples (Fig. 7) and its source is uncertain. Sterenes and steradienes were not present as significant constituents. Also, the polyolefinic hydrocarbons detected in the shallow Southern California Bight sediments (Simoneit and Kaplan, 1980) were not present in these samples.

Traces of the diterpenoid hydrocarbon derivatives retene, dehydroabietin, simonellite, dehydroabietane, norsimonellite and methyl phenanthrene and cadalene were detected in some samples. Coupled with the presence of low amounts of dehydroabietic acid, this indicates a minor influx of resinous higher plant detritus (Simoneit, 1977).

The presence of organic or elemental sulfur has been used as an indicator of anoxic sedimentary conditions (Didyk et. al., 1978). With the present GC/MS system, the elemental sulfur could be speciated into some polysulfide moieties. Thus, the polysulfide peaks corresponding to S_8, S_7 and S_6 are resolved in the GC/MS data (Fig. 8) and their molecular weights confirmed by the mass spectra. Samples 467-3-3, 467-8-5, 467-18-5, 467-41-4, 467-110-3, and. 469-2-2 contained these polysulfides indicating euxinic sedimentary conditions as was also concluded from the other lipid data.

Kerogen:

Kerogen combustion followed by manometric measurement of the resultant gases for a determination of C, H, N and O in the original kerogen generally has given the elemental results listed in Table 1. Some of the variability can be attributed to the high ash content in all but one of the kerogen samples (7--Hole 468). Cores 467 and 469 contained variable amounts of pyrite (FeS_2), which was also detected in the initial core analyses on-board ship, thus high ash values in the kerogen are not surprising. The H/C values for samples 5 and 9 are therefore high and the values for samples 1, 3, 4, 6and 8 fall in the more aromatic range, whereas samples 2, 5, 7 and 9 are more aliphatic. (cf., Table 1).

The $\delta^{13}C$, $\delta^{15}N$ and δD data for the kerogens are listed in Table 1. Values for $\delta^{13}C$ fall within the range of -20 to -23°/0. , and are indicative of chiefly marine planktonic source material with minor input of terrestrial higher plant detritus (Sackett, 1964; Peters *et al.*, 1978; Stuermer *et al.*, 1978).

In addition to source elucidation, $\delta^{13}C$ data have been used to indicate structural modification of kerogen resulting from microbial breakdown or from elevated thermocatalytic effects due to increased burial. Figure 9 shows a plot of kerogen $\delta^{13}C$ versus depth within each core. In Hole 467, shallow samples become isotonically heavier with depth, reaching a maximum value at 381 m subbottom (sample 4), and then decreasing to the lowest $\delta^{13}C$ value in the core at the concomitant greatest depth of 1035 m (sample 6). This $\delta^{13}C$ profile may be the result of two competing processes: the microbial or oxidative alteration of kerogen substrate moieties enriched in ^{12}C, and the inorganic thermal decomposition of kerogen carboxyl functionalities which are enriched in ^{13}C. It is well established that less energy is required to break ^{12}C-^{12}C bonds than it is for ^{13}C-^{12}C linkages (Stevenson et al., 1948; Brodskii et al., 1959); therefore, degradation of kerogen would be expected to preferentially utilize ^{12}C-^{12}C fractions, leaving the residual kerogen heavier in $^{13}C/^{12}C$. Indeed, this appears to be the dominant process for Hole 467 until at a depth of 381 m (4}, there is a reversal and $\delta^{13}C$ becomes increasingly lighter. That phenomenon may be attributed to the overriding effects of thermal decomposition of kerogen portions that are ^{13}C-enriched in conjunction with the waning fractionation of ^{12}C-rich groups from the microbial or oxidative degradation of kerogen. Slight systematic enrichment in ^{12}C in the residual kerogen which is derived from the elimination of -COOH groups heavy in ^{13}C has previously been demonstrated (Abelson and Hoering, 1961; Galimov, 1973; 1978; Rohrback, 1979). It is not clear that the pumiceous tuff located in the sedimentary column between 700 to 820 meters might have accelerated the rate of decarboxylation reactions in the kerogen since there are no major discontinuities in the decreasing $\delta^{13}C$ trend with depth for the data points at 381 m (4), 800 m (5) and at 1035 m (6). More Information is needed for samples taken within close proximity both above and below the tuff interval in order to clarify the situation. Similarly, Hole 468 shows an increase in $\delta^{13}C$ from a depth of 7.5 m (7) to the deepest subsample taken at 160 m (8). Apparently, temperature effects were not great. enough to initiate decarboxylation of kerogen, and decomposition by microbes or oxidation was the dominant process, yielding kerogen residues heavier in $\delta^{13}C$. Conversely, Hole 469 shows nearly a constant $\delta^{13}C$ value with depth (-22.20"/00), which could mean that microbial/oxidative and thermal decomposition processes for the refractory organic material were roughly in balance with one another throughout the core intervals sampled. However, this should be interpreted with caution due to the limited data, until additional $\delta^{13}C$ analyses can be conducted on further samples taken between samples 9 and 10.

Deuterium ratios for the ten kerogen samples demonstrate greater variance, showing a distribution between -140 to +29 ‰ . Before an assignment of organic source material can be made on the basis of δD variance, limitations to the usage of the deuterium ratio must be understood. Generally, δD results are thought to provide a less concrete basis for the elucidation of organic source material, since deuterium values have previously been shown to be intrinsically related to the δD ratios of meteoric waters which drain into a given geographic location, rather than to inherent biological fractionation processes of marine and terrestrial biota (Hoering, 1975). However, Nissenbaum (1974) detected slight differences among δD measurements of various marine and terrestrial humic acids and found that for a given restricted geographic location, δD ratios of -102 to -110 ‰ for humic material in the underlying recent marine sediments, and attributed this range to contributions primarily by marine plankton. Comparing this δD range to the δD values of these kerogen samples (Table 1), only samples 1 and 8 of Quaternary and Lower/Middle Miocene ages, respectively, coincide with the -102 to -110 ‰ interval. Clearly, the δD values generated in this study do not support the corresponding ^{13}C data which irrevocably point to a marine planktonic origin for these kerogens. Factors which may have induced the wide variations in δD measured in the other eight sample intervals include the following:

1) presence of heavy minerals in the isolated kerogen fractions could either increase or diminish δD during the separation and pyrolysis phases of kerogen analysis (Durand and Monin, 1978),
2) fractionation due to equilibration or exchange of kerogen hydrogen during analytical procedures (Hoering, ?975),
3) fractionation of the hydrogen fraction contained in humates during

diagenetic processes that lead to kerogen formation; thus, -102 to -110 ‰ measured in humates, is fundamentally not applicable to kerogen, and

4) application of varying degrees of thermal stress to the kerogen after burial within the sediment.

Knowledge of the thermal stress within a given sediment may be used to demonstrate the changes in δD with depth, and thus, correlate increasing temperature due to burial within a geothermal gradient. Thus, it may be possible to document paleothermal events by analysis of anomalous δD fluctuations with depth (Fig. 10). For Hole 467, δD remains nearly constant to a depth of 381 m (4), then increases to a maximum value at 800 m (5), and finally decreases in the deepest kerogen sample. The substantial depletion of ^{12}C at a depth of 800 m also coincides with the appearance of a pumiceous tuff. It seems evident that the heat from this nearly cooled volcanic material was sufficient enough to cause mass fractionation of the lighter isotope, leaving behind a deuterium enriched kerogen residue. Moreover, in terms of D/H content, the sample at 800 m (5) is diagenetically more mature than the lower kerogen sample from 1035 m (6). This anomalous maturation in the tuff vicinity may be interpreted as a Rayleigh distillation effect in which the lighter isotope is distilled off first, the magnitude of which is related to the absolute distance from the heat source. A similar phenomenon has been observed in the thermal alteration of Cretaceous black shale by basaltic intrusions in the Eastern Atlantic (Simoneit <u>et al.</u>, 1978).

For Site 468, δD increases with depth, however, the deepest sample is only 160 m (8). Apparently, the sediment in this interval of 7.5 to 160 m did not experience an unusual thermal stress, since the δD lies within the same range as for the shallow kerogen at site 467, despite the fact that volcanic ash layers appear in the core lithology at a depth of about 230 m.

Similar behavior is not true for Hole 469, in which δD is enriched by 40 to 70°/00 in the core relative to the δD values in either Hole 467 or 468. The organic matter in Hole 469 exhibits a high diagenetic maturity in terms of very large D/Ii ratios, which may well have been induced by the high thermal stress imparted by the observed diabase intrusion. Moreover, the intrusion appears to be of an Upper Quaternary age in order to account for the high δD value in the shallow 10.0 m (9) sample that was formed during this era. Therefore, when comparing the relative thermal stress induced by volcanic debris or alternatively, the greatest extent of diagenetic maturity of the organic matter, the following is true: the core from Hole 469 shows extensive thermal degradation, followed by localized zones of moderately heated kerogen in Hole 467, and finally, no significant thermal alteration of kerogen from Hole 468.

When a correlation is made between δD and $\delta^{13}C$ for each kerogen sample (Figure 11) a compelling segregation of drill holes 457 and 468 from 469 is evident. This separation of data points may be a manifestation of differential thermal stress on the various kerogen fractions by a non-uniform thermal gradient or by non-homogeneous heating by volcanic debris. That is assuming the effects of experimental fractionation, heavy mineral interaction, meteoric deuterium values and organic source material are roughly equivalent among all ten kerogen samples. Overall, $\delta^{13}C$ shows minor deviation (-20 to -23 ‰), while δD values demonstrate significant variability (-140 to +29 ‰). By plotting the changes in δD and $\delta^{13}C$ among kerogen from a single drill site, consistent progressions become apparent. For Site 467, shallow samples are clustered together (1 to 4), having low δD ratios. Deeper samples (5 and 6) show an enrichment in deuterium of about 40°/00, relative to the shallow kerogen. Carbon values are more or less in the same range for all analyzed kerogen, with a variability of approximately 2 70.. Thus, with depth there is a rapid increase of δD relative to $\delta^{13}C$, and this relation may indicate the accelerated effect of biological and abiological kerogen alteration processes acting upon the lighter element. This same trend is noted for Hole 469 and less pronounced for Hole 468. Consequently, when considering diagenetic alteration of kerogen, changes of greater magnitude occur for hydrogen components than for carbon components. This generalization is supported by simulated laboratory thermal alterations of kerogens (Baedecker et al., 1977; Ishiwatari et al., 1977; Sackett, 1978; Rohrback, 1979; Durand and Monin, 1978) which show the degree of elemental loss in the order of O > H > N > C.

The $\delta^{15}N$ data for the kerogens are also listed in Table 1 and they range from +1.4 to +11.8 ‰ , with considerable scatter and error due to the low levels of nitrogen contents. The correlation of $\delta^{15}N$ versus $\delta^{13}C$ is shown in Fig. 12 and the correlation line (slope 1.1) for organic matter from the continental shelf sediments of the Northeast Pacific (Peters et al., 1978) is also indicated. The interpretation of the data is limited but it shows that all these kerogens are of a mixed composition derived from terrestrial and marine detritus. Based on the $\delta^{15}N$ values, the samples from Site 469 are distinctly more marine in character.

CONCLUSIONS

The nature and composition of the lipids and kerogens of selected core samples from Sites 467 to 469 were determined and the genetic origin and maturity of that organic matter could be evaluated from these data.

Lipids:

The lipids had a multiple origin from primary autochthonous marine production (i.e., microbial residues) and from allochthonous sources.

The allochthonous influx was comprised of terrigenous detritus, primarily higher plant wax and traces of resin residues, and geologically mature bitumen from seepage or from recycled older sedimentary material. These inferences are based on the homolog distributions of the n-alkanes and n-fatty acids, with the shape and magnitude of the unresolved branched and cyclic hydrocarbons (the hump), and the structural and stereochemical compositions of the molecular indicators.

The Pr/Ph values ranged from 0.7 to 2.0 and perylene and polysulfide sulfur were present in most samples, indicating partial euxinic paleoenvironmental conditions of sedimentation.

Kerogen

The δD and $\delta^{13}C$ values of the kerogen samples demonstrate that sites 467 to 469 contain organic material principally derived from marine planktonic sources, with a minor input of terrestrial higher plant components. Although these sites are within close proximity to each other, the respective sediments show varying degrees of thermal stress, based upon the variation of δD with depth. Hole 469 shows anomalously high δD values, which support the idea of localized heating by a recent (Quaternary) diabase intrusion. Alternatively, Site 467 was moderately heated within close proximity of a vitric tuff, while Hole 468 does not show any significant alteration of kerogen by a far removed lapili tuff. Moreover, the in situ thermal alteration of the organic matter shows these overall trends:

1) δD increases with increasing depth, in a normal diagenetic sequence as a result of the preferential loss of the lighter isotope with increasing temperature (mass fractionation),
2) $\delta^{13}C$ increases with increasing depth, initially, due to microbial degradation, and then decreases with depth due to inorganic breakdown (thermal stress),

3) loss of H is more rapid than loss of C during the normal diagenetic sequence of events.

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REFERENCES

Abelson, P.H. and T.C. Hoering {1961). Carbon isotope fractionation in formation of amino acids by photosynthetic organisms. Proc. Nat. Acad. Sci. U.S. 47; 623-632.

Ageta, H., Shioima, K. and Arai, Y. (1968). Fern constituents: Neohopane, hopene-II, neohopadiene and fernadiene isolated from Adiantum species, Chem. Comm. 1968; 1105-1107.

Baedecker, M.J., R. Ikan, R. Ishiwatari and I.R. Kaplan (1977). Thermal alteration experiments on organic matter in recent marine sediments as a model for petroleum genesis. In: Chemistry of Marine Sediments, (T.F. Yen, Ed.), Ann Arbor Science, Ann Arbor, Mich; pp. 55-72.

Brodskii, A.M., R.A. Kalinenko and K.P. Lavroskii (1959). On the kinetic isotope effect in cracking. Int'l. J. Appl. Radiat. Isotopes 7; 118.

Craig, t-1. (1957). Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acts 12; 133-149.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C. and Eglinton, G. (1978). Organic geochemical indicators of paleoenvironmental conditions of sedimentation, Nature 272, 216-222.

Djerassi, C., Theobald, N., Kokke, W.C., Pak, C.S. and Carlson, R.M.K. (1979). Recent progress in the marine sterol field, Pure Appl. Chem. 51, 1815-1828.

Durand, B. and Monin, J.C. (1978). Elemental analysis of kerogens. Chapter 4, in: Kerogen -- Insoluble Organic Matter From Sedimentary Rocks. 6. Durand, cd., Paris: Editions Technip. , pp. 113-142.

Galimov, E.M. (1978). $^{13}C/^{12}C$ ratios in kerogen. In: Kerogen -- Insoluble Organic Matter From Sedimentary Rocks. B. Durand, cd"' Paris: Editions Technip, pp. 271-299.

Galimov, E.M. (1973). Carbon isotopes in oil and gas geology. English translation: Washington, NASA TT F-682.

Haq, B., Yeats, R.S., Barren, J.A. et al. (1979). Eastern Pacific Boundary Currents, Geotimes 24 (4), 30-31.

Hoering, T.C. (1975). The biogeochemistry of the stable hydrogen isotopes. Annual Report of the Director, Geophysical Laboratory, Carnegie Inst., 1974-1975, Washington, D.C., Vol. 1975, pp. 598-604.

Huang, N.-Y. and Meinschein, W.G. (1979). Sterols as ecological indicators, Geochim. Cosmochim. Acts 43, 739-745.

Ishiwatari, R., Ishiwatari, M., Rohrback, B.G. and Kaplan, I.R. (1977). Thermal alteration experiments on organic matter from recent marine sediments in relation to petroleum genesis. Geochim. Cosmochim. Acts 41, 815-828.

Nissenbaum, A. (1974)0 The organic geochemistry of marine and terrestrial humic substances: Implications of carbon and hydrogen isotope studies. In: Advances in Organic Geochemistry 1973, B. Tissot and F. Bienner, eds., Editions Technip, Paris, pp. 39-52.

Ourisson, G., Albrecht, P. and Rohmer, M. (1979). The hopanoids. Paleochemistry anti.biochemistry of a group of natural products, Pure Appl. Chem. 51_, 709-729.

Peters, K.E., Sweeney, R.E. and Kaplan, I.R. (1978). Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23, 598-604.

Rohrback, B.G. (1979). Analysis of low molecular weight products generated by thermal decomposition of organic matter in recent sedimentary environments. Ph.D. Thesis, University of California at Los Angeles, 195 pp.

Sackett, W.M. (1978). Carbon and hydrogen isotope effects during the thermo-catalytic production of hydrocarbons in laboratory simulation experiments. Geochim. Cosmochim. Acts 42, 571-580.

Sackett, W.M. (1964). The depositional history and isotopic organic carbon composition of marine sediments. Marine Geol. 2, 173-185.

Seifert, W.K., Moldowan, J.M., Smith, G.W. and Whitehead, E.V. (1978). First proof of structure of a C_{28}-pentacyclic triterpane in petroleum. Nature 271, 436-437.

Simoneit, B.R.T. (1977). Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acts 41, 463-476.

Simoneit, B.R.T. (1978). The organic chemistry of marine sediments, in Chemical Oceanography, J.P. Riley and R. Chester, eds., Academic Press, New York, Vol. 7, pp. 233-311.

Simoneit, B.R.T. (1979a). Lipid geochemistry of Cretaceus black shales from the Bay of Biscay, Site 402, and of Eocene mudstone from the Rockall Plateau, Site 404. in: Initial Reports of the DSDP, Vol. 48, Montadert, L., Roberts, D.G. et al., U.S. Govt. Printing Office, Washington, D.C., pp. 935-941.

Simoneit, B.R.T. (1979b). Organic geochemistry of the shales from the north-western Proto-Atlantic, DSDP Leg 43, In: Initial Reports of the DSDP Tucholke, B.E., Vogt, P.R., et al., Vol. 43, U.S. Govt. Printing Office, Washington, D.C., pp. 643-649.

Simoneit, B.R.T. (1980). Organic geochemistry of Mesozoic sediments from Deep Sea Drilling Project Site 3 0, Falkland Plateau. In: Initial Reports of the Deep Sea Drilling Project, Vol. 50, Lancelot, Y., Winterer, E.L. et al., U.S. Govt. Print. Office, Washington, D.C., pp. 637-642.

Simoneit, B.R.T. and Kaplan, I.R. (1980). Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern California Bight, Mar Environ. Res. 3_, 113-128.

Simoneit, B.R.T., Mazurek, M.A., Brenner, S., Crisp, P.T., and Kaplan, I.R. (1979). Organic geochemistry of recent sediments from Guaymas Basin, Gulf of California, Deep-Sea Res. 26A, 879-891.

Stevenson, D.P., Wagner, C.D., Beeck, O. and tros, J.W. (1948). Isotope effect in thermal cracking of propane-1-^{13}C . J. Chem. Phys. 16, 993.

Stuermer, D.H., Peters, K.E. and Kaplan, I.R. (1978). Source indicators of humic substances and proto-kerogen. Stable isotope ratios, elemental. compositions and electron spin resonance spectra. Geochim. Cosmochim. Acts 42, 989-997.

Venkatesan, M.I., Brenner, S., .Ruth, E., Bonilla, J. and Kaplan, I.R. (1980). Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochim. Cosmochim. Acta 44, 789-802.

Table Sample descriptions, analyses and analytical results for the lipids and kerogen of sediments from Leg 63.

Sample Designation	Location	Water Depth (m)	Subbottom Depth (m)	Age	Lithology	Carbon[1]		$CaCO_3$[1]	LIPIDS										0 G			
						Total (%)	Org. (%)	(%)	Total Lipids (μg/g)[2]	HC (μg/g)	n-Alkanes CPI[3]	n-Alkanes Max.[4]	Pr/Ph[5]	n-Fatty Acids (μg/g)[2]	CPI[3]	Max.[4]	Yield	H/C	O/C	$\delta^{13}C$	δD (‰)[6]	$\delta^{15}N$ (‰)[6]
467-3-3 35-120cm)	120°45.47'W	2128	15.5	Quat.	Diatom. silty clay	4.0	1.1	24	700	10	1.3	17,19,29	1.4	14	8.8	16,26	2.5	1.01	0.072	-22.3	-114	+6.2
467-8-5 30-117cm)	33°50.97'N 120°45.47'W	2128	70.0	Quat.	Diatom. nanno clay	5.	1.9	27	100	14	.9	17,23,29	0.9	18	6.1	16,26	1.9	1.13	0.057	-21.5	-133	+5.6
467-13-5 -118cm)	33°50.97'N 120°45.47'W	2128	165.0	Upper Plio.	Diatom. silty clay	8.9	3.4	45	2500	43	2.2	,23,29	0.7	45	7.1	16,28	4.5	0.40	0.062	-21.4	-135	+4.5
467-41-4 00-121cm)	33°50.97'N 120°45.37'W	2128	381.0	Lower Plio.	Nanno Claystone	7.6	3.0	40	2180	7	1.6	17,23,29	0.9	15	3.4	16,26	4.5	0.89	0.056	-20.8	-128	+3.0
467-85-4 05-116cm)	33°50.97'N 120°45.47'W	2128	800.0	Mid-Mioc.	Lithic tuff with nanno clay chalk	8.7	0.7	67	635	7	1.0	7,Pr,23	.9	8	3.7	16,22	3.7	1.97	0.058	-21.5	- 36	+
67-110-3 (5-9cm)	33°50.97'N 120°45.47'W	2128	1035.0	Mid-Mioc.	Calcareous silty claystone	3.3	0.9	20	2040	260	0.9	18,Pr,22,29	2.0	104	2.3	16,24	2.5	1.00	0.046	-22.9	- 96	+6.7
68-2-3 00-120cm)	32°37.03'N 120°07.07'W	1849	7.5	Mid-Mioc.	Diatom. Nanno ooze	9.8	0.9	74	2750	25	.5	17,23,29	1.2	65	5.1	16,28	3.5	1.24	0.059	-22.4	-136	+3.4
168-18-3 -119cm)	32°37.03'N 120°07.07'W	1849	159.5	Lower Mioc.	Diatom. Nanno ooze	5.0	2.8	19	1850	3	.0	17,23	1.6	3	6.2	12,16	2.9	0.99	0.054	-21.8	-107	+4.8
169-2-2 36-150cm)	32°37.00'N 120°32.99'W	3790	10.0	Upper Quat.	Gray clay	0.7	0.6		2440	24	2.8	23,29	1.3	13	4.8	16,28	0.8	1.97	0.079	-22.2	- 20	+ .8
169-43-1 31-150cm)	32°37.00'N 120°32.90'W	3790	388.0	Lower Mioc.	Clayey Nanno chalk	7.7	0.3	62	1800	12	.5	3,17,29	1.2	5	3.4	16,24,28	2.7	--	0.053	-22.3	+ 28	+ 9.

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ata supplied by the Deep-Sea Drilling Project, Scripps Institution of Oceanography, University of California at San Diego.

ased on dry sediment weight.

rbon Preference summed from C_{10} to C_{35}, alkanes odd-to-even, acids even-to-odd.

he dominant s underscored.

ristane-to-phytane ratio.

alues reported versus PDB for $\delta^{13}C$ SMOW for δD and atmospheric N_2 for $\delta^{15}N$.

Table 2. Approximate concentrations of some molecular markers of sediments from Leg 63.

Sample	Perylene (ng/g)[1]	Alkylcyclohexanes (ng/g)	Extended diterpanes (ng/g)	Triterpenoids (ng/g)	Steranes (ng/g)
Site 467					
1) 3-3	n.d.[2]	130	800	1200	250
2) 8-5	1000	105	660	1800	83(I
3) 18-5	3200	48	340	930	22,000
4) 41-4	900	82	100	190	460
5) 85-4	30	27	20	70	130
6) 110-3	200	840	380	2040	9600
Site 468					
7) 2-3	100	170	190	300	n.d.
8) 18-3	n.d.				
Site 469					
9) 2-2	10	730	270	530	95
10) 43-1	20				

---

[1] Based on dry sediment weight.
[2] n.d. - not detected.

Table 3. Inferred sources of lipids and kerogen of Leg 63 samples based on organic geochemical data.

Sample	Lipids	Kerogen
467-3-3	marine/terrigenous[1]	marine
8-5	marine/terrigenous	marine
18-5	marine/terrigenous	marine/terrigenous[1]
41-4	marine/terrigenous	marine
85-4	marine	marine
110-3	marine/terrigenous	marine
468-2-3	marine/terrigenous	marine
18-3	marine	marine
469-2-2	marine/terrigenous	marine/terrigenous
43-1	marine/terrigenous	marine

---

[1] Dominant source of two is underscored.

FIGURE LEGENDS

Fig. 1. Location map of sites 467-469 in the California Continental Borderland.

Fig. 2. Distribution diagrams for the n-alkanes (A-F) and n-fatty acids (G-L) of the samples from Site 467. (...indicates isoprenoids, --- dehydroabietic acid).
A,G: sample 467-3-3, 105-120 cm
B,H: sample 467-8-5, 100-117. cm
C,I: sample 467-18-5, 100-118 cm
D,J: sample 467-41-4, 100-121 cm
E,K: sample 467-85-4, 105-116 cm
F,L: sample 467-110-3, 5-9 cm

Fig. 3. Distribution diagrams for the n-alkanes (A-D) and n-fatty acids (E-H) of the samples from Sites 468 and 469. (... indicates isoprenoids, --- dehydroabietic acid).
A,E: sample 468-2-3, 100-120 cm
B,F: sample 468-18-3, 110-119 cm
C,G: sample 469-2-2, 136-150 cm
D,H: sample 469-43-1, 131-150 cm

Fig. 4. Distribution diagrams for the n-alkylcyclohexanes of the samples from Sites 467-469.
(A) sample 467-3-3, 105-120 cm; (B) sample 467-8-5, 100-117 cm; (C) sample 467-18-5, 100-118 cm; (D) sample 467-41-4, 100-121 cm; (E) sample 467-35-4, 105-116 cm; (F) sample 467-110-3, 5-9 cm; (G) sample 468-2-3, 110-120 cm; (H) sample 469-2-2, 136-150 cm.

Fig. 5. Relative distribution diagrams for extended diterpanes and triterpenoids (the concentrations are based on the relative intensity of the m/z 191 mass chromatograms and gas chromatographic response). The R and S diastereomers of the extended homologs are also indicated and the C_{28} compound is 17a(H), 18a(H), 21β(H)-28,30-bisnorhopane..
A) sample 467-3-3, 105-120 cm
B) sample 467-8-5, 100-117 cm
C) sample 467-18-5, 100-118 cm
D) sample 467-41-4, 100-121 cm
E) sample 467-85-4, 105-116 cm
F) sample 467-110-3, 5-9 cm
G) sample 468-2-3, 100-120 cm
H) sample 469-2-2, 136-150 cm
I) sample BLM 193, 25-31 cm, Southern California Bight (Simoneit and Kaplan, 1980)
J) sample 30 G-5, Gus>-mas Basin (Simoneit et al., 1979)

Fig. 6. Selected mass spectra of molecular markers in lipids of sample 467-18-5, 100-118 cm.
A) 17a(H), 18a(H), 21β(H) -28, 30-Bisnorhopane (III)
B) <u>iso</u> - Hop-13(18)-ene (IV)
C) 28-Norbishomohopanoic acid (as methyl ester) (VII)

Fig. 7. Distribution diagrams for steranes (also sterenes . ..) of the samples from Sites 467 to 469.
A) sample 467-3-3, 105-120 cm
B) sample 467-8-5, 100-U7 cm
C) sample 467-18-5, 100-118 cm
D) sample 467-41-4, 100-121 cm
E) sample 467-85-4, 105-116 cm
F) sample 467-110-3, 5-9 cm
G) sample 469-2-2, 136-150 cm
H) sample BLM 193, 25-31 cm, Southern California Bight (Simoneit and Kaplan, 1980)

Fig. 8. GC/MS data for the polysulfides, (A) mass chromatogram for m/z 64, the base peak of S_6, S_7 and S_8, (B) total ion current trace.

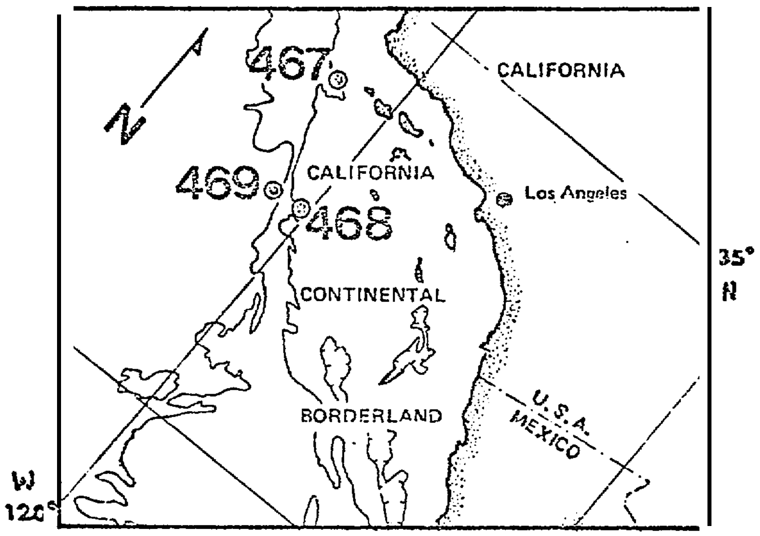
Fig. 9. Plot of the $\delta^{13}C$ data versus depth for the kerogens from Sites 467 to 469.

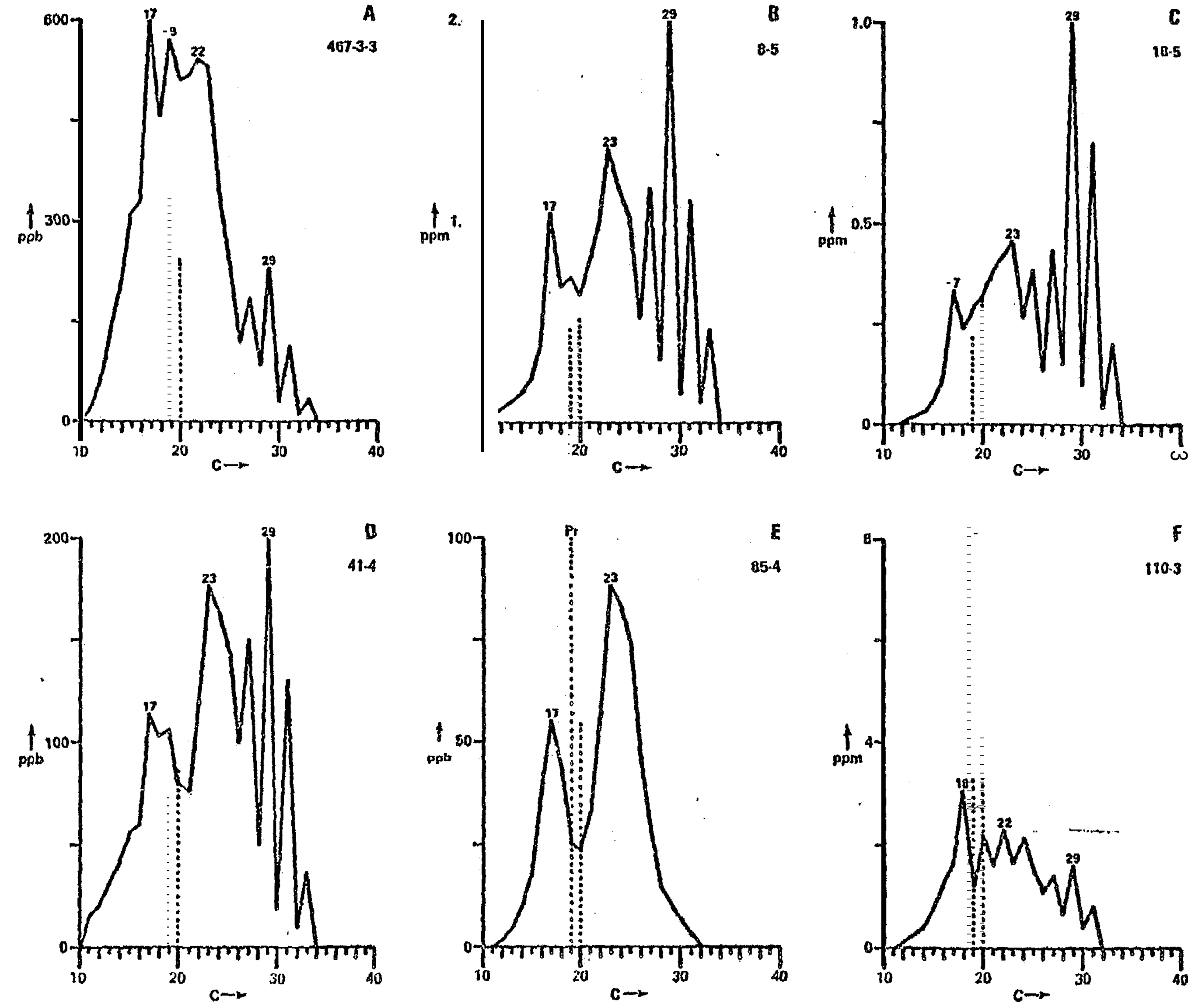
Fig. 10. Plot of the δD data versus depth for the kerogens from Sites 467 to 469.

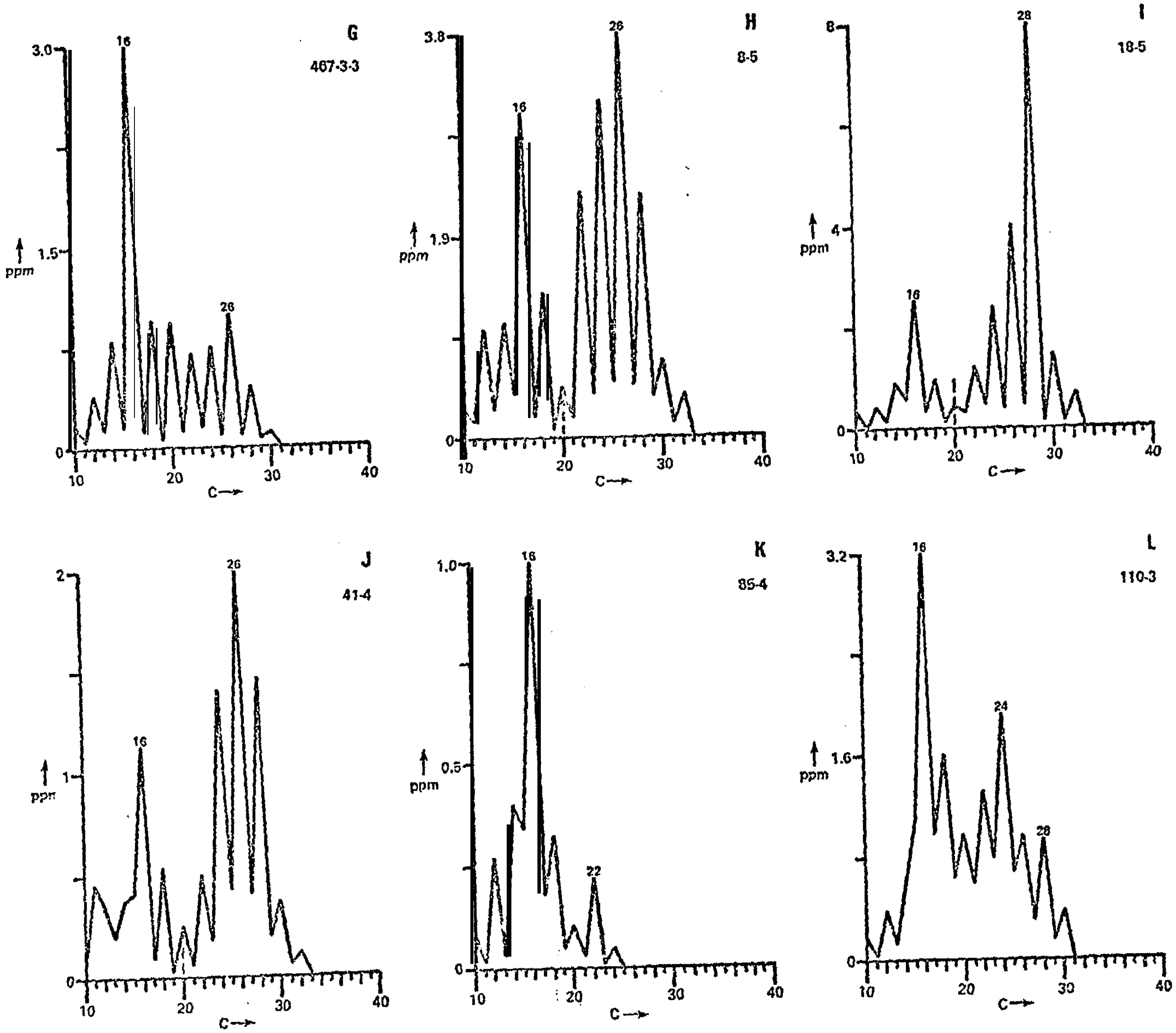
Fig. 11. Correlation diagram of δD versus $\delta^{13}C$ for the kerogens from Sites 467 to 469.

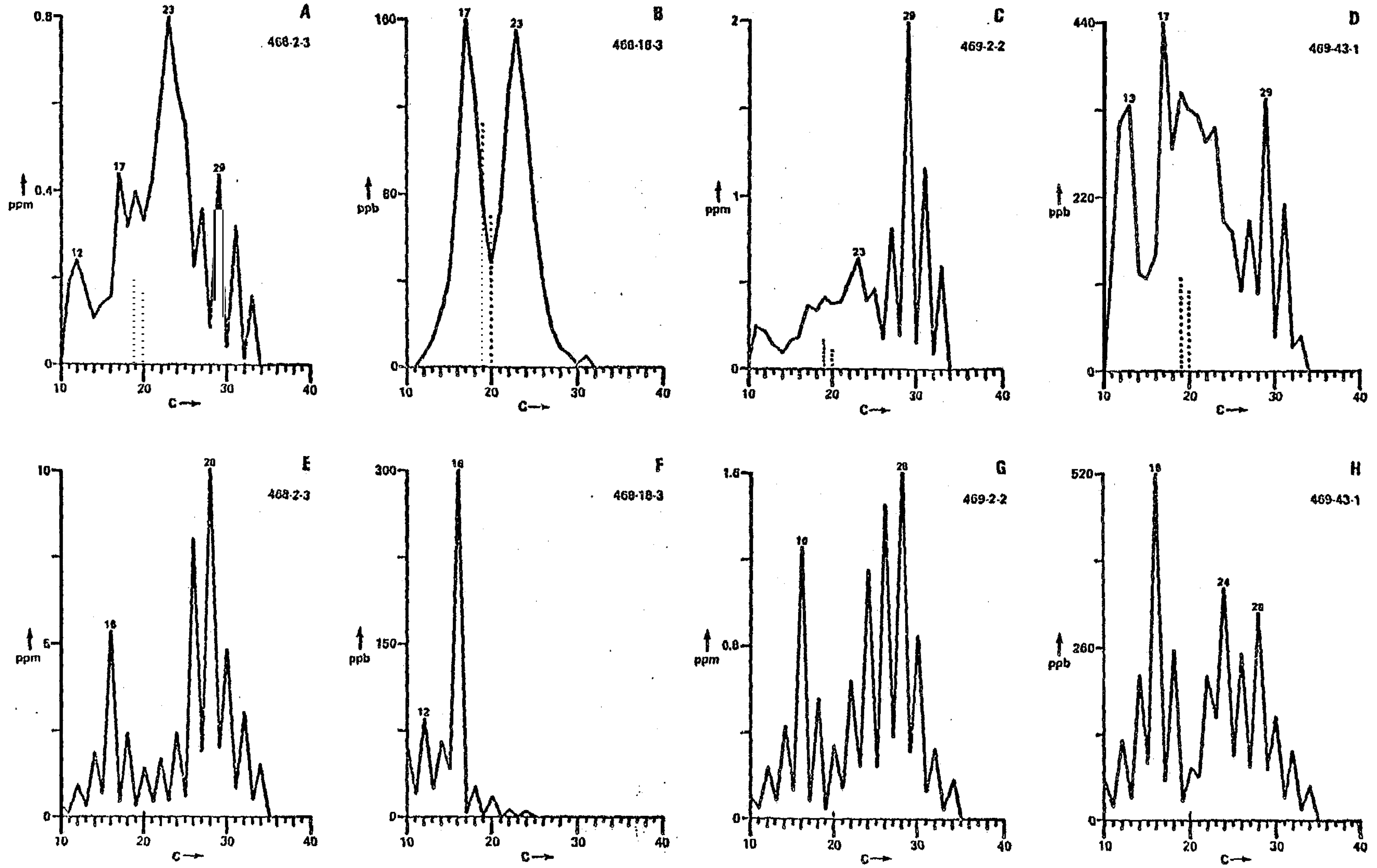
Fig. 12. Correlation diagram of $\delta^{15}N$ versus $\delta^{13}C$ for the kerogens from Sites 467 to 469.

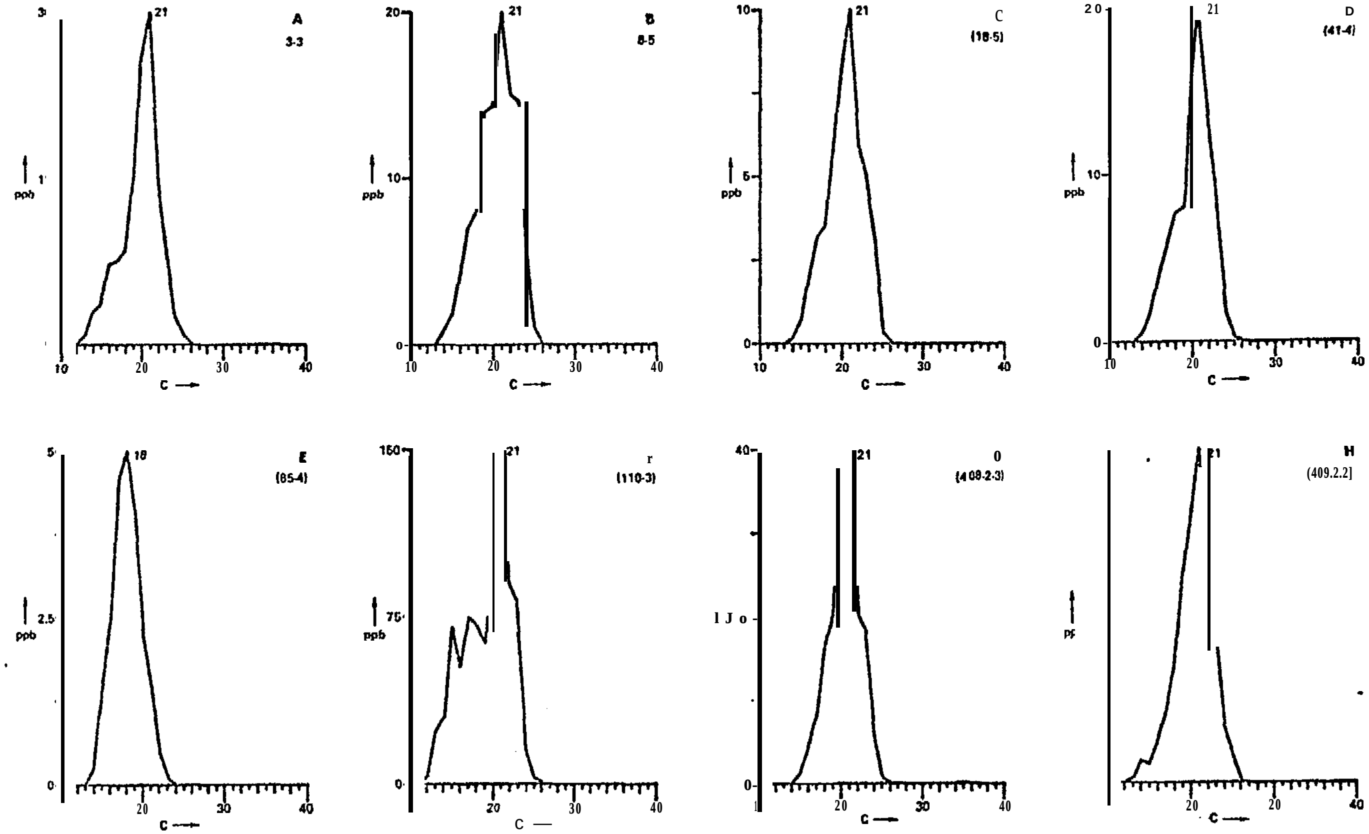
Appendix I. Chemical Structures Cited


N
467
469
468
CALIFORNIA
CALIFORNIA
CONTINENTAL
BORDERLAND
Los Angeles
U.S.A.
MEXICO
35° N
W 120°

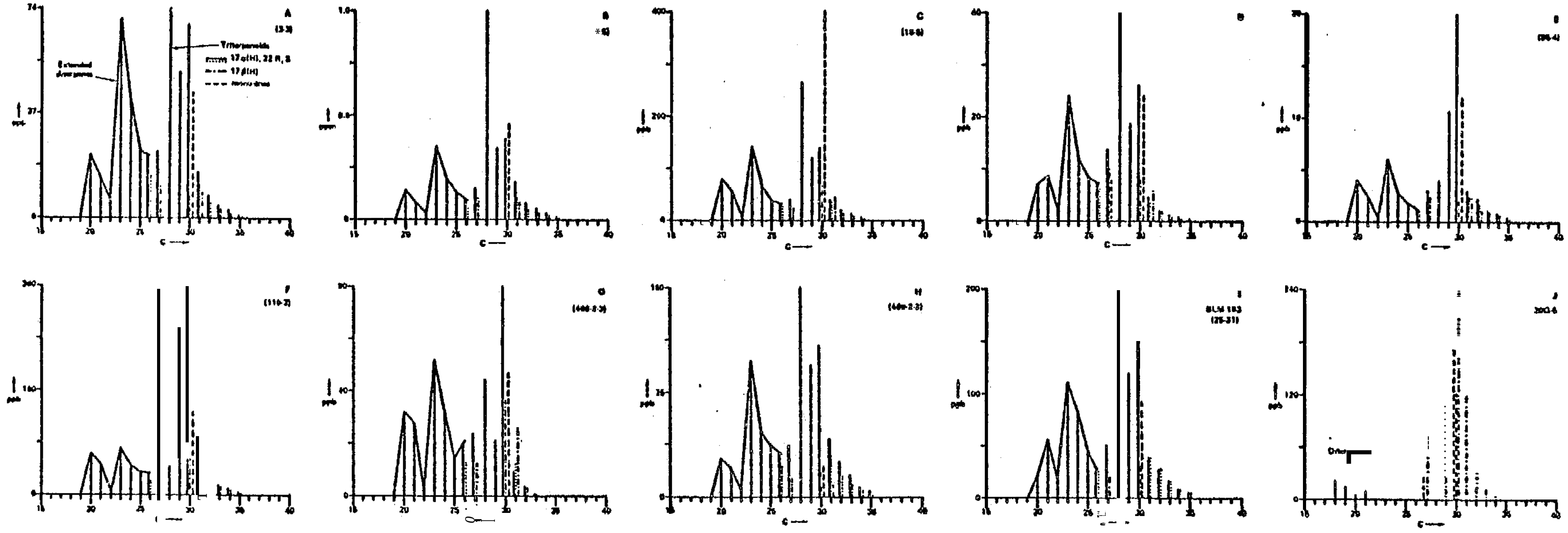

A
467-3-3
600
300
0
ppb
17
-9
22
29
10
20
30
40
C→
B
8-5
2.
1.
ppm
17
23
29
20
30
40
C→
C
18-5
1.0
0.5
0
ppm
-7
23
29
10
20
30
3
C→
D
41-4
200
100
0
ppb
17
23
29
10
20
30
40
C→
E
85-4
100
50
0
ppb
Pr
17
23
10
20
30
40
C→
F
110-3
8
4
0
ppm
18
22
29
10
20
30
40
C→

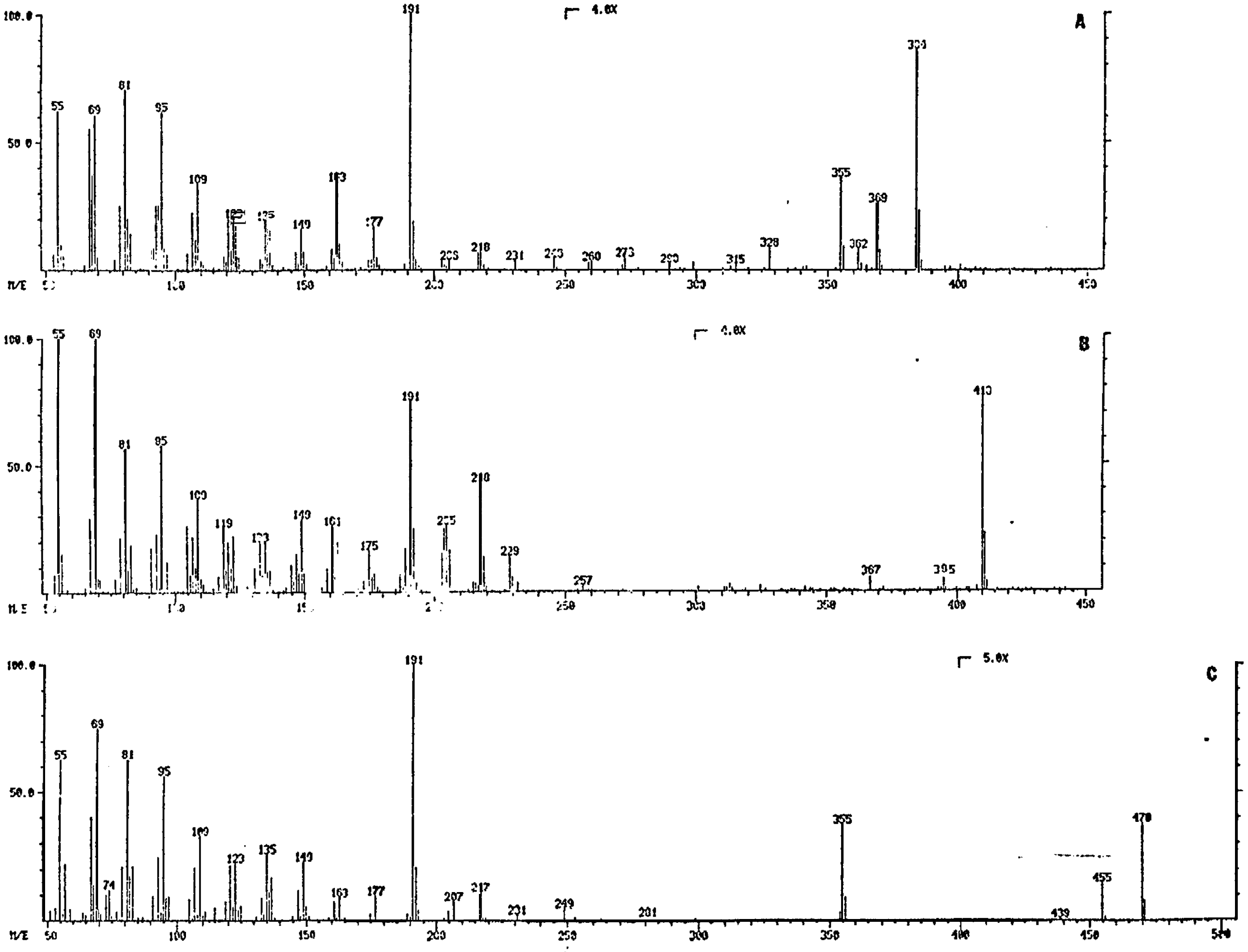

G
467-3-3
3.0
1.5
ppm
0
16
26
10
20
30
40
C→
H
8-5
3.8
1.9
ppm
0
16
26
10
20
30
40
C→
I
18-5
8
4
ppm
0
16
28
10
20
30
40
C→
J
41-4
2
1
ppm
0
16
26
10
20
30
40
C→
K
85-4
1.0
0.5
ppm
0
16
22
10
20
30
40
C→
L
110-3
3.2
1.6
ppm
0
16
24
28
10
20
30
40
C→

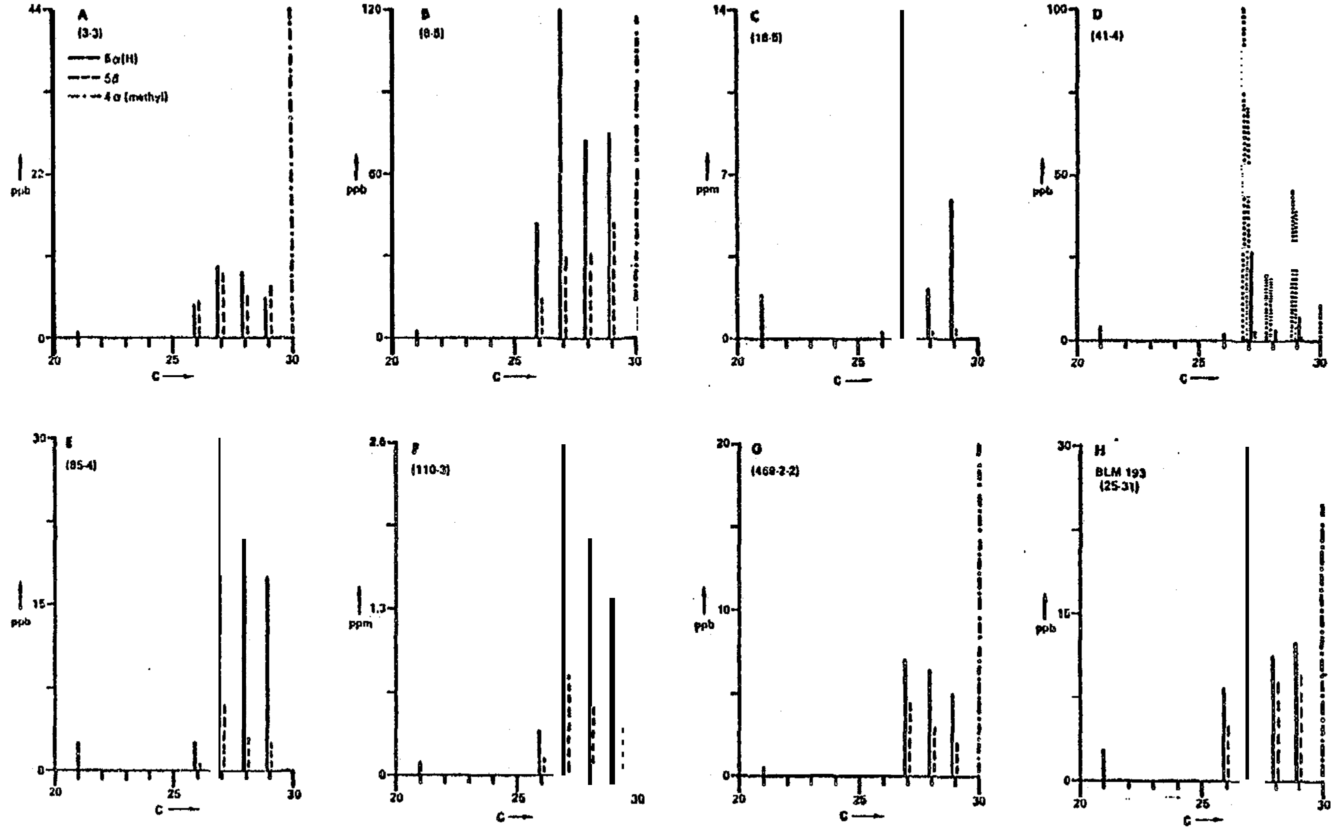

A
468-2-3
0.8
0.4
0
ppm
12
17
23
29
10
20
30
40
C→
B
468-18-3
160
80
0
ppb
17
23
10
20
30
40
C→
C
469-2-2
2
1
0
ppm
23
29
10
20
30
40
C→
D
469-43-1
440
220
0
ppb
13
17
29
10
20
30
40
C→
E
468-2-3
10
5
0
ppm
16
28
10
20
30
40
C→
F
468-18-3
300
150
0
ppb
12
16
10
20
30
40
C→
G
469-2-2
1.6
0.8
0
ppm
16
28
10
20
30
40
C→
H
469-43-1
520
260
0
ppb
16
24
28
10
20
30
40
C→

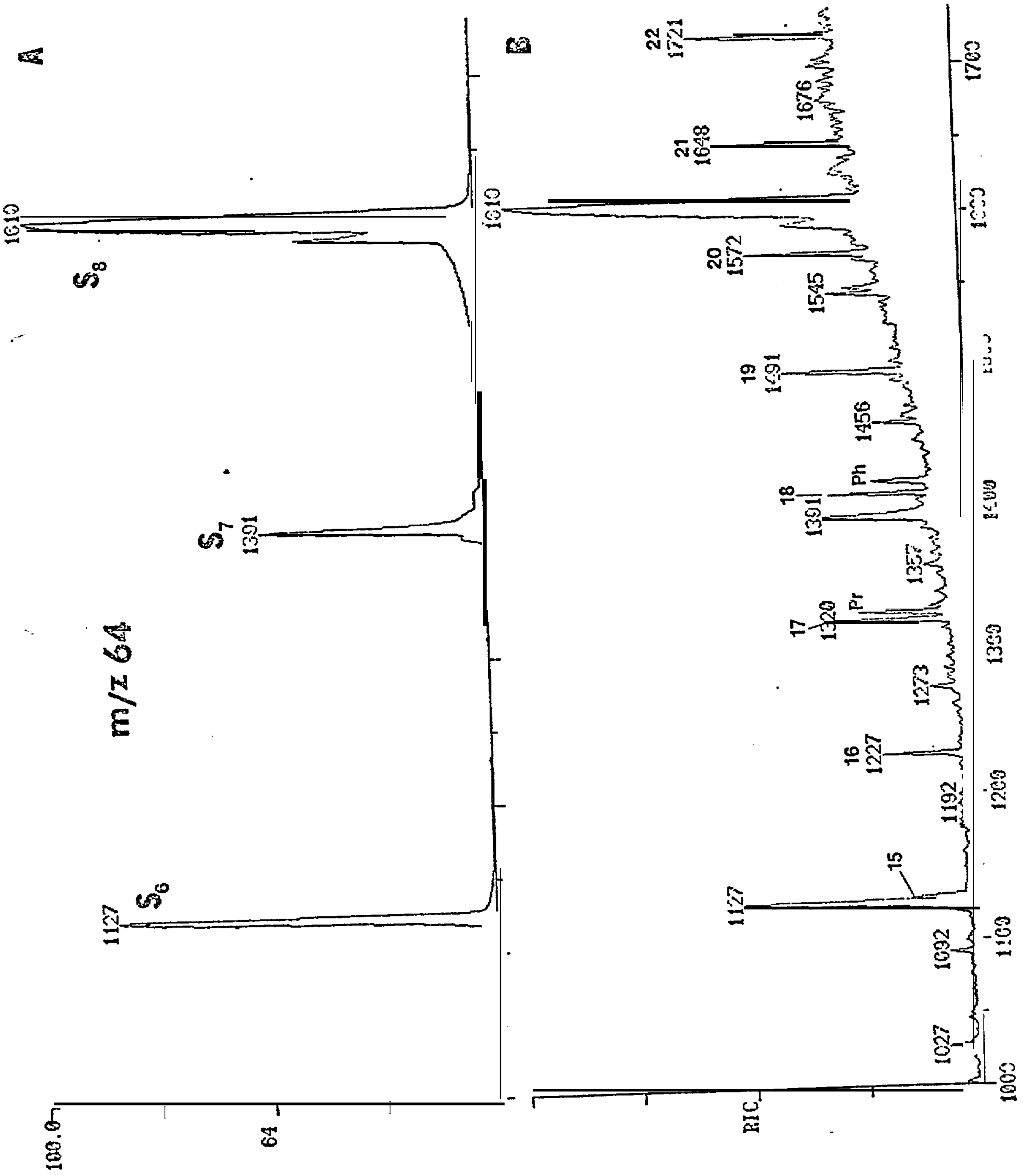


A
3·3
21
ppb
C →
10
20
30
40
B
8·5
21
20
10
0
ppb
C →
C
(18·5)
21
10
5
0
ppb
C →
D
(41·4)
21
20
10
0
ppb
C →
E
(85·4)
18
5
2.5
0
ppb
C →
r
(110·3)
21
150
75
0
ppb
C —
0
(408·2·3)
21
40
0
C →
H
(409.2.2]
21
C →

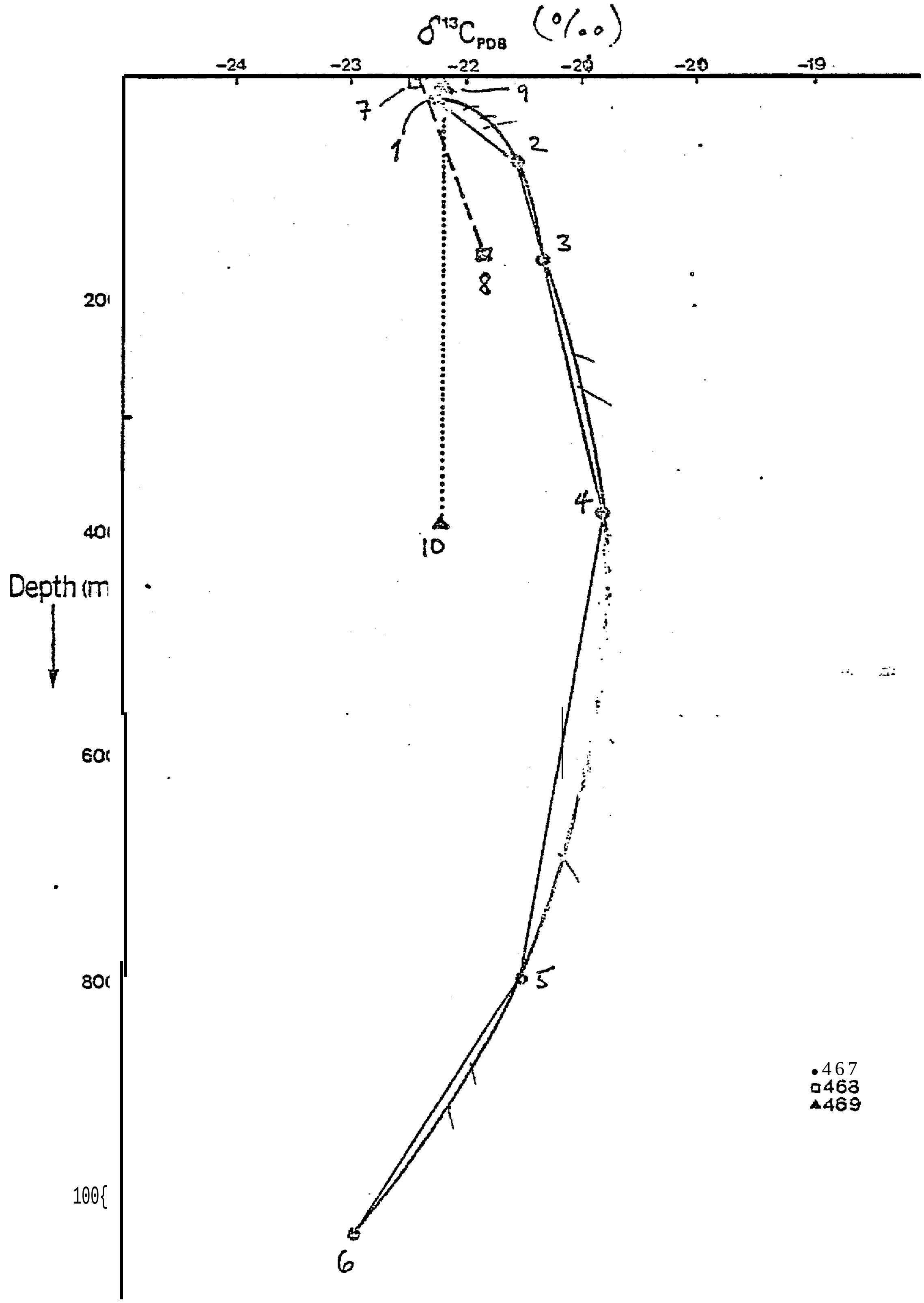

A
(3-3)
Extended
Isoprenoids
Triterpanoids
17α(H), 22 R, S
17β(H)
74
37
0
ppb
15
20
25
30
35
40
C →
B
1.0
0.5
ppm
C
(18-8)
400
200
D
40
20
E
(96-4)
20
10
F
(110-2)
300
150
G
(466-2-3)
80
40
H
(46a-2-3)
150
75
I
BLM 183
(25-31)
200
100
J
300-6
240
120

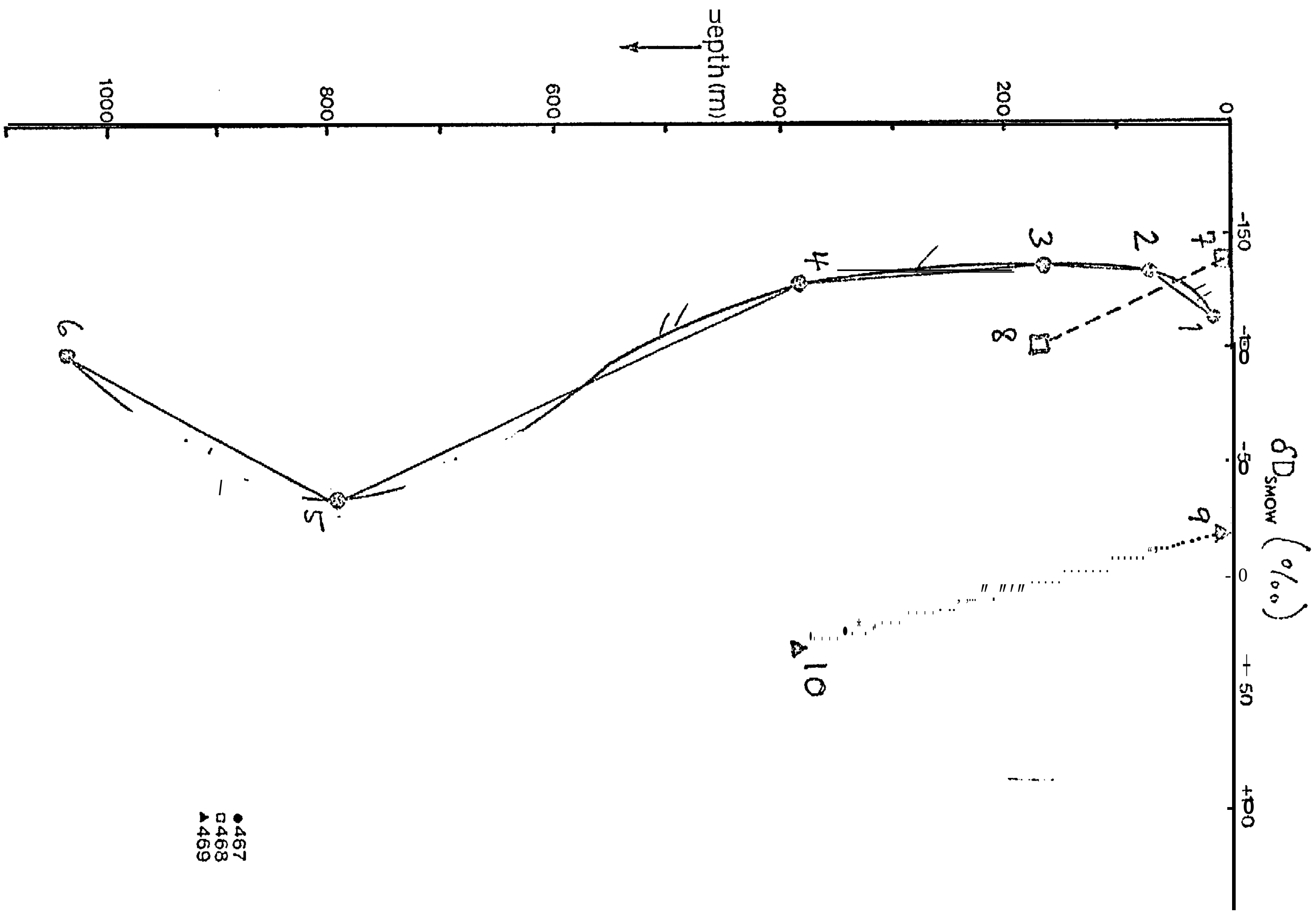

A
B
C
100.0
50.0
M/E
4.0X
4.0X
5.0X
50
100
150
200
250
300
350
400
450
500
55
69
81
95
109
123
135
149
163
177
191
205
218
231
245
260
273
290
315
328
355
362
369
384
119
133
161
175
229
257
367
395
410
74
207
217
249
281
439
455
470


A
(3·3)
5α(H)
5β
4α (methyl)
44
22
0
ppb
20
25
30
C ⟶
B
(8·8)
120
60
0
ppb
C ⟶
C
(18·8)
14
7
0
ppm
C ⟶
D
(41·4)
100
50
0
ppb
C ⟶
E
(85·4)
30
15
0
ppb
C ⟶
F
(110·3)
2.6
1.3
0
ppm
C ⟶
G
(468·2·2)
20
10
0
ppb
C ⟶
H
BLM 193
(25-31)
30
15
0
ppb
C ⟶

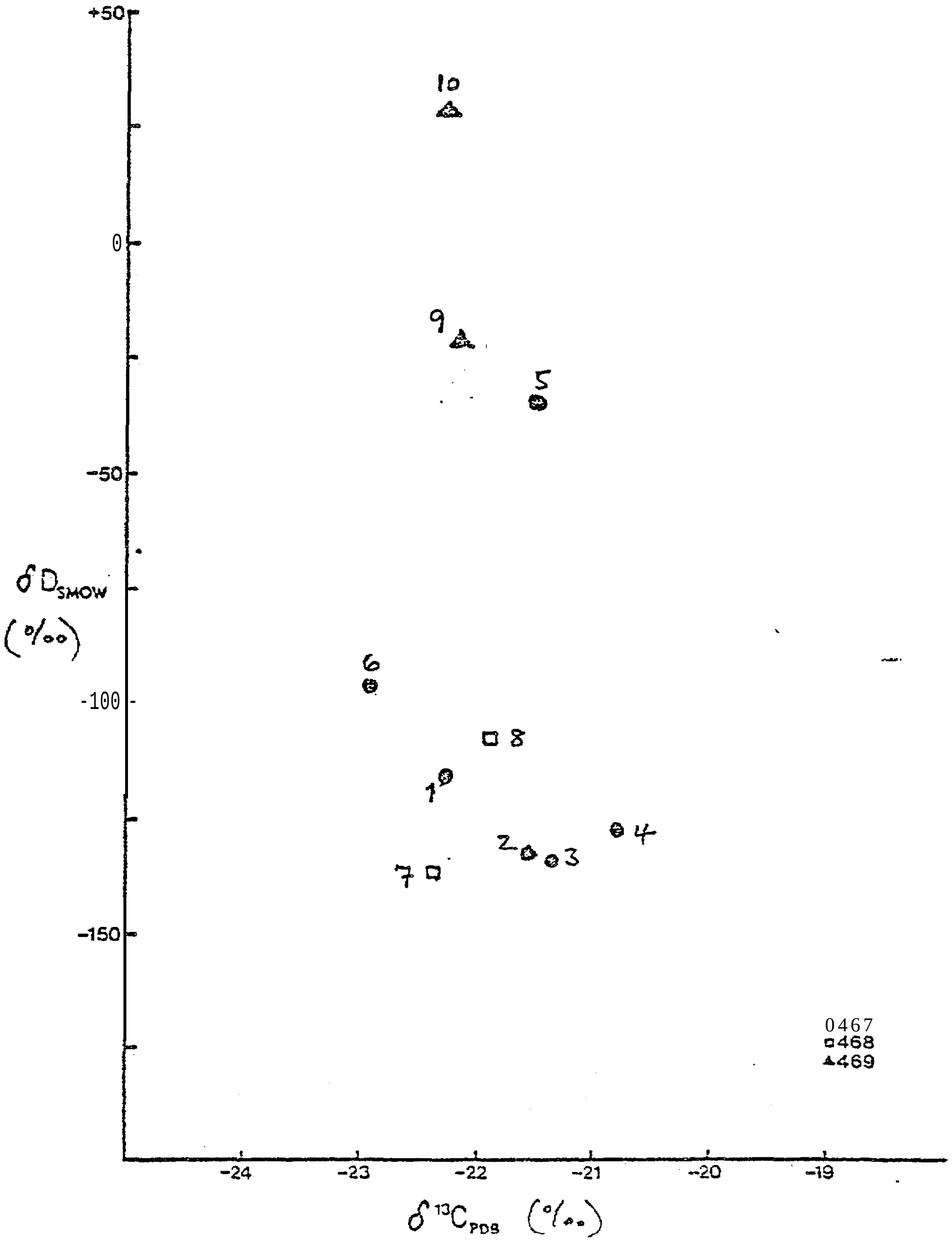

A
m/z 64
100.0
64
1127
S6
1391
S7
1610
S8
B
RIC
1000
1027
1092
1100
1127
15
1192
1200
16
1227
1273
1300
17
1320
Pr
1357
18
1391
Ph
1400
1456
19
1491
1500
1545
20
1572
1610
1600
21
1648
1676
22
1721
1700

F.9

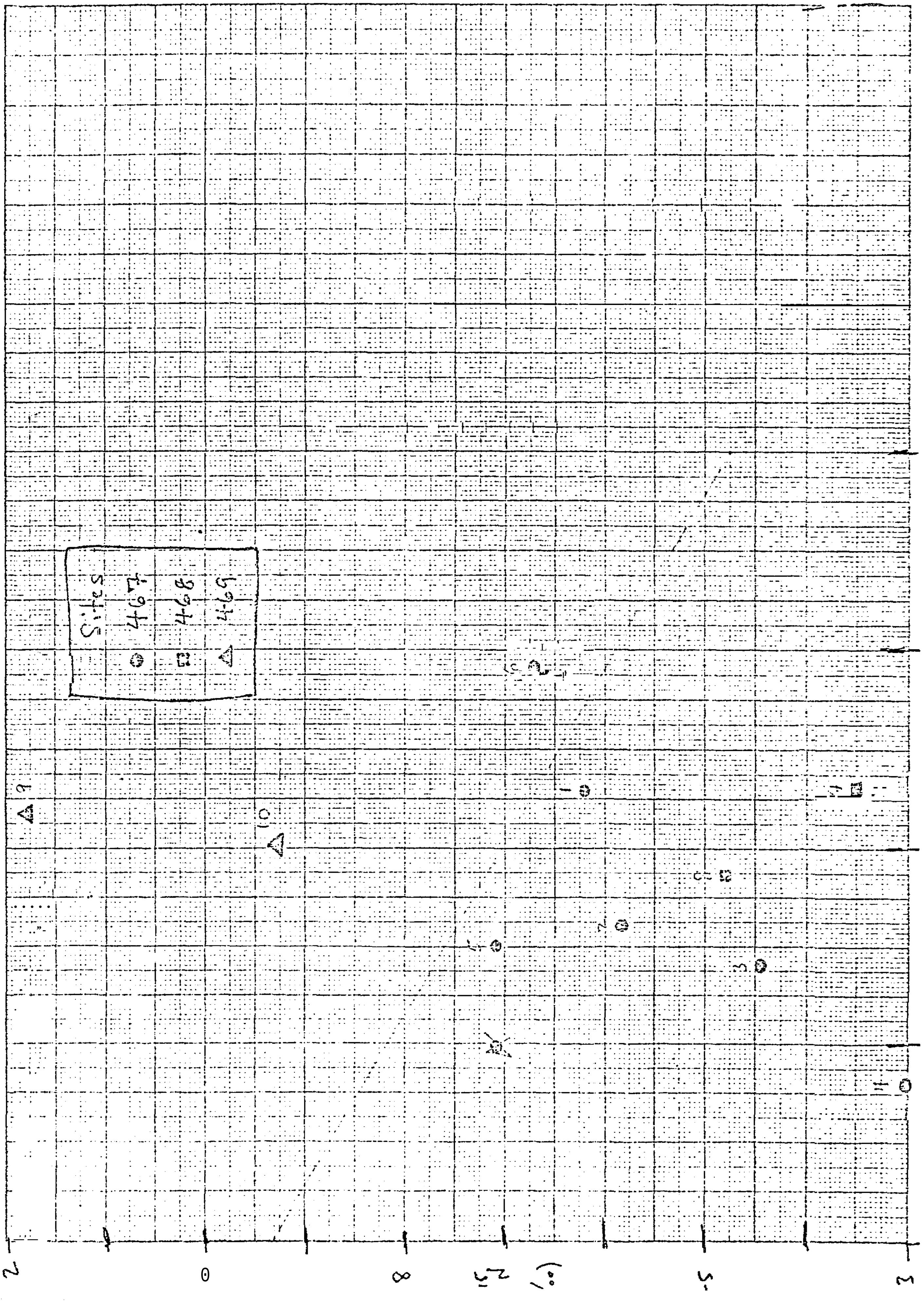

δ13CPDB (0/00)
-24
-23
-22
-20
-20
-19
20
40
60
80
100
Depth (m
1
2
3
4
5
6
7
8
9
10
•467
□468
▲469


δD_SMOW (‰)
-150
-100
-50
0
+50
+100
depth (m)
0
200
400
600
800
1000
1
2
3
4
5
6
7
8
9
10
●467
□468
▲469

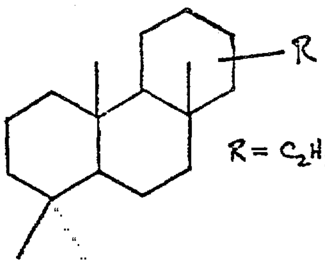
F. 1


+50
0
-50
-100
-150
δD_SMOW
(‰)
10
9
5
6
8
1
2
3
4
7
0467
□468
▲469
-24
-23
-22
-21
-20
-19
δ13C_PDB (‰)

F. 12 (12)

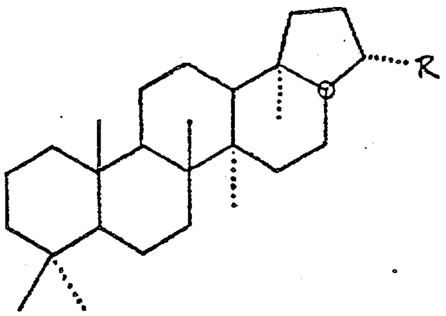


Appendix I. Chemical Structures Cited

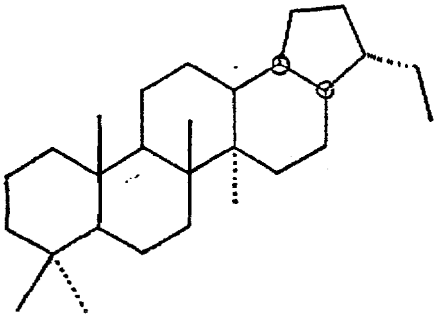


$R = C_2H_5 - C_8H_{17}$

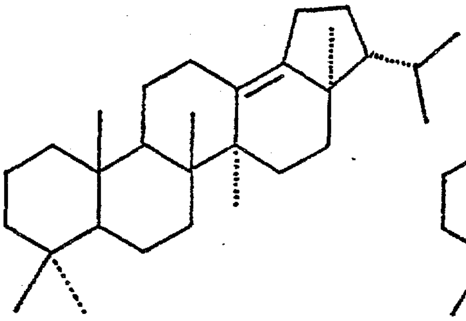
I. Extended diterpanes



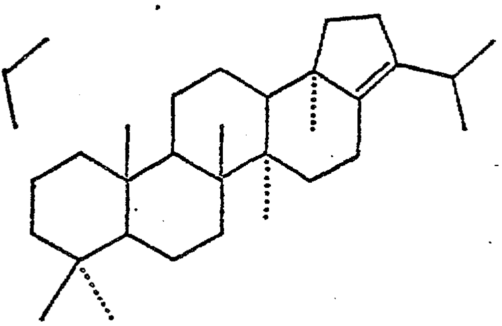
II. 17α(H)-Hopanes



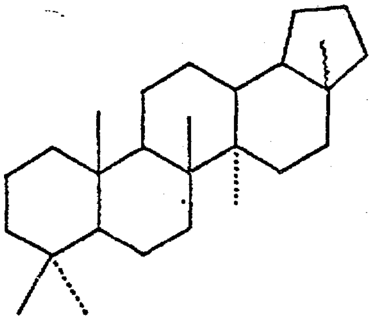
III. 17α, 18α, 21β(H)-28,30-Bisnor-hopane



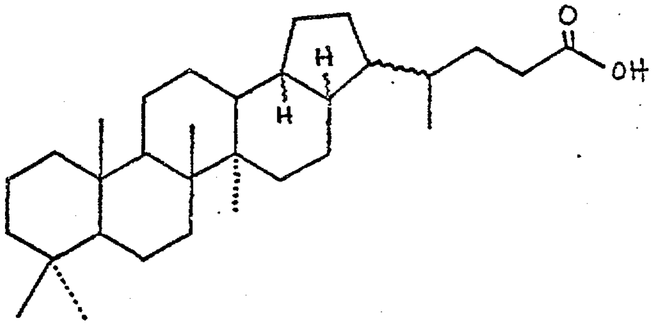
IV. iso-Hop-13(18)-ene



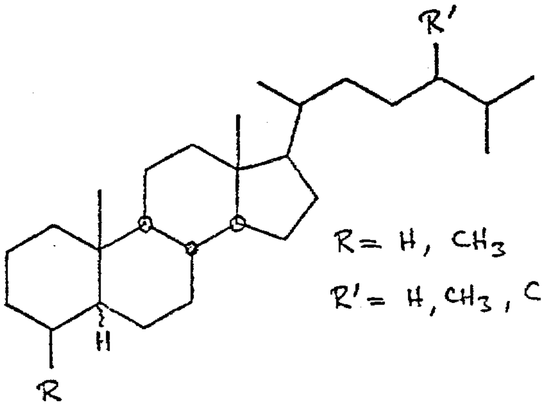
V. Hop-17(21)-ene



VI. iso-Trisnorhopane



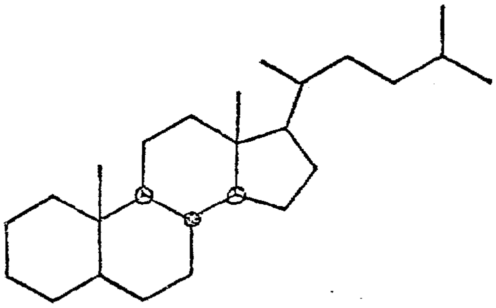
VII. 28-Norbishomohopanoic acid



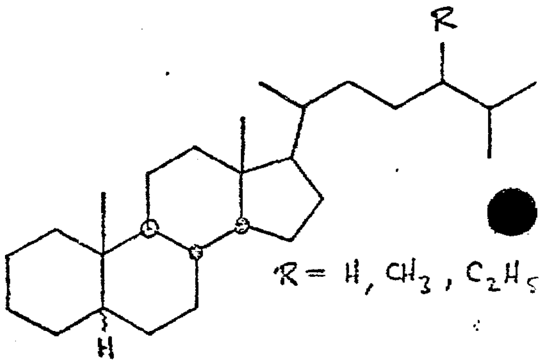
$R = H, CH_3$

$R' = H, CH_3, C_2H_5$

VIII. Steranes

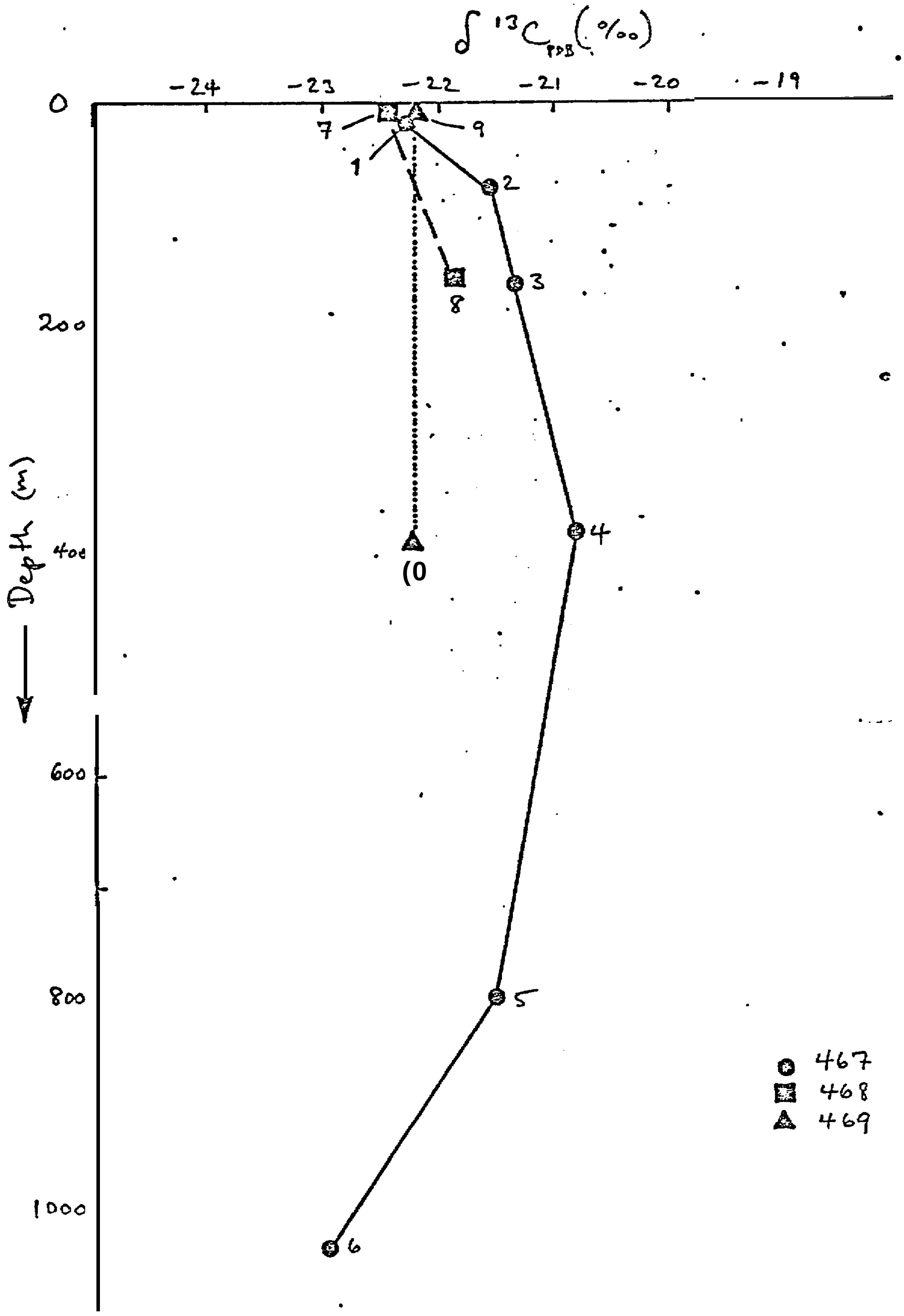


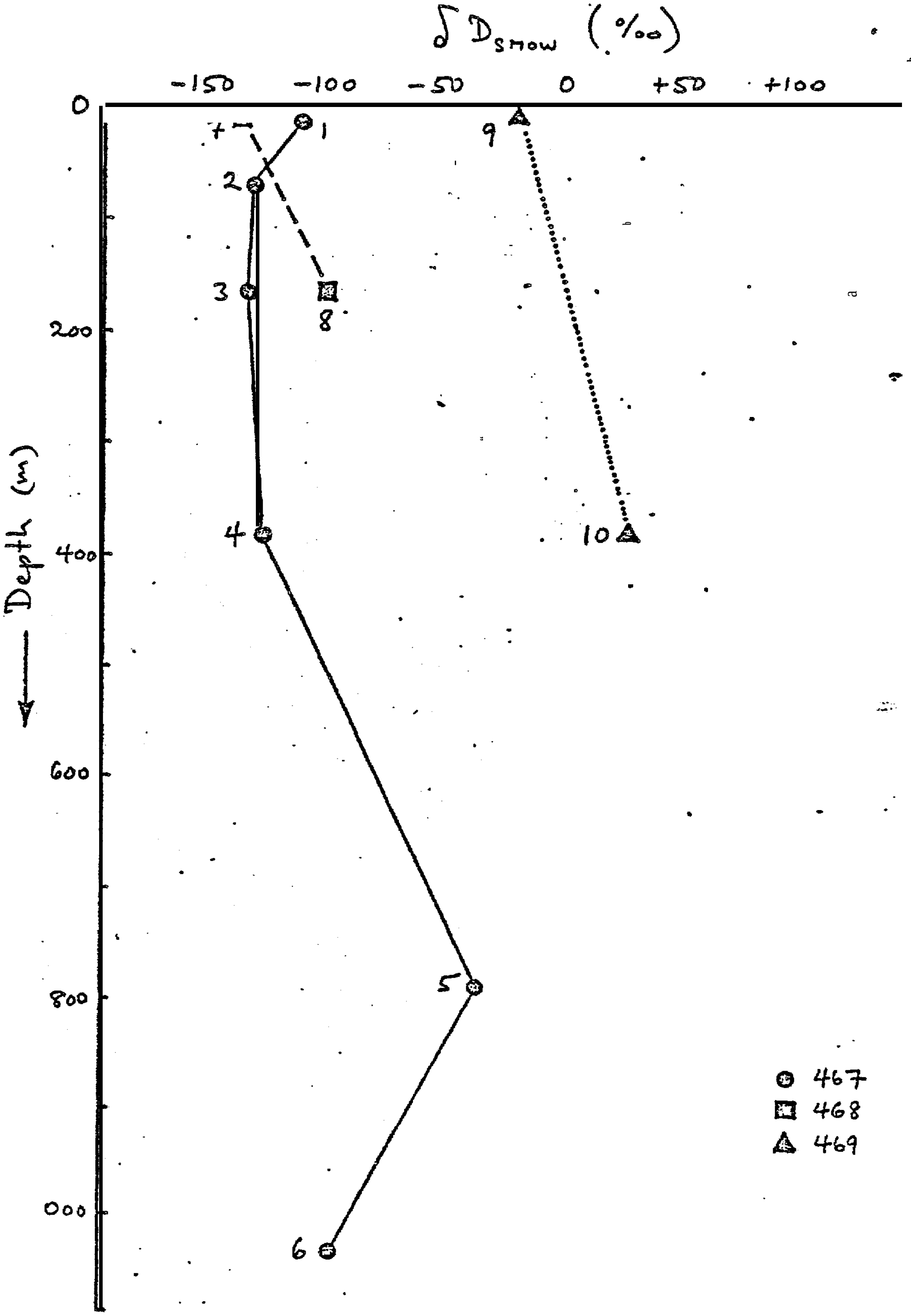
IX. Norcholestane

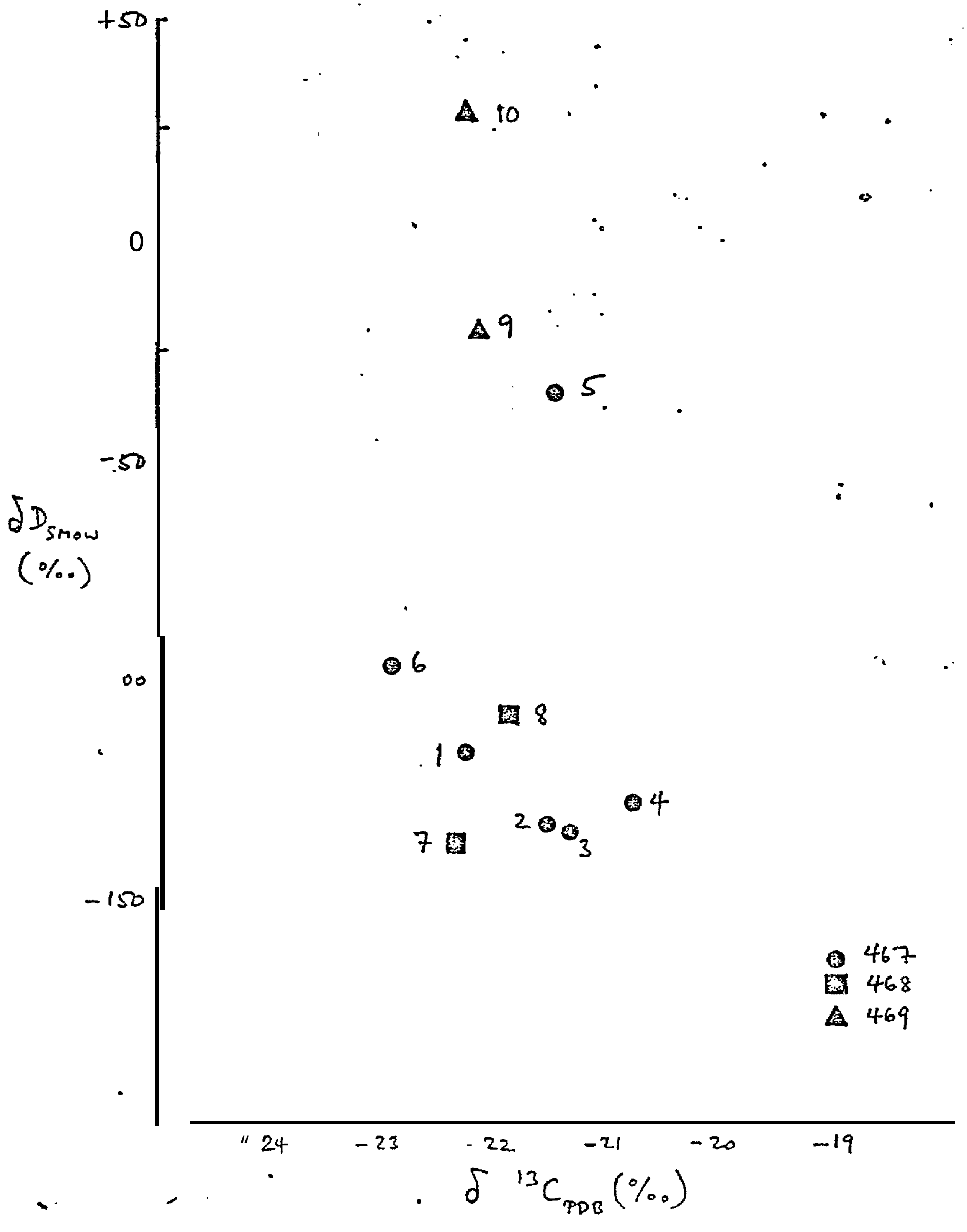


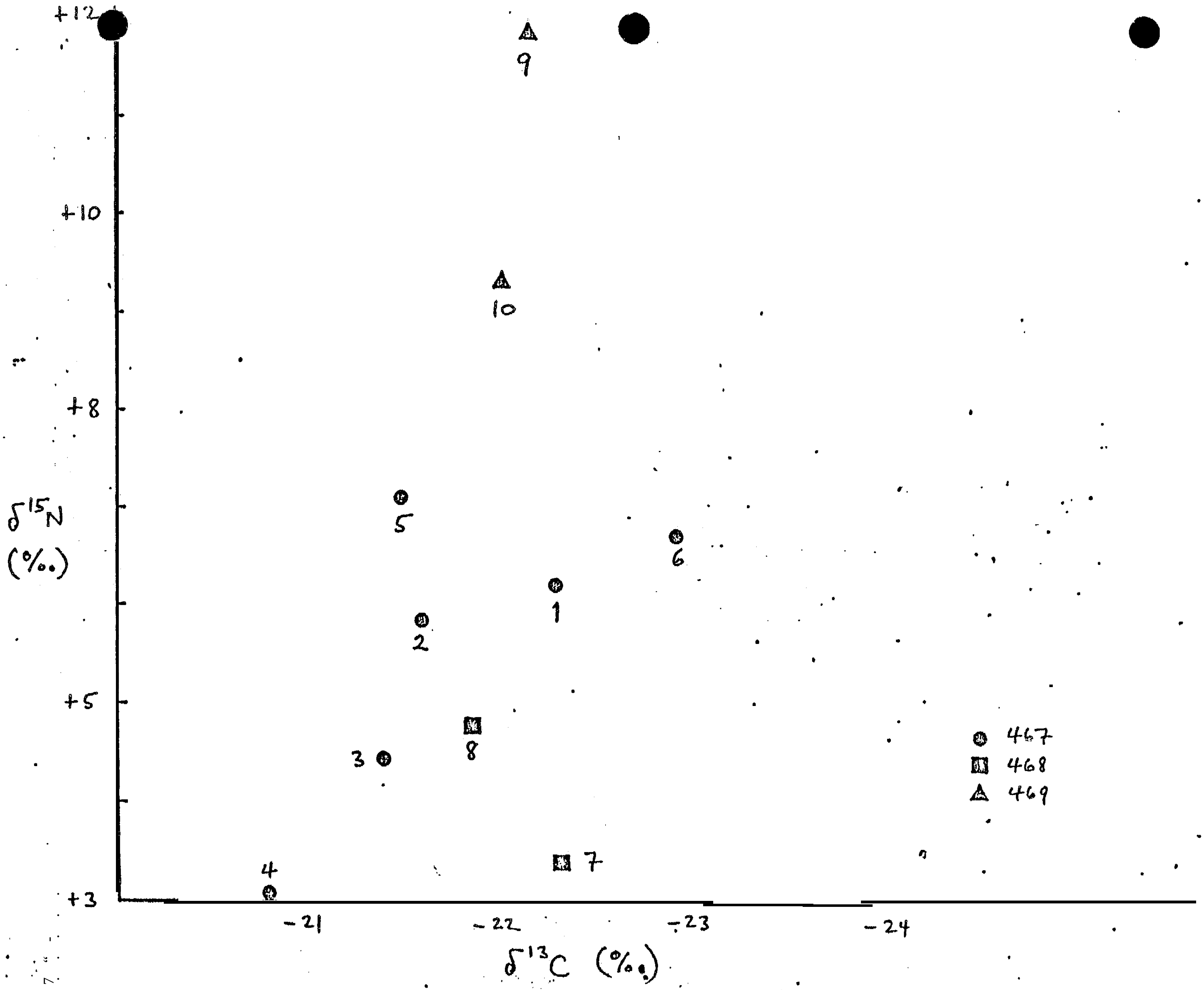
$R = H, CH_3, C_2H_5$

X 8β 14β(H)-Steranes

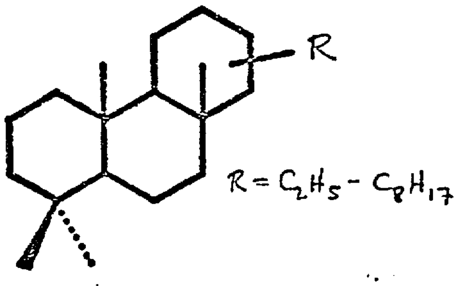

δ 13C PDB (‰)
-24
-23
-22
-21
-20
-19
0
200
400
600
800
1000
Depth (m)
1
2
3
4
5
6
7
8
9
10
467
468
469


δ D_SMOW (‰)
-150
-100
-50
0
+50
+100
0
200
400
600
800
000
Depth (m)
1
2
3
4
5
6
7
8
9
10
467
468
469

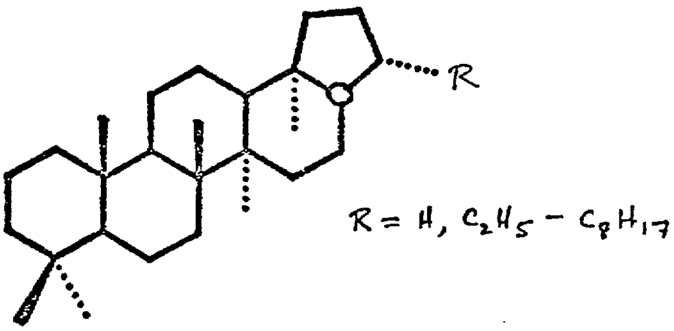

+50
0
-50
00
-150
δD_SMOW (‰)
10
9
5
6
8
1
4
2
3
7
● 467
■ 468
▲ 469
-24
-23
-22
-21
-20
-19
δ 13C_PDB (‰)


+12
+10
+8
+5
+3
$\delta^{15}N$ (‰)
-21
-22
-23
-24
$\delta^{13}C$ (‰)
1
2
3
4
5
6
7
8
9
10
● 467
■ 468
▲ 469

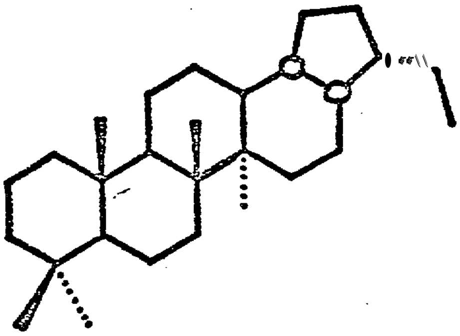
Appendix 2. Chemical structures cited



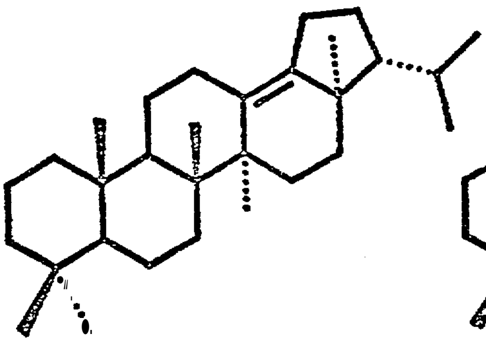
I. Extended diterpanes



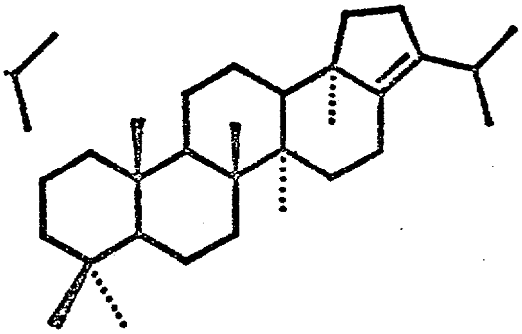
II. 17α(H)-Hopanes



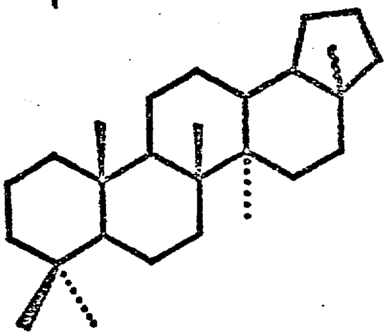
III. 17α, 18α, 21β(H)-28,30-Bis-norhopane



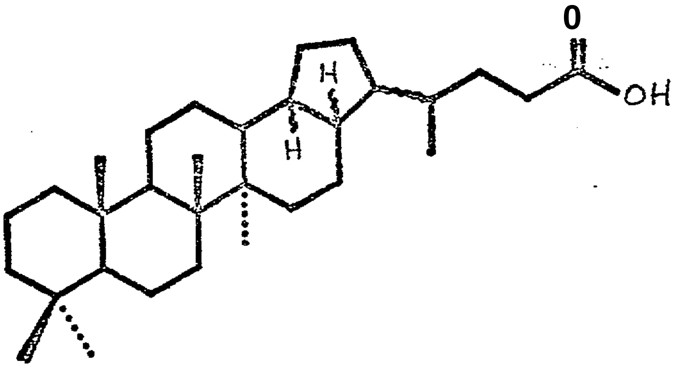
IV. iso-Hop-13(18)-ene



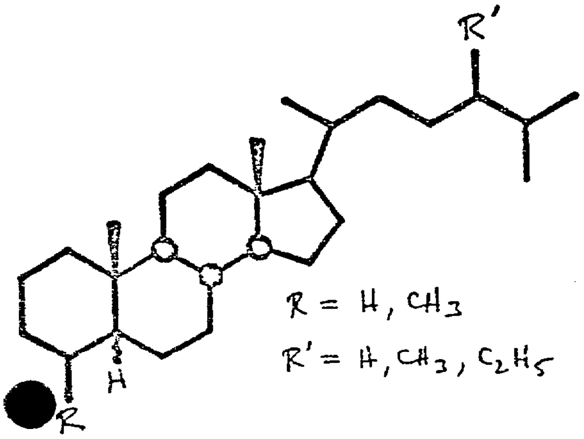
V. Hop-17(21)-ene



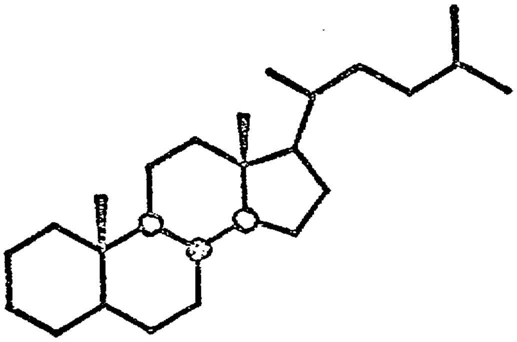
VI. (iso-) Trisnorhopane



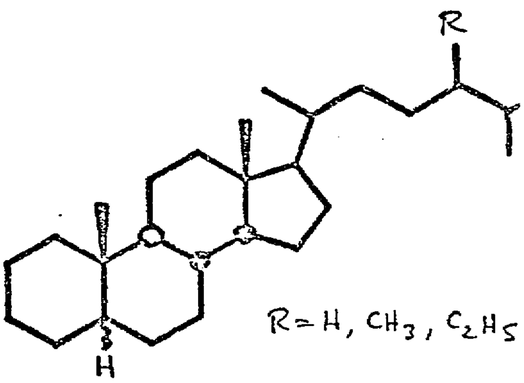
VII. 28-Norbishomohopanoic acid



VIII. Steranes



IX. Norcholestane



X. 8β, 14β(H)-Steranes

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Utility of Molecular Markers and Stable Isotope Compositions in the Evaluation of Sources and Diagenesis of Organic Matter in the Geosphere [1,2]

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ABSTRACT

The analytical techniques of organic geochemistry are used to examine organic matter in terms of its structural and compositional makeup. The sources and transport mechanisms to a sedimentary environment and the geothermal history of this organic matter can be evaluated from such data.

Organic matter is best examined in four separated fractions,. where to some extent (a) gas and mainly (b) lipids (bitumen) are characterized by various molecular markers and homolog distributions in terms of their biogenic precursors and diagenetic alterations, and both (c) humates (and fulvates; in older sediments--the asphaltenes) and (d) kerogen (and protokerogen) are characterized by their bulk properties (eg., H/C, N/C, stable isotope ratios, pyrolysis-GC, and ESR) in terms of their biogenic origins and diagenetic and catagenetic evolution. The transport of organic matter. to sedimentary environments consists of autochthonous production with a varying allochthonous influx of detritus by predominantly potamic, eolian and in some cases, ice-rafting mechanisms, followed usually by redistribution from turbidite and contour flows. Predation takes place throughout the transport and especially once deposited, which is followed by diagenesis and eventually catagenesis.

All of these processes contribute to the ultimate fingerprint of the organic matter in sediments. Thus, the overall analyses of organic matter with the effects of its influx on the environment, need to be carried out in such detail, in order to delineate the origins, with the geologic history, of that organic matter and to correlate the organic geochemistry of the Recent realm with that of the geologically ancient realm (i.e., chemical evolution).

INTRODUCTION

The isolation and identification of fossil. pigments from geological samples by Treibs (1934, 1936) set the stage for modern organic geochemistry. The concept of the chemical evolution of life based on the elucidation of molecular fossils (markers) (Calvin, 1969) has been an active academic persuit since the advent of modern analytical. instrumentation (eg., Eglinton and Murphy, 1969). Innumerable diversifications and applications of organic geochemical methodology have occurred since (eg., Nriagu, 1976; Krumbein, 1978; Hunt, 1979; Tissot and Welte, 1978; Swain, 1970; Colombo and Hobson, 1964; Hobson and Louis, 1966; Hobson and Speers, 1970; Schenck and Havenear, 1969; Gaertner and Wehner, 1972; Tissot and Bienner, 1974; Campos and Goñi, 1977).

The biogenetic and/or geogenetic origin of carbonaceous sediments is reflected in the constitution of their organic matter as well as their mineralogy and lithology. Aquatic sediments are the ultimate depositories of posthumus organic debris. This organic matter is composed of both autochthonous residues and detritus derived from allochthonous sources (Simoneit, 1975). Modern aquatic sediments receive organic detritus from natural and anthropogenic sources. Thus, the pollutant chemistry is en integral part of the "natural" chemistry and is subject to the same environmental processes (eg., Eglinton et al., 1975).

The preservation of organic matter in sediments depends on the initial diagenetic processes involving microbial degradation and chemical conversion, coupled with the environmental conditions of acidity and redox potential (eg., Didyk et al., 1978).. Examples of these processes for the marine environment are shown in Fig. 1. Then, during subsequent sediment maturation and lithification, the organic matter is modified by the effects of temperature, pressure and petrology (eg., Hunt, 1979; Tissot and Welte, 1978; Simoneit, 1978a; Tissot et al., 1971).

The analytical techniques of organic geochemistry are ideally suited to examine the character of such organic matter in terms of its structural and compositional makeup (Simoneit, 1978a). The sources, the diagenetic and catagenetic histories and the transport mechanisms to the sedimentary environment of this organic matter can then be evaluated from such data. It should be noted that in the following discussion, organic matter is comprised of gas, lipids (bitumen), humic substances (with fulvic substances) and kerogen (with "protokerogen").

Here, I shall illustrate and summarize some of the analytical techniques with examples of typical data for the various types of organic. matter found in sediments.

ANALYSES OF ORGANIC MATTER

A typical. experimental flow schematic for sample workup is shown in Figure 2. This basic organic geochemical procedure has been in routine use. for several years, with only minor modifications tailored to specific problems (eg., Simoneit, 1980a; Simoneit et al., 1979; Boon et al., 1978; Deroo et al., 1978).

Interstitial gas analyses are usually accomplished by gas chromatography (GC) and confirmed by gas chromatography-mass spectrometry (GC/MS) (eg., Hunt, 1975; Simoneit et al., 1979). Stable isotope analyses have also been carried out to delineate sources and genetic origins of gases (eg., Claypool and Kaplan, 1974).

The wet sediments are commonly freeze-dried, powdered and extracted in a Soxhlet apparatus or by ultrasonic or shaker agitation (Recent sediments are extracted directly without drying). The extracted lipids or bitumens are separated by column (liquid)-, thin layer- (TLC), gel permeation- or high-pressure liquid chromatography into discrete fractions, which are then analyzed by GC and GC/MS (eg., Simoneit, 1978a). Prior to separation, the lipids can also be derivatized (eg., esterification of free fatty acids) to reduce the polarity of some compounds. Saponification of whole sediment or lipids can be employed to de-esterify bound lipids (eg., waxes). Argentation-TLC can be utilized to separate saturated from olefinic compounds. Complex fractions can be further separated by molecular sieving or urea (also thiourea) adduction into normal and branched-cyclic components.

Other ancillary techniques which can be applied to lipid analyses are stable isotope ratios, W-visible spectrophotometry, infrared spectrophotometry and nuclear magnetic resonance spectroscopy.

RESULTS AND DISCUSSION

The organic matter of sediments can be divided into the following categories based on the limitations imposed by the analytical procedures

Gas	Lipids (bitumen)	Humates (with fulvates)	Kerogen
(cl-c*, + CO_2, H_2S, etc.)	(C_8-C_{40}+)	(Macromolecular, M.W. ∿10^3 to >10^6)	(Macromolecular , > humates)
Minor amount of total $C_{org.}$	Minor amt. (Max. ∿10%)	Variable amount	Major amount

Gas

Interstitial hydrocarbon gases consist primarily of methane with [illegible] amounts of ethane and higher hydrocarbons to about C_8. Biogenic hydrocarbon *gases* usually have $CH_4/(C_2H_6 + C_3H_8)$ ratios greater than 1000, while [illegible] a petrogenic (thermogenic) origin have ratios less than 50 (Bernard [illegible] 1976) . For example, the $C_1/(C_2+C_3)$ ratios for shallow sediment gases [illegible] Guaymas Basin, Gulf of California range from 41-150 and thus indicate a mixed origin of biogenic (CH_4) and thermogenic (C_2-C_8) hydrocarbons (Simoneit <u>et</u> <u>al</u>., 1979). More detailed analyses of the trace components in interstitial gas can be found in the work of Hunt and Whelan (1978) and Thompson (1979) . Stable isotope analyses of carbon and nitrogen have been us as guides to sources of natural gas (eg.,Stahl,*1977}*. For example, biogenic methane has a mean $\delta^{13}C$ range of about -60 to -75 ‰ , with isolated values outside this spread (eg., Degens, 1979; Simoneit <u>et al</u>., 1979 . for mature thermogenic methane, the $\delta^{13}C$ values cluster from -20 to .,, [illegible] (Stahl, 1977).

More data are needed to identify the origins and to different. [illegible] biogenic hydrocarbons other than CH_4 (eg., ethylene, propylene, etc. [illegible] the thermogenic analogs (eg., neopentane, thiophene, etc.).

Humic and fulvic substances are separated from exhaustively extracted sediments (after removal. of carbonates by HCl treatment) by shaking with aliquots of 0.1-0.3 M sodium hydroxide solution until the extracts are colorless (Stuermer et al., 1978; Stuermer and Simoneit, 1978). The combined attracts are then centrifuged' and the supernatant is acidified with hydrochloric acid to pH 1 to precipitance the humic substances. The supernatant, after removal of humic substances contains the fulvic material, which can be separated by lyophilization after dialysis or after ion exchange chromatography which remove the salts. The humic substances are washed with 0.01 M HCl and lyophilized to yield the protonated form.

The residual sediment is then treated with hydrofluoric acid to remove silicate minerals yielding a kerogen concentrate. Kerogen with a low ash content can be obtained by density flotation (Stuermer et al., 1978).

Both humates and kerogens have been characterized mainly by bulk properties and to a limited extent by chemical degradation (especially kerogen). These analyses consist of. elemental composition (eg., H/C, O/C, N/C, etc.), stable isotope composition (eg., $\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$, δD, etc.), electron spin resonance and nuclear magnetic resonance spectrometry, and for kerogens also a determination of the vitrinite reflectance (Simoneit, 1978a). Pyrolysis GC and pyrolysis GC/MS have also proven to be of utility for analysis of kerogen and humates, since they provide a fingerprint pattern and are rapid analytical methods (eg., Van de Meent et al., 1980; Larter and Douglas, 1978; Philp et al., 1978).

Lipids

The lipids of sediments, especially the hydrocarbons, have been most extensively examined. The compound classes which are commonly analyzed as lipid components and which have reasonable stability over geologic time periods are: hydrocarbons (n-, iso-, anteiso-, alkenes, aromatic and isoprenoidal), fatty acids (n-, iso-, anteiso-, unsaturated, isoprenoid and dicarboxylic), fatty alcohols, ketones, wax esters, steroids, terpenoids (sesqui-, di-, sester-, tri- and tetra-), and tetrapyrrole pigments (Simoneit, 1978a, 1980). The following additional compound classes are analyzed primarily in Recent sediments, since their geologic half-lives are short: chlorin and carotenoid pigments, amino acids and peptides, purines and pyrimidines, and carbohydrates (Simoneit, 19.78a). The homolog distributions and molecular markers of the first category of compound classes will be briefly illustrated with some examples 'and further details can be found elsewhere (Simoneit, 1978a, and references cited therein].

Distributions of Homologs

Some typical examples of homologous compound distributions in lipids of sediments are shown in Figures 3 and 4. Sample 36-330-10-1, 95-102 cm, which is of Jurassic age from the South Atlantic, exhibits n-alkanes maximizing at n-C_{17} and n-C_{19} (Fig. 3A) and even carbon numbered n-fatty acids with a maximum at n-C_{16} (Fig. 3E). Both these distributions are indicative of primary bacterial lipid residues and there are only traces of allochthonous homologs > C_{21}. These lipids are of a marine origin (Simoneit, 1980b). The n-alkanes are superimposed on a minor unresolved complex mixture of branched and cyclic hydrocarbons (hump) which maximizes in the GC retention region of C_{17}. Such humps were found for bacterial residues in surface sediments at natural gas emanations in Chile (Simoneit and Didyk, 1978; Simoneit et al., 1980).

Sample ML71-2-23, 8.0m is from Mangrove Lake, Bermuda, of Recent origin in a highly productive sapropelic environment (Hatcher et al., I-977, 1980). The n-alkanes (Fig. 3B) show maxima at n-C_{17} from primary algal synthesis, at n-C_{22} from microbial degradation of algal detritus and a minor one at n-C_{29}, with a strong odd carbon number predominance $> C_{26}$, derived from higher plant wax (Simoneit, 1975). The maximum at n-C_{22} with no carbon number predominance is superimposed on an unresolved hump which also maximizes in that retention region. The n-fatty acids (Fig. 3F) exhibit a bimodal distribution where the predominant maximum at C_{28} and C_{30} is of a plant wax origin and the minor homologs $< C_{20}$ are of a marine (or lacustrine) derivation.

The Black Sea is a sink for terrigenous lipids from plant wax as indicated by the example (Fig. 3C, G). The n-alkanes exhibit a maximum at n-C_{29} with a strong odd-to-even carbon number predominance, typical of higher plant wax (Simoneit, 1974, 1977b, 1978b). This is corroborated by the n-fatty acids with their maxima at n-C_{16} and n-C_{26} and strong even carbon number predominance, where the homologs $> C_{20}$ are of an allochthonous terrigenous origin (Simoneit, 1977b, 1978b).

Sample 18-175-2-2, 45-47 cm is an example of a reducing microenvironment, where the n-alkanes (Fig. 3D) exhibit a strong even-to-odd carbon number predominance for the homologs $< C_{24}$ and the distribution follows that of the n-fatty acids $< C_{24}$ (Fig. 3H). These even n-alkanes ($< C_{24}$) may be derived from reduction of fatty acids or of olefins from fatty alcohols (Simoneit, 1977a; Tissot and Welte,1978). The n-alkanes $> C_{24}$ with the odd carbon number predominance and maximum at n-C_{29} are derived from plant wax.

Strong euxinic conditions of sedimentation are reflected in the saturated hydrocarbons by an excess of phytane to pristane as for example, for the Cretaceus black shale from the Cape Verde Basin (Fig. 4A) (Simoneit, 1980a). The n-alkanes exhibit a bimodal distribution with an odd-to-even carbon number predominance and maxima at n-C_{17} and n-C_{31}. The homologs c C_{21} are of an autochthonous origin and those > C_{22} are derived from plant wax. The n-fatty acids (Fig. 4E) also have this same dual. origin, as indicated by the maxima at n-C_{16} and n-C24, with the strong even carbon number predominance. The presence of pristanic and phytanic acids should be noted, *as well* as the large amount of phytane. The preservation of the $C_{20}>C_{19}$ isoprenoid skeleton is a consequence of the anoxic depositional environment (Didyk et al.., 1978).

The n-alkane distribution of a seep oil from the Norwegian-Greenland Sea is shown in Fig. 4B. It exhibits a maximum at C_{20} and has no carbon number predominance. The n-alkanes are superimposed on the broad unresolved hump which has a maximum at about C_{25} retention and range from C_{12} to C_{31}.

Alkan-2-ones are also found in sediments and they are derived from microbial alteration of n-alkanes or n-fatty acids (Arpino, 1973; Simoneit, 1980a). The n-alkan-2-ones of the Pleistocene sample 42B-381-1-4, 104-115 cm from the Black Sea are shown in Fig. 4F. They exhibit a strong odd carbon number predominance with *a* maximum at C_{29}, reflecting an origin from alkanes of higher plant wax. The 6,10,14-trimethylpentadecan-2-one (Structure I) and 6,10-dimethylundecan-2-one (.11) are the predominant isoprenoidal ketones present.

Fatty alcohols are ubiquitous in sediments (Sever and Parker, 1969) and an example *is* shown in Fig. 4D. Sample 12-114-5-5, 80-140 cm is of Oligocene age from the North Atlantic and consists of terrigenous clay (Simoneit, 1980a). The n-fatty alcohols exhibit a bimodal , distribution with a major maximum at n-C_{28}, a minor one at n-C_{16} and a strong even carbon number predominance. The homologs > C_{20} are typical of higher plant wax alcohols.

Eolian particulates are carried by trade winds far out to sea and they contain lipids composed of primarily plant wax blown off from continental sources (Simoneit *et al*., 1977; Simoneit, 1977c). Dust sample DC 5 from over the Atlantic Ocean is shown as an example in Fig. 4C and G for comparison purposes. The n-alkanes show a strong odd carbon number predominance and maximum at n-C_{31} only. The n-fatty acids show a bimodal distribution with a strong even carbon number predominance and maxima at n-C_{16} and n-C_{26}. The n-alkanes > C_{20} and the n-fatty acids > C_{20} are typical. of plant wax. The n-fatty acids < C_{20} have probably a dual origin from the sea slick and from desiccated lacustrine muds. Then_-fatty alcohols of dust sample E2 from over the Atlantic are shown in Fig. 4H. They exhibit a bimodal distribution with a strong even carbon number predominance and maxima at C_{18} and C_{28} The homologs > C_{20} are again typical of higher plant wax alcohols.

The distribution patterns of homologous compounds in lipids can be *used* to make partial assessments of the genetic origins of those compounds. *This* approach can be further strengthened by coupling it with the analysis and interpretation of the molecular fossils in the lipids. Lipids have also been analyzed for stable carbon isotope content which can lend further support *to* their genetic origin (eg., Simoneit, 1980a).

Molecular Markers

Molecular markers which are characteristic of a biogenic (terrigenous and/or marine) or of a petrogenic origin can be identified in lipid fractions. The n-alkanes, n-fatty acids, n-alkan-2-ones, n-fatty alcohols and isoprenoids can be considered as molecular markers based on their homolog distributions.

However, structurally more complex molecules have a much greater information content. The terpenoids are the compound groups which have had the greatest utility as specific markers.

The sesquiterpenoi'ds that have been identified in sedimentary environments are primarily cadalene (III), with various tetrahydro analogs. They are of both a marine (algal) and terrigenous origin (Simoneit and Kaplan, 1980).

The diterpenoids that have been characterized fit into two classes, those derived from terrigenous sources (Simoneit, 1977a) and extended diterpanes of a probable *marine* origin (Simoneit, unpublished data). The terrigenous diterpenoids consist of a large number of compounds and the most abundant analogs are dehydroabietic acid (IV), dehydroabietin (V), dehydroabietane (VI), simonellite (VII) , retene (VIII) , tetrahydroretene (IX), fichtelite (X), pimanthrene (XI), 17-nordehydroabietane (XII), iosene (XIII), 13-methylpodocarpa-8,11,13-triene (XIV), and norsimonellite (XV) (Simoneit, 1977a, in preparation). The extended diterpanes were first identified in shale and petroleum (eg., Reed, 1977), where they are ubiquitous, and then in Recent sediments. Most of their occurrences were coupled with the presence of the 17α(H)-hopane series of triterpanes, which are geologically mature, i.e., old (Simoneit and Kaplan, 1980). These extended tricyclic diterpanes range from $C_{19}H_{34}$ to $C_{26}H_{48}$ and sometimes to $C_{29}H_{54}$ with very similar distributions. The inferred skeleton for the C_{19}-C_{24} homologs is Structure XVI. The $C_{26}H_{48}$ homolog (in some cases to $C_{29}H_{54}$) is resolved on capillary GC into an R and S diastereomeric pair (Simoneit and Kaplan, 1980). Some distributions are shown as examples in Figure 5. The samples from the Southern California Bight (Fig. 5C,D) are contaminated by petroleum seepage, indicating that the extended diterpanes are syngenetic with the 17α(H)-hopane series. However, the extended diterpanes in the Recent sample from Walvis Bay (Fig. 5B) must be derived from a marine source, since no petroleum contamination is evident.

The triterpenoids found in most pelagic sediments are of an autochthonous origin and are usually comprised of the hopane and to a lesser extent the moretane series. Hemipelagic and lacustrine sediments can also receive triterpenoid residues from terrigenous sources. The homologs consist of trisnorhopane (XVII, R=H), norhopane (XVII, $R=C_2H_5$), hopane (XVII $R=C_3H_7$) and extended hopanes ranging from C_{31} *to* C_{35} (XVIII) with minor amounts of the corresponding moretanes (XIX). The 17β(H) stereochemistry predominates in Recent, immature sediments (Dastillung and Albrecht, 1976) and various triterpenes such as diploptene (XX), 17β(H)-hop-21(22)-ene (XXI) and hop-17(21)-ene (XXII) are also Present (Brooks et al., 1977). The Recent sediments from the Gulf of California and Walvis Bay (Fig. 5A and B) illustrate this point in that only 17β(H)-hopanes and hopenes *are* present. The extended 17β(H)-hopanes occur as only the 22S diastereomer in Recent sediments as the direct markers of biosynthesis. In ancient sediments or crude oil, the hopanes occur "as the 17α(H)-stereomers and the extended 17α(H)-hopanes are found as 22R and 22S diasteromeric pairs, where full maturity is indicated by an S/R ratio of one (Dastillung and. Albrecht, 1976; Brooks et al., 1977; Simoneit and Kaplan, 1980). The samples from the Southern California Bight {Fig. 5C and D) show this type of distribution, where in sample 193 only petroleum residues and matured 17α(H)-hopanes are found and in sample 575, a mixture of Recent and ancient triterpenoids and allied lipids are present. Also, a $C_{28}H_{48}$ triterpane is a major analog in the Southern California Bight sediments and it has been identified as 17α(H),18α(H),21β(H)-28,30-bisnorhopane (XXIII)(Seifert et al., 1978; Simoneit and Kaplan, 1980). This compound appears to be a specific marker for Southern California petroliferous residues, as it is not commonly found in other areas (Simoneit and Kaplan, 1980).

Steroidal compounds are common in sediments and they undergo complex diagenetic reactions yielding various series of hydrocarbons, alcohols and ketones (XXIV)(Gaskell, 1974; Lee et al., 1977, 1979; Huang and Meinschein 1979). The saturated hydrocarbons are comprised of the steranes [XXV, eg., cholestane, 5α(H) vs. coprostane, 56(H)], diasteranes (XXVI) and traces of other isomers. Examples of sterane distributions are shown in Fig. 6 for a Cretaceus and a Jurassic sample from the South Atlant ic. The 5α stereomers predominate over the 5β (Simoneit, 10b). Unsaturated hydrocarbons are found mainly as ster-2-enes, ster-4-enes, diasterenes and monoaromatic steranes (XXVII), and functionalized analogs are found as stan-3-ols and stan-3-ones. Various series of 4-methylsteroids have also been identified in some environments (eg., Mattern et al., 19.70; Simoneit, 1974, 1977b).

Other minor components that can be utilized as molecular markers are tetraterpenoids, iso- and anteiso- alkanes or fatty acids, hydroxy fatty acids (eg., Boon et al., 1977), wax esters (Boon and deLeeuw, 1979), tetrapyrrole pigments {Baker, this volume) and aromatic hydrocarbons (eg., Windsor and Hites, 1979). The tetraterpenoids are generally quite labile (eg., carotenoids), but can be preserved in anoxic environments (Watts and Maxwell, 1977). Tetrapyrrole pigments have been extensively studied and they are excellent molecular markers as well as geothermal sensors (eg., Baker and Smith, 19.74; Baker, this volume).

Aromatic hydrocarbons are found in hemipelagic sediments and are composed mainly of polynuclear aromatic compounds with limited alkyl substitution. These polynuclear aromatic hydrocarbons are proposed as markers of pyrogenic activity (eg., Windsor and Hites, 1979). In anoxic sediments (Recent to Cretaceus), significant amounts of perylene (XXVIII) are found (Didyk et al., 1978; Simoneit, 1978b). This compound appears to be derived primarily from the diagenetic alteration of naphthol pigments under reducing conditions and not from pyrolytic sources. Aromatic hydrocarbons can also be derived from olefinic cyclic precursors of natural origin by disproportionation or dehydrogenation reactions (eg., Spyckerelle et al., 1977; Spyckerelle, 1975). The major examples of such compounds which have been identified in sedimentary environments are summarized in Fig. 7. The compounds in rows a and b are derived from sesquiterpenoids of both marine and terrigenous origins and from diterpenoids of a terrigenous origin (Simoneit, 1977a). The aromatized steranes (XXVII) are derived from diasterenes (ring D olefin of XXVI) (Spyckerelle, 1975). The compounds in row c are derived from the olefins (ring E or side-chain) of the hopane and/or moretane series by successive dehydrogenation which proceeds from ring D to A (Greiner et al., 1977). These compounds can be considered as markers of a predominantly marine (microbial) origin, since their precursors are widespread in these environments (Rohmer, 1975; Rohmer and Ourisson, 1976). The compounds in row d are derived from triterpenoids of higher plants by loss of the functionalized A ring (Spyckerelle, 1975; Spyckerelle et al., 1977). They occur as minor components in environments receiving terrigenous detritus. Pentacyclic aromatic hydrocarbons (analogs to those of row c, Fig. 7), where the aromatization occurred from ring A to D, and the series in row d (Fig. 7) have been identified in environments receiving dominantly terrigenous drainage (eg., in Indonesia, P. Albrecht, private communication; Amazon River, R. Hites, private communication). These compounds can be considered as indicators of terrestrial higher plants.

Humates (and fulvates)

Both humic and fulvic substances are mixtures of complex macromolecules, and the latter are of lower molecular weights and thus soluble in dilute HCl. Little is known about the detailed structures of the compounds concerned and the analytical data consist of their various bulk properties (eg., Schnitzer and Khan, 1972; Stuermer, 1975; Hue, 1973, 1978). It has been shown that humic substances decrease in concentration with. depth of burial or geologic age and are probably incorporated into the kerogenous material (eg., Nissenbaum and Kaplan, 1972; Stuermer and Simoneit, 1978). This trend is illustrated in Fig. 8 showing the decrease of humates with depth to the upper Jurassic for DSDP site 44-391 (Stuermer and Simoneit, 1978). The abundance of humates at this site at depths of 600-1000 m sub-bottom indicates that a significant contribution of land-derived organic matter had occurred (Deroo et al., 1978). Humic substances from Recent environments have been characterized by bulk properties such as elemental (C,H,O) composition, stable isotope ratios (C,H,N), and electron spin resonance (Stuermer et al., 1978). The sources of this organic matter could be delineated by coupling these parameters with the same data for the respective kerogens. Data for fulvates are sparse, although they are being determined in sea waters. Both these carbon fractions should be characterized for more environments to yield better baseline data.

Kerogen

Kerogens are also complex mixtures of high molecular weight moieties of various, essentially unknown structures. The end members of kerogen sources are coals for terrigenous and alginites for marine origins. Most kerogens of the aquatic realm are admixtures of all input sources (eg., Tissot et al., 1974). Kerogen is an invaluable endogenous paleoenvironmental marker for the origin of the bulk of the organic matter. This could be enhanced if its bulk structure, and thus its genetic origin, could be further characterized. The elemental composition and H/C and O/C ratios of kerogen can be correlated using Van Krevelen (1961) diagrams to assess the magnitude of the allochthonous influx and the extent of diagenesis and catagenesis (eg., Deroo *et al.*, 1978). Using the stable carbon isotope ratios in a correlation versus H/C (eg., Fig. 9) of kerogens of Recent to Cretaceus age reveals a clustering which reflects the genetic origin, i.e., terrigenous, marine or a mixture of both (Simoneit 1980c). Ancient kerogen can be eroded from continental geologic formations and recycled to marine sediments (eg., Sackett *et al.*, 1974). Recent sediments, eg., algal mats, yield a "protokerogen" which is a lipoid macromolecular material, constitutionally less complex than ancient kerogen but related to it (eg., Philp and Calvin, 1976, 1977; Stuermer *et al.*, 1978).

Kerogen is sensitive to thermal stress from either the normal gradient due to depth of burial (eg., Tissot *et al.*, 1971; Tissot and Welte, 1978) or from transients such as intrusions (Simoneit *et al.*, '~97~)- This catagenesis results in the generation of bitumen (petroleum) from the kerogen, which in turn becomes more aromatic. This is illustrated in Fig. 10, where an igneous sill intrusion into Cretaceus shale resulted in the loss of volatiles and decrease in H/C in the major sill proximity (Simoneit *et al.*, 1978). This same phenomenon an be observed in a correlation of H/C versus N/C (Simoneit *et al.*, 1978). Kerogen, on microscopic examination, can be subdivided into phytoclasts such as spores, pollen, resin and vitrinite. Vitrinite particles have been used as the best petrographic component for the determination of organic maturity (eg., Hunt, 1979; Tissot and Welte, 1978). The vitrinite reflectance values of the intruded Cretaceus shale correlate with the H/C (Fig. 11) again reflecting the thermal stress of the intrusion. (Peters *et al.*, 1979). Thus, the bulk parameters of kerogen can be good indicators of the thermal history of the sediment.

Since kerogen represents the major portion of the sedimentary organic matter, more extensive analyses are needed and should be forthcoming.

Transit Modes of Organic Matter

Autochthonous organic detritus from the euphotic zone undergoes extensive modification on passing through the food web down to the sea floor (Fig. 12a). The residual organic matter from the bottom fauna then becomes incorporated into the sediment (Demaison and Moore, 1980; Simoneit, 1975; 1978a).

The amount of allochthonous organic matter reaching the deep sea is usually small. However, over geological time spans such material makes a significant contribution to hemipelagic sediments. The major transport mechanisms for terrestrial organic detritus are the rivers, wind and ice-rafting (.Fig. 12) (Simoneit, 1975, 1978a; Davies and Gorsline, 1976). Although river transport is obviously the major input mechanism for terrigenous organic matter to the marine environment, little is known about quantities and general makeup of the material. This potamic influence is evident in the Black Sea (Simoneit, 1974, 1977b, 1978a) and in the Amazon outflow (Aizenshtat et al., 1973). Eolian transport carries terrigenous organic detritus far out to sea (Simoneit et al., 1977; Simoneit, 1977c), but is a minor input mechanism for most areas. Ice-rafting is also a minor and localized input mechanism for organic debris (eg., Sackett et al., 1974). The type and amount of organic matter that is preserved in a sediment is highly dependent on the rates of autochthonous production and allochthonous influx and the environmental conditions of sedimentation (Fig. 1 and Fig. 12)(Didyk et al., 1978; Demaison and Moore, 1980). High production and rapid influx of terrigenous detritus, coupled with anoxic conditions both in the sediment and water columns result in the maximum preservation of organic matter.

Natural seepage of both petroleum and gas into the marine environment can be a significance contributor of organic matter in limited areas. Wilson et al. (1974) have summarized the known seeps (about 190) and estimated that they amounted to about $0.6x10^9$ kg/year. Reed and Kaplan (1977) have studied the chemistry of marine petroleum seeps of the California borderland and the Gulf of Alaska. Paleoseep contamination was demonstrated to be prevalent in sediments throughout the California borderland (Simoneit and Kaplan, 1980; Reed and Kaplan, 1977).

SUMMARY

The application of organic geochemistry is of great value for the investigation of organic matter in the geosphere, both in Recent and ancient environments. The characterization of the gas, lipid, humate (with fulvate) and kerogen fractions of sediments (also hydrosphere and atmosphere) can provide information about the origin of the organic matter. It can also provide some insight into the paleoenvironmental conditions prevailing during deposition and the diagenetic and thermal history of the sediments. Such data can complement results from other disciplines which examine geological phenomena such as paleogeography, paleoclimatology, paleo-oceanography and economic geology (i.e., oil., gas and coal exploration, etc.). Detailed analyses of all the fractions of organic matter can aid in the interpretation of isolated analyses and put them into an overall perspective (eg., pollutant hydrocarbon analyses and how they interface with the natural hydrocarbons). The link between Recent and ancient sedimentary environments (i.e., chemical evolution) and the flux mechanisms have been addressed (Demaison and Moore, 1980; Didyk <u>et al</u>., 1978; Tissot and Welte, 1978; Simoneit, 1978a; Calvin, 1969; Cloud, 1978) but need more work.

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REFERENCES

Aizenshtat, Z. , M.J. Baedecker and I.R. Kaplan (1973). Distribution and diagenesis of organic compounds in JOIDES sediment from Gulf of Mexico and western Atlantic. Geochim. Cosmochim. Acts 37; 1881-1898.

Arpino, P. {1973]. Les lipides des sédiments lacustres éocènes, Thèse, L'Université Louis Pasteur de Strasbourg, France.

Baker, E.W. and G.D. Smith (1974). Pleistocene changes in chlorophyll pigments, in: Advances in Organic Geochemistry 1973, B. Tissot and F. Bienner, eds., Editions Technip , Paris; pp. 649-660.

Bernard, B.B., J.M. Brooks and W.M. Sackett (1976). Natural gas seepage in the Gulf of Mexico. Earth Planet. Sci. Lett. 31; pp. 48-54.

Boon, J.J., F.W. v.d. Meer, P.J.W. Schuyl, J.W. de Leeuw, P.A. Schenck, and A.L. Burlingame (1978?.. Organic geochemical analyses of core samples from site 362, Walvis Ridge, DSDP Leg 40, in Initial Reports of the Deep Sea Drilling Project, Vol. 40, Suppl., U.S. Govt. Printing Office, Washington, D.C., pp. 627-637.

Boon, J.J., F. deLange, P.J.W. Schuyl, J.W. deLeeuw and P.A. Schenck (1977). Organic geochemistry of Walvis Bay diatomaceous ooze--II. Occurrence and significance of the hydroxy fatty acids, in: Advances in Organic Geochemistry 197S, R. Campos and J. Goñi, eds. , ENADIMSA, Madrid; pp. 255-272.

Boon, J.J. and J.W. deLeeuw (1979). The analysis of wax esters, very long mid-chain ketones and sterol ethers isolated from Walvis Bay diatomaceous ooze. Mar. Chem. 7; 117-132.

Brooks, P.W.; G. Eglinton, S.J. Gaskell, D.J. McHugh, J.R. Maxwell and R.P. Philp (1977). Lipids of Recent sediment, Part 11. Branched and cyclic alkanes and alkanoic acids of some temperate lacustrine and subtropical lagoonal/tidal-flat sediments, Chem. Geol. 20; 189-204.

Calvin, M. {1969]. Chemical Evolution, Oxford University Press, New York; 278 pp.

Campos, R. and J. Goñi, eds. (1977). Advances in Organic Geochemistry 1975, ENADIMSA, Madrid; 911 pp.

Colombo, U. and G.D. Hobson, eds. (1964). Advances in Organic Geochemistry, MacMillan-Pergamon Press, New York; 488 pp.

Claypool, G.E. and I.R. Kaplan (1974). The origin and distribution of methane in marine sediments, in Natural Gases in Marine Sediments, I.R. Kaplan, cd., Plenum Publishing Corp., New York; pp. 99-139.

Cloud P. (1978). Cosmos, Earth, and Man, Yale University Press, New Haven; 372 pp.

Dastillung, M. and P. Albrecht (1976). Molecular test for oil pollution in surface sediments. Mar. Poll. Bull. 7; 13-15.

Davies, T.A. and D.S. Gorsline (1976). Oceanic sediments and sedimentary processes, in Chemical Oceanography, J.P. Riley and R. Chester, eds., Vol. 5, Academic Press; pp. 1-80.

Degens, E.T. (1969]. Biogeochemistry of stable isotopes, in Organic Geochemistry, Methods and Results, G. Eglinton and M.T.J. Murphy, eds., Springer Verlag, New York; pp. 304-329.

Demaison, G.J. and G.T. Moore (1980). Anoxic environments and oil source bed genesis. Org. Geochem. {in press).

Deroo, G., J.P. Herbin, J. Roucaché, B. Tissot, P. Albrecht and J. Schaeffle (1977). Organic geochemistry of some Cretaceus black shales from sites 367 and 368, Leg 41, Eastern North Atlantic, in Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., U.S. Govt. Print. Office, Washington, D.C.; 865-873.

Deroo, G., J.P. Herbin, J.R. Roucaché, B. Tissot, P. Albrecht and M.” Dastillung (1978). Organic geochemistry of some Cretaceus claystones from site 391, Leg 44, Western North Atlantic, in Initial Reports of the Deep Sea Drilling Project, Vol. 44, W.E. Benson R.E. Sheridan, et al., U.S. Govt. Printing Office, Washington, D.C.; pp. 593-598.

Didyk, B.M., B.R.T. Simoneit, S.C. Brassell, and G. Eglinton (1978). Organic geochemical indicators of paleoenvironmental conditions of sedimentation. Nature 272; 216-222.

Eglinton, G. and M.T.J. Murphy, eds. (1969). Organic Geochemistry, Methods and Results, Springer Verlag, Berlin; 828 pp.

Eglinton, G., B.R.T. Simoneit and J.A. Zero (1975). The recognition of organic pollutants in aquatic sediments. Proc. Roy. Sot. Lend. B189; pp. 415-442.

Gaertner, H.R. von and H. Wehner, eds. (1972). Advances in Organic Geochemistry 1971, Pergamon Press, New York; 736 pp.

Gaskell, S.J. (1974). The environmental geochemistry of sterols, Ph.D. Thesis, University of Bristol, England; 321 pp.

Greiner, A.C., C. Spyckerelle, P. Albrecht and G. Ourisson (1977). Aromatic hydrocarbons from geological sources. Part V. Mono- and di-aromatic hopane derivatives. J. Chem. Res. (S) 1977; pp. 334.

Hatcher, P.G., B.R. Simoneit, and S.M. Gerchakov (1977). The organic geochemistry of a Recent sapropelic environment: Mangrove Lake, Bermuda, In Advances in Organic Geochemistry 1975, R. Campos and J. Goñi, eds., ENADIMSA, Madrid; pp. 469-484.

Hatcher, F.G., B.R.T. Simoneit, F.T. Mackenzie, A.C. Neumann, D.C. Thorstenson and S.M. Gerchakov (1980). Organic geochemistry of Mangrove Lake, Bermuda. Organic Geochem., submitted for publication.

Hobson, G.D. and M.C. Louis, eds. (1966). Advances in Organic Geochemistry 1964, Pergamon Press, New York; 330 pp.

Hobson, G.D. and G.C. Speers, eds., (1970). Advances in Organic Geochemistry 1966, Pergamon Press, New York; 557 pp.

Huang, W.-Y. and W.G. Meinschein (1979). Sterols as ecological indicators. Geochim. Cosmochim. Acts 43; 739-745.

Huc, A.Y. (1973). Contribution à l'étude de l'humus marin et de ses relations avec les kérogènes. Thèse Docteur-ingenieur, Université de Nancy, France.

Huc, A.Y. (1978). Geochimie organique des schistes bitumineux du Toarcien du bassin de Paris, Thèse Docteur es-Sciences, l'Université Louis Pasteur de Strasbourg, France; 137 pp.

Hunt, J.M. (1975). Origin of gasoline range alkanes in the deep sea. Nature 254; pp. 411-413.

Hunt, J.M. (1979). Petroleum Geochemistry and Geology, W.H. Freeman and Company, San Francisco; 617 pp.

Hunt, J.M. and J.K. Whelan (1978). Dissolved gases in Black Sea sediments, in Initial Reports of the Deep Sea Drilling Project, Vol. 42B, D.A. Ross, Y. Neprochnov et al., U.S. Govt. Printing Office, Washington, D.C.; pp. 661-665.

Krumbein, W.E., ed. (1978). Environmental Biogeochemistry and Geomicrobiology, Ann Arbor Science Publishers, Inc., Ann Arbor; 1055 pp.

Larter, S. and A.G. Douglas (1978). Low molecular weight aromatic hydrocarbons in coal maceral pyrolysates as indicators of diagenesis and organic matter type, in Environmental Biogeochemistry and Geomicrobiology, W.E. Krumbein, cd., Ann Arbor, Vol. 1; pp. 373-386.

Lee, C., R.B. Gagosian and J.W. Barrington (1977). Sterol diagenesis in Recent sediments from Buzzard's Bay, Massachusetts. Geochim. Cosmochim. Acts 41; pp. 985-992.

Lee, C., J.W. Barrington and R.B. Gagosian (1979). Sterol geochemistry of sediments from the western North Atlantic Ocean and adjacent coastal areas. Geochim. Cosmochim. Acts 43; pp. 35-46.

Mattern, G., P. Albrecht and G. Ourisson (1970). 4-Methyl-sterols and sterols in Messel shale (Eocene). Chem. Comm. 1970; pp. 1570-1571.

Nriagu, J.O., ed. (1976). Environmental Biogeochemistry, Ann Arbor Science Publishers, Inc., Ann Arbor; 797 pp.

Peters, K. E., B.R. T. Simoneit, S. Brenner and I.R. Kaplan (1979). Vitrinite reflectance-temperature determinations of intruded Cretaceus Black Shale in the Eastern Atlantic, in Symposium Low Temperature Metamorphism of Kerogen and Clay Minerals, D.F. Oltz, cd., Pacific Section, Sot. Econ. Paleontol. Mineral., Los Angeles; pp. 53-58.

Philp, R.P. and M. Calvin (1976). Kerogen structures in recently-deposited algal mats at Laguna Mormons, Baja California: A model system for the determination of kerogen structures in ancient sediments, in Environmental Biogeochemistry, J.O. Nriagu, cd., Ann Arbor, Vol. 1; pp. 131-148.

Philp, R.P. and M. Calvin (1977). Kerogenous material in Recent algal mats at Laguna Mormons, Baja California, in Advances in Organic Geochemistry 1975, R. Campos and J. Goñi, eds., ENADIMSA, Madrid, pp. 735-752.

Philp, R.P., M. Calvin, S. Brown and E. Yang (1978}. Organic geochemical studies on kerogen precursors in recently-deposited algal mats and oozes. Chem. Geol. 22; pp. 207-231.

Reed, W.E. (1977). Molecular compositions of weathered petroleum and comparison with its possible source. Geochim. Cosmochim. Acts 41; pp. 237-247.

Reed, W.E. and I.R. Kaplan (1977). The chemistry of marine petroleum seeps. J. Geochem. Explor. 7; pp. 255-293.

Rohmer, M. (1975). Triterpenoïdes de procaryotes, Ph.D. Thesis, Université Louis Pasteur de Strasbourg, France; 100 pp.

Rohmer, M. and G. Ourisson (1976). Derivés du bactériohopane: Variations structurales et repartition. Tetr. Lett. 1976; pp. 3637-3640.

Sackett, W.M., C.W. Poag and B.J. Eadie (1974). Kerogen recycling in the Ross Sea, Antarctica. Science 185; pp. 1045-1047.

Sever, J. and P.L. Parker (1969). Fatty alcohols (normal and isoprenoid) in sediments. Science 164; pp. 1052-1054.

Schenck, P.A. and 1. Havenaar, eds. (1969). Advances in Organic Geochemistry 1968, Pergamon Press, New York; 736 pp.

Schnitzer, M. and S.U. Khan (1972). Humic Substances in the Environment, Marcel Dekker, New York; 327 pp.

Simoneit, B.R. (1974). Organic analyses of Black Sea cores, in The Black Sea-Geology, Chemistry and Biology, E.T. Degens and D.A. Ross, eds., Memoir 20, Amer. Assoc. Petrol. Geol., Tulsa; pp. 477-498.

Simoneit, B.R.T. (1975). Sources of organic matter in oceanic sediments, Ph.D. Thesis, University of Bristol, England; 300 pp.

Simoneit, B.R.T. (1977a].. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41; pp. 463-476.

Simoneit, B.R.T. (1977b). The Black Sea, A sink for terrigenous lipids. Deep-Sea Res. 24; pp. 813-830.

Simoneit, B.R.T. (1977c). Organic matter in eolian dusts over the Atlantic Ocean. Proc. of Symp. on Concepts in Marine Organic Chemistry , Mar. Chem. 5; pp. 443-464.

Simoneit, B.R.T. (1978a). The organic chemistry of marine sediments, in Chemical Oceanography, 2nd Edition, J.P. Riley and R. Chester, eds., Academic Press, New York, Vol. 7, Chap. 39; pp. 233-311.

Simoneit, B.R.T. (1978b). Organic geochemistry of terrigenous muds and various shales from the Black Sea, DSDP Leg 42B, in Initial Reports of the Deep Sea Drilling Project, vol. 42, Part 2, D. Ross, Y. Neprochnov et al., U.S. Govt. Printing Office, Washington, D.C.: pp* 749-753.

Simoneit, B.R.T. (1980a). Terrigenous and marine organic markers and their input to marine sediments, in Proceedings of Symp. on Organic Geochemistry of Deep Sea Drilling Project Sediments, E.W. Baker, cd., Science Press, Princeton, N.J., in press.

Simoneit, B.R.T. (1980b). Organic geochemistry of Mesozoic sediments from the Falkland Plateau, DSDP Leg 36, Site 330,. in Initial Reports of the Deep Sea Drilling Project, Vol. SO, Y. Lancelot, E. Winterer, et al., U.S. Government Printing Office, Washington, D.C., in press.

Simoneit, B.R.T. (1980c). Organic geochemistry of the shales and sapropels of the Cretaceus Atlantic, in Advances in Organic Geochemistry 1977, USSR Acad. Sciences, in press.

Simoneit, B.R.T. and B.M. Didyk (1978). Organic geochemistry of a Chilean paraffin dirt. Chem. Geol. 23; 21-40.

Simoneit, B.R.T. and I.R. Kaplan (1980). Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern California Bight. Mar. Environ. Res., in press.

Simoneit, B.R.T., R. Chester and G. Eglinton (1977). Biogenic lipids in particulate from the lower atmosphere over the Eastern Atlantic: Nature 267; pp. 682-685.

Simoneit, B.R.T., S. Brenner, K.E. Peters and I.R. Kaplan (1978). Thermal alteration of Cretaceus black shale by basaltic intrusions in the Eastern Atlantic. Nature 273; pp. 501-504.

Simoneit, B.R.T., M.A. Mazurek, S. Brenner, P.T. Crisp and I.R. Kaplan (1979) . Organic geochemistry of Recent sediments from Guaymas Basin, Gulf of California. Deep-Sea Res. 26A; pp. 879-891.

Simoneit, B. R. T., P.T. Crisp, B.G. Rohrback and B. Il. Didyk (1980). Chilean paraffin dirt--II. Natural gas seepage at an active site and its geochemical consequences, in Advances in Organic Geochemistry 1979, A.G. Douglas and J.R. Maxwell, eds., in press.

Spyckerelle, C. (1975). Constituents aromatiques de sédiments, Ph.D. Thesis, Université Louis Pasteur de Strasbourg, France; 108 pp.

Spyckerelle, C., A.C. Greiner, P. Albrecht and G. Ourisson (1977). Aromatic hydrocarbons from geological sources. III . A tetrahydrochrysene derived from triterpenes, in Recent and old sediments: 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene, J. Chem. Res. (5), 1977; pp. 330-331.

Stahl., W.J. (1977). Carbon and nitrogen isotopes in hydrocarbon research and exploration. Chem. Geol. 20; pp. 121-149.

Sturmer, D.H. (1975). The characterization of humic substances in seawater, Ph.D. Thesis, Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, WoodsHole; 188 pp.

Stuermer, D.H. and B.R.T. Simoneit (1978). Varying sources for the lipids and humic substances at site 391, Blake-Bahama Basin, DSDP Leg 44, in Initial Reports of the Deep Sea Drilling Project, Vol. 44, W.E. Benson, R.E. Sheridan et al., U.S. Government Printing Office, Washington, D.C.: pp. 587-591.

Stuermer, D.H., K.E. Peters and I.R. Kaplan (1978). Source indicators of humic substances and protokerogen: Stable isotope ratios, elemental compositions and electron-spin resonance spectra. Geochim Cosmochim. Acts 42; pp. 989-997.

Swain, F.M. (1970). Non-marine Organic Geochemistry, Cambridge University Press, Cambridge; 445 pp.

Thompson, K.F.M. (1979). Light hydrocarbons in subsurface sediments. Geochim. Cosmochim. Acts 43; pp. 657-672.

Tissot, B. and F. Bienner, eds. (1974). Advances in Organic Geochemistry 1973, Editions Technip, Paris; 1080 pp.

Tissot, B.P. and D.H. Welte (1978). Petroleum Formation and Occurrence, A New Approach to Oil and Gas Exploration, Springer-Verlag, Berlin; 538 pp.

Tissot, B., Y. Califet-Debyser, G. Deroo and J.L. Oudin (1971). Origin and evolution of hydrocarbons in Early Toarcian shales. Amer. Assoc. petrol. Geol. Bull. 55; pp. 2177-2193.

Tissot, B., B. Durand, J. Espitalie and A. Combaz (1974). Influence of natural and diagenesis of organic matter in formation of petroleum, Amer. ASSOC. petrol. Geol. Bull. 58; pp. 499-506.

Treibs, A. (1934). Chlorophyll- und Häminderivate in bituminösen Gesteinen, Erdölen, Erdwachsen und Asphalten, Ann. Chem. (Liebig) 510; pp. 42-62.

Treibs, A. (1936). Chlorophyll- und Häminderivate in organischen Mineralstoffen, Angew. Chemie 49; pp. 682-686.

van de Meent, D., S.C. Brown, R.P. Philp and B.R.T. Simoneit (1980). Pyrolysis-high resolution gas chromatography and pyrolysis-gas chromatography-mass spectrometry of kerogens and kerogen precursors. Geochim. Cosmochim Acts, submitted for publication.

Watts, C.D. and J.R. Maxwell (1977]. Carotenoid diagenesis in a marine sediment. Geochim. Cosmochim. Acts 41; pp. 493-497.

Wilson, R.D., P.H. Monaghan, A. Osanik, L.C. Price and M.A. Rogers (1974). Natural marine oil seepage. Science 184; pp. 857-865-

Windsor, J.G., Jr. and R.A. Hites (1979). Polycyclic aromatic hydrocarbons in Gulf of Maine sediments and Nova Scotia soils. Geochim. Cosmochim. Acts 43; pp. 27-33.

FIGURE LEGENDS

Fig. 1: Schematic representations of typical sedimentary environments (Didyk et al., 1978). The water column is divided into three zones: euphotic, disphotic and aphotic and three levels of the oxicity/anoxicity interface (-·-·) are shown.

Fig. 2: Schematic for the experimental procedures for separating various carbon fractions.

Fig. 3: Distribution diagrams of n-alkanes (A-D) and n-fatty acids (E-H) (. ..isoprenoids, ---diterpenoids) :

(A,E) Sample 36-330-10-1, 95-102 cm, S. Atlantic (Simoneit, 1980b)
(B,F) Sample ML71-2-23, 8.0 m, Mangrove Lake, Bermuda (Hatcher et al., 1979)
(C,G) Sample AII49-1462K, 5.0 m, Black Sea (Simoneit, 1977b)
(D,H) Sample 18-175-2-2, 45-47 cm, N.E. Pacific (Simoneit, 1980a).

Fig. 4: Distribution diagrams of n-alkanes (A-C), n-fatty acids (E-G), n-alkan-2-ones (F) and n-fatty alcohols (D,H)(. ..isoprenoids, ---unsaturated):

(A,E) Sample 41-367-19-4, 10-15 cm, Cape Verde Basin, N. Atlantic (Simoneit, 1980a)
(B) Sample 38-345-4-1, 130-140 cm, Norwegian-Greenland Sea, Seepage (Simoneit, 1980a)
(C,G) Eolian dust DC5, North Atlantic (Simoneit, 1977c)
(D) Sample 12-114-5-5, 80-140 cm, N. Atlantic (Simoneit, 1978b)
(F) Sample 42B-381-1-4, 104-115 cm, Black Sea (Simoneit, 1978b)
(H) Eolian dust E2, N. Atlantic (Simoneit, 1977c)

Fig. 5: ' Relative distribution histograms for diterpenoids and triterpenoids (based on the m/z 191 mass chromatograms or gas chromatographic response) of some examples. The R and S diastereomers are also indicated and ^{c}28 Hopane I is 17α(H),18α(H),21β(H)-28,30-bisnorhopane.

(A) Sample 30G-I (102-105 cm), Guaymas Basin, Gulf of California (Simoneit et al., 1979).
(B) Sample AII 93/3-18 (197-201 cm), Walvis Bay, SW Africa (Simoneit and Kaplan, 1980)
(C) Sample 193 (25-31 cm), Santa Barbara Coastal Area, Southern California Bight (Simoneit and Kaplan, 1980)
(D) Sample 575 (25-31 cm), Tanner Basin, Southern California Bight (Simoneit and Kaplan, 1980).

Fig. 6: Concentrations of steranes: (A) Sample 36-330-4-2 (120-126 cm), (B) Sample 36-330-10-1 (95-102 cm)(Simoneit, 1980b).

Fig. 7: Some aromatic compounds derived from diagenesis of sesqui-, di- and triterpenoids and steroids (T = terrigenous and M = marine origin).

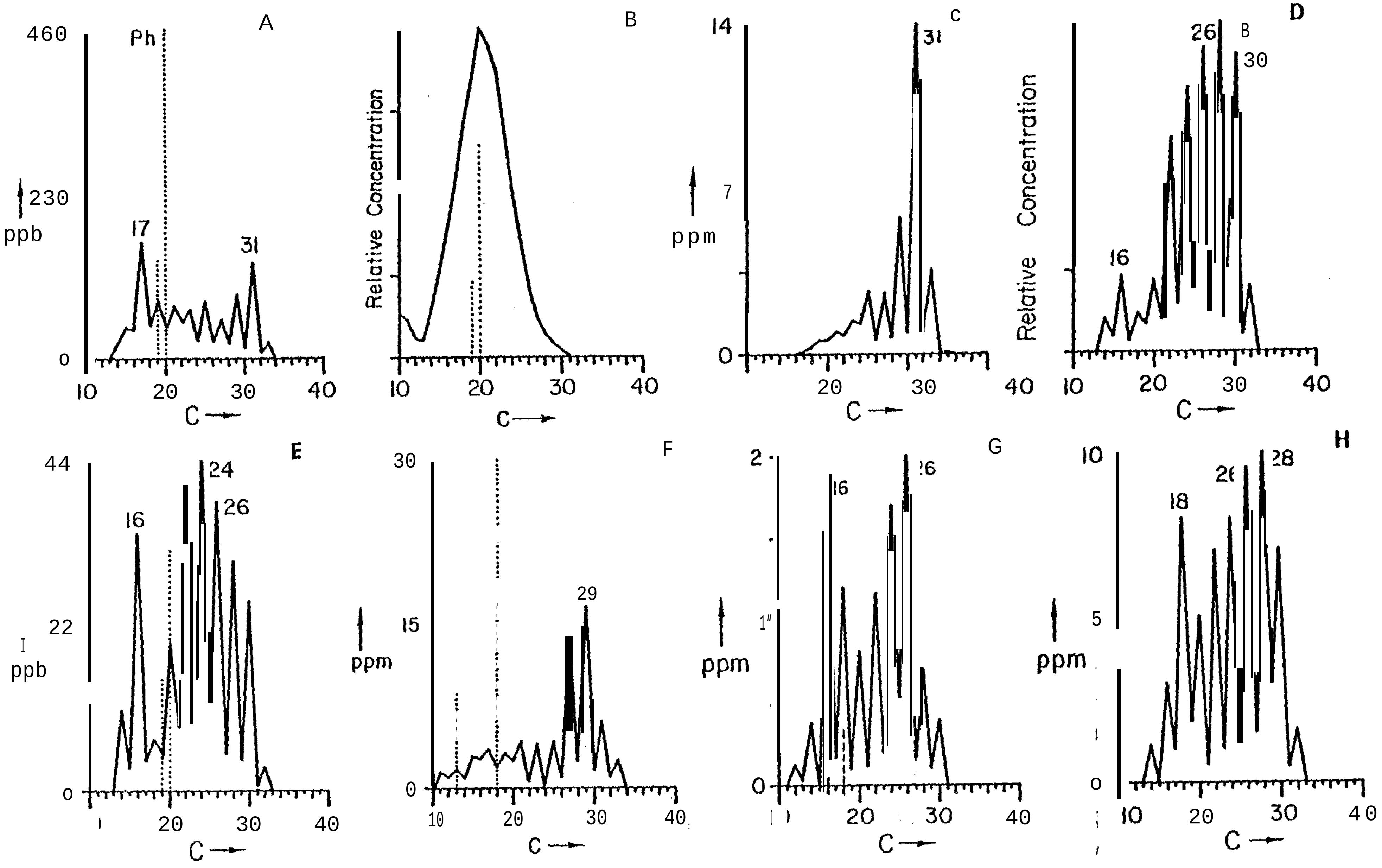
Fig. 8: Plot of percent humic acid carbon with respect to total organic carbon versus sediment depth at DSDP site 44-391 (Stuermer and Simoneit, 1978).

Fig. 9: Correlation diagram of H/C versus $\delta^{13}C$ for some kerogens and humates (▲ Recent kerogen; ● Cretaceus kerogen; ■ Ret-t kerogen from work of Stuermer *et al*., 1978; A Recent and 0 Cretaceus humates).

Fig. 10: Plot of the atomic H/C of the kerogens at DSDP site 41-368 versus depth in the sediment (Simoneit *et al*., 1978). The intrusions are indicated by the hatched areas.

Fig. 11: Correlation diagram of vitrinite reflectance value versus atomic H/C or kerogens at DSDP site 41-368 (Peters *et al*., 1979) .

Fig. 12 Examples of near-shore environments (Didyk *et al*., 1978): a) oxic water and sediments, b} anoxic midcolumn water, giving anoxic sediments on rise, and c) anoxic basin water and sediments.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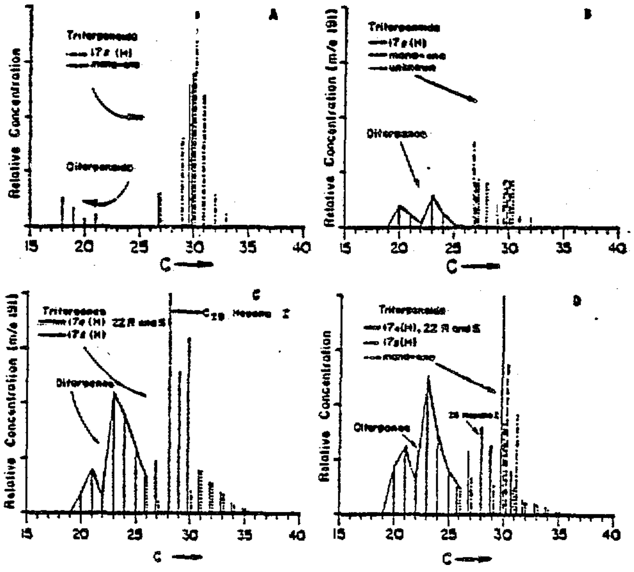
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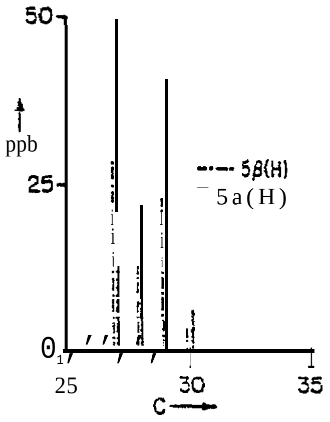
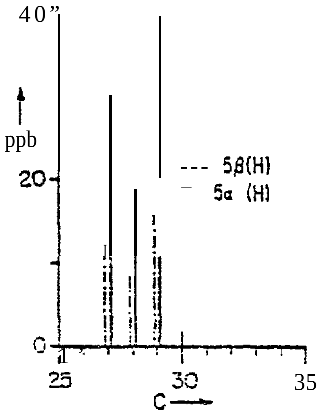
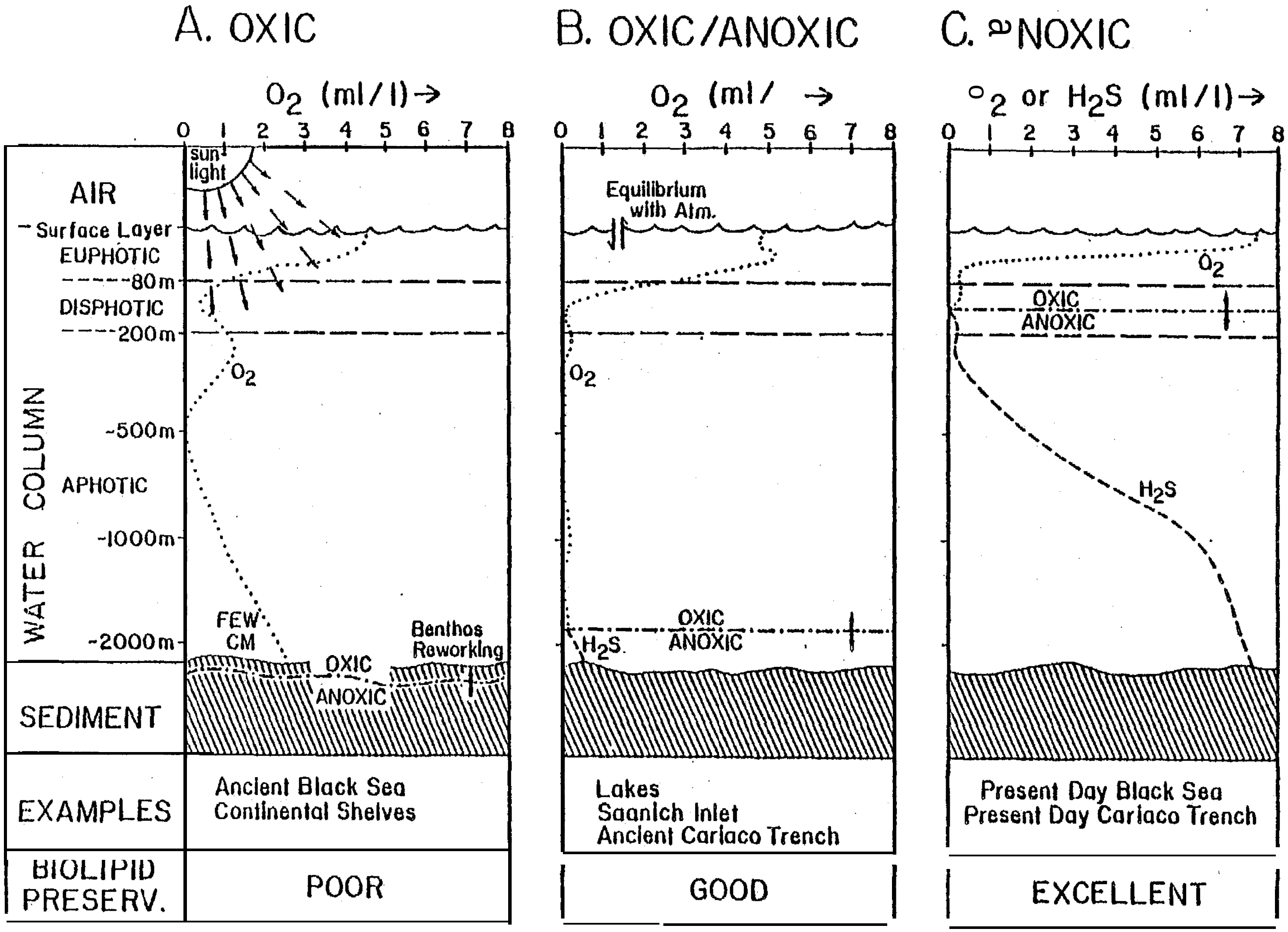
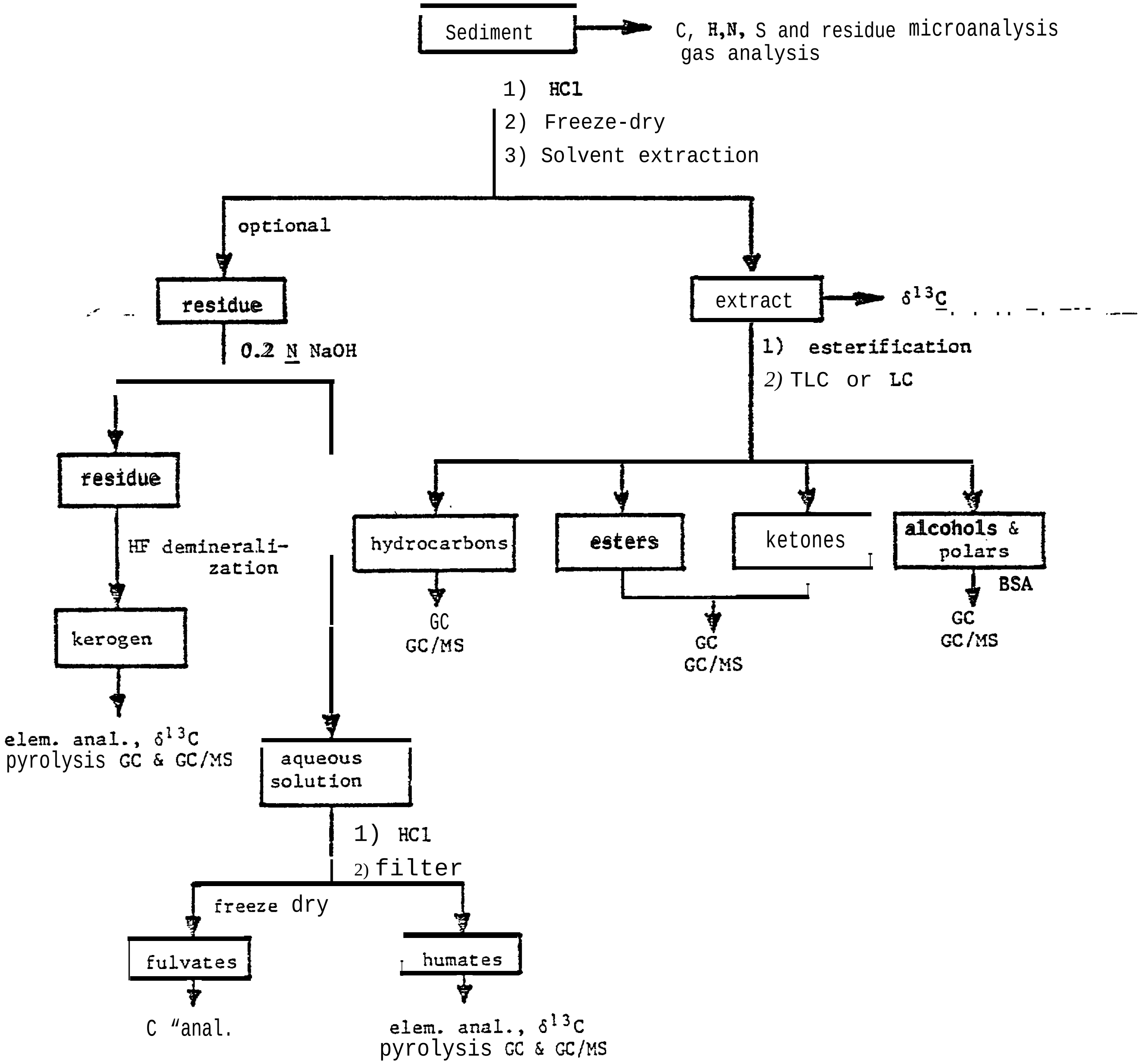
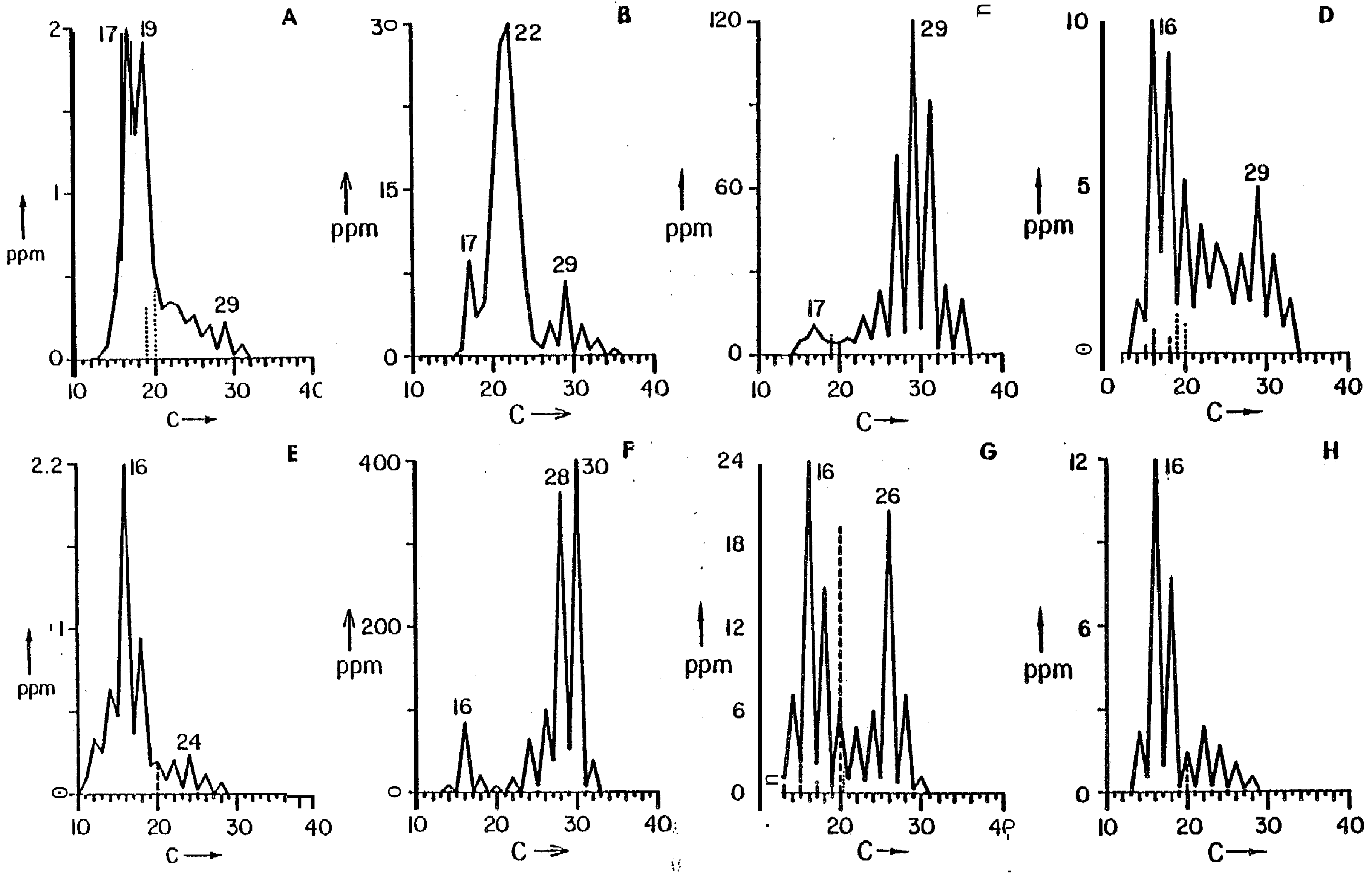
15
20
25
30
35
40
C
B
Triterpanoids
17α (H)
moretane
unknown
Diterpanoids
Relative Concentration (m/e 191)
C
Triterpanes
17α (H) 22 R and S
17β (H)
C_{28} Hopane
Diterpanes
Relative Concentration (m/e 191)
D
Triterpanoids
17α(H), 22 R and S
17β(H)
moretane
28 Hopane
Diterpanes
Relative Concentration

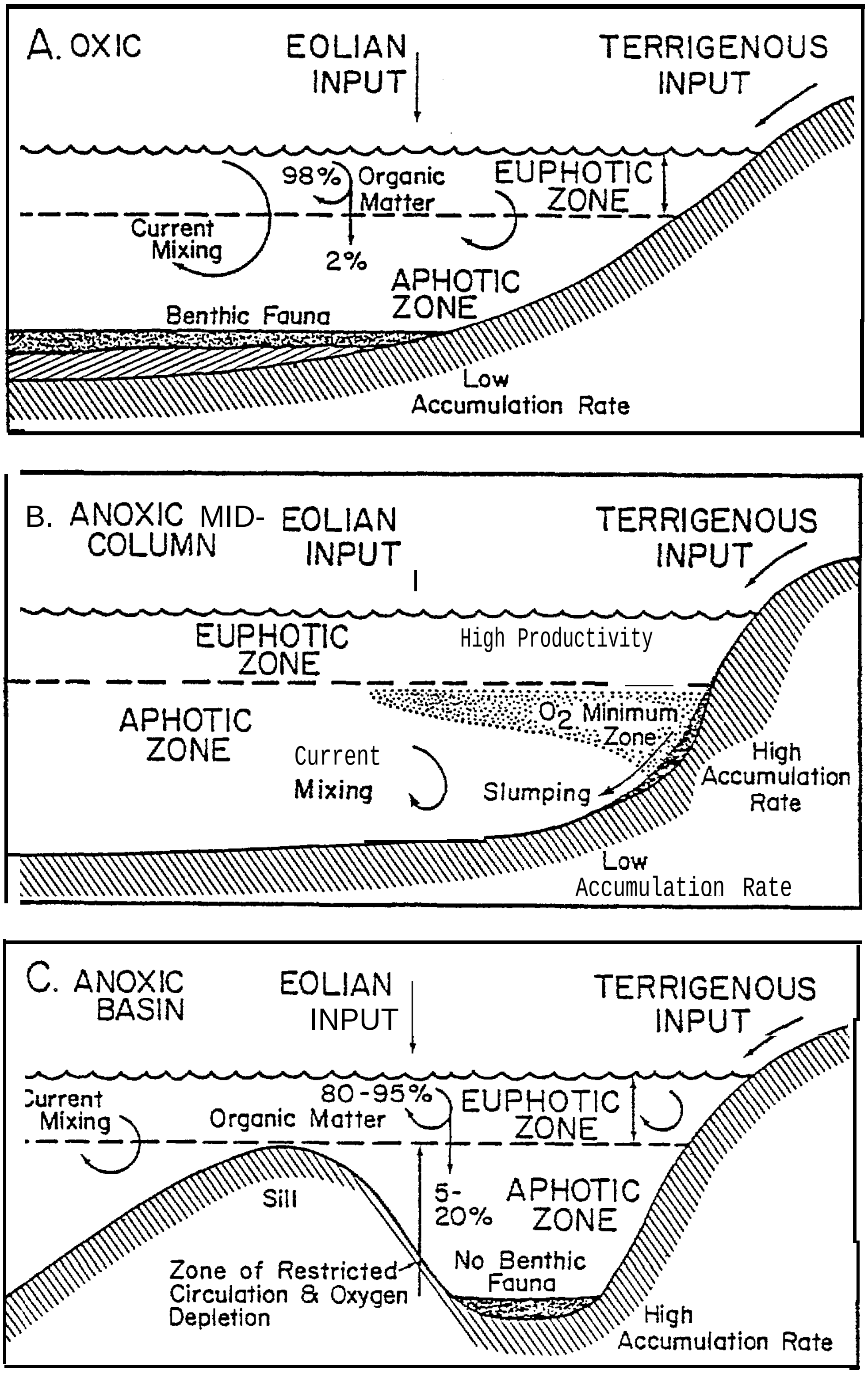

50
25
0
ppb
5β(H)
5α(H)
25
30
35
C


40
20
0
ppb
5β(H)
5α (H)
25
30
35
C

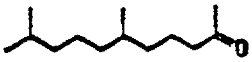

A. OXIC
B. OXIC/ANOXIC
C. ANOXIC
O_2 (ml/l)→
O_2 (ml/ →
O_2 or H_2S (ml/l)→
0
1
2
3
4
5
6
7
8
sun light
AIR
Surface Layer
EUPHOTIC
-80m
DISPHOTIC
-200m
WATER COLUMN
-500m
APHOTIC
-1000m
-2000m
SEDIMENT
EXAMPLES
BIOLIPID PRESERV.
O_2
FEW CM
OXIC
ANOXIC
Benthos Reworking
Equilibrium with Atm.
H_2S
Ancient Black Sea
Continental Shelves
Lakes
Saanich Inlet
Ancient Cariaco Trench
Present Day Black Sea
Present Day Cariaco Trench
POOR
GOOD
EXCELLENT


Sediment
C, H,N, S and residue microanalysis
gas analysis
1) HCl
2) Freeze-dry
3) Solvent extraction
optional
residue
extract
$\delta^{13}C$
0.2 N NaOH
1) esterification
2) TLC or LC
residue
HF demineralization
hydrocarbons
esters
ketones
alcohols & polars
BSA
GC
GC/MS
GC
GC/MS
GC
GC/MS
kerogen
elem. anal., $\delta^{13}C$
pyrolysis GC & GC/MS
aqueous solution
1) HCl
2) filter
freeze dry
fulvates
humates
C "anal.
elem. anal., $\delta^{13}C$
pyrolysis GC & GC/MS

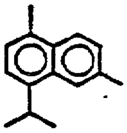

A
2
1
0
ppm
17
19
29
10
20
30
40
C →
B
30
15
0
ppm
17
22
29
10
20
30
40
C →
C
120
60
0
ppm
17
29
10
20
30
40
C →
D
10
5
0
ppm
16
29
0
20
30
40
C →
E
2.2
1
0
ppm
16
24
10
20
30
40
C →
F
400
200
0
ppm
16
28
30
10
20
30
40
C →
G
24
18
12
6
0
ppm
16
26
20
30
40
C →
H
12
6
0
ppm
16
10
20
30
40
C →


A. OXIC
EOLIAN INPUT
TERRIGENOUS INPUT
98%
Organic Matter
EUPHOTIC ZONE
Current Mixing
2%
APHOTIC ZONE
Benthic Fauna
Low Accumulation Rate
B. ANOXIC MID-COLUMN
EOLIAN INPUT
TERRIGENOUS INPUT
EUPHOTIC ZONE
High Productivity
APHOTIC ZONE
O_2 Minimum Zone
Current Mixing
Slumping
High Accumulation Rate
Low Accumulation Rate
C. ANOXIC BASIN
EOLIAN INPUT
TERRIGENOUS INPUT
Current Mixing
80-95%
Organic Matter
EUPHOTIC ZONE
Sill
5-20%
APHOTIC ZONE
No Benthic Fauna
Zone of Restricted Circulation & Oxygen Depletion
High Accumulation Rate

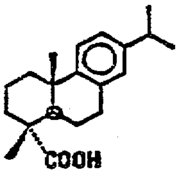
I. 6. 10.164rfme*YIe-2**



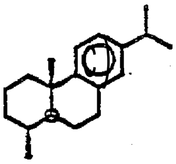
II. 6,10-dimethylundecan-2-one



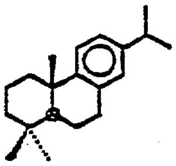
III. cadalene



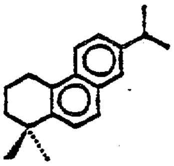
IV. dehydroabietic acid



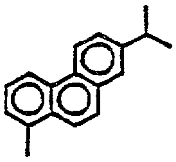
V. dehydroabietin



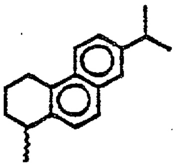
VI. dehydroabietane



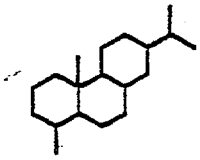
VII. simonellite



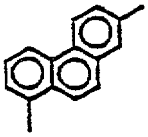
VIII. retene



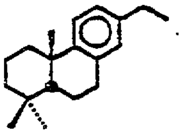
IX. tetrahydroretene



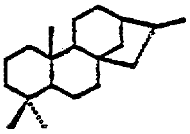
X. fichtelite



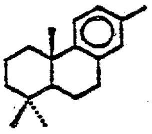
XI. pimanthrene



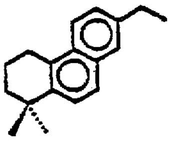
XII. 17-nordehydroabietane



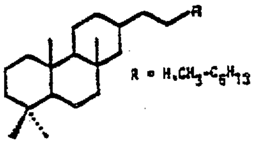
XIII. iosene



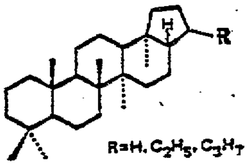
XIV. 13-methylpodocarpa-8,11,13-triene



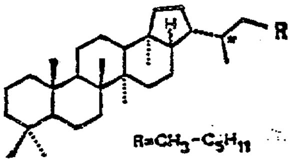
XV. norsimonellite



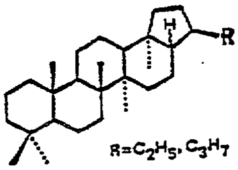
XVI. extended diterpanes



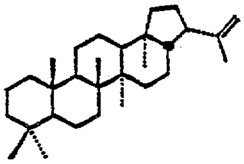
XVII. hopanes



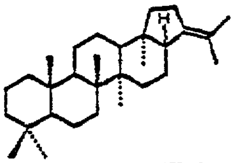
XVIII. extended hopanes



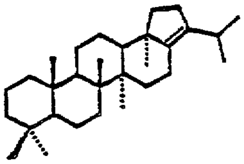
XIX. moretanes



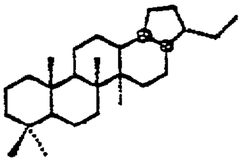
XX. diploptane



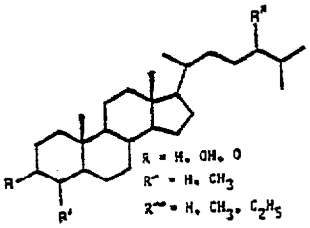
XXI. hop-21(22)-ene



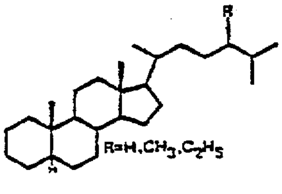
XXII. hop-17(21)-ene



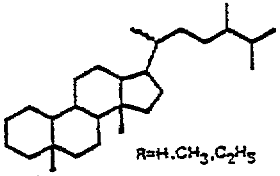
XXIII. 17α(H), 18α(H), 21β(H)-28,30-bisnorhopane



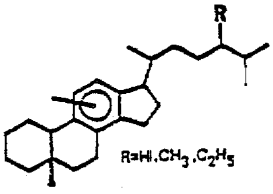
XXIV. steroidal derivatives



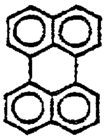
XXV. steranes, 5α/β(H)



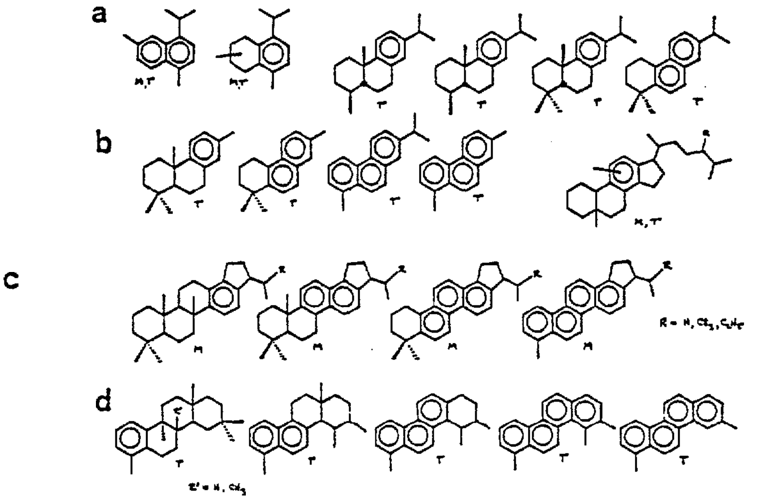
XXVI. diasteranes



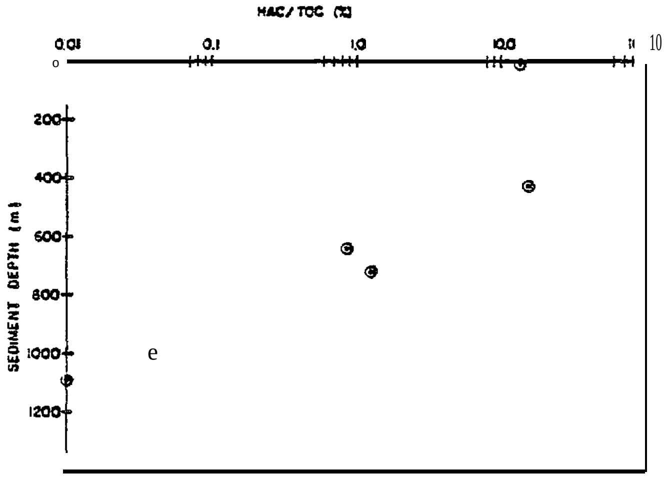
XXVII. monoaromatic steranes

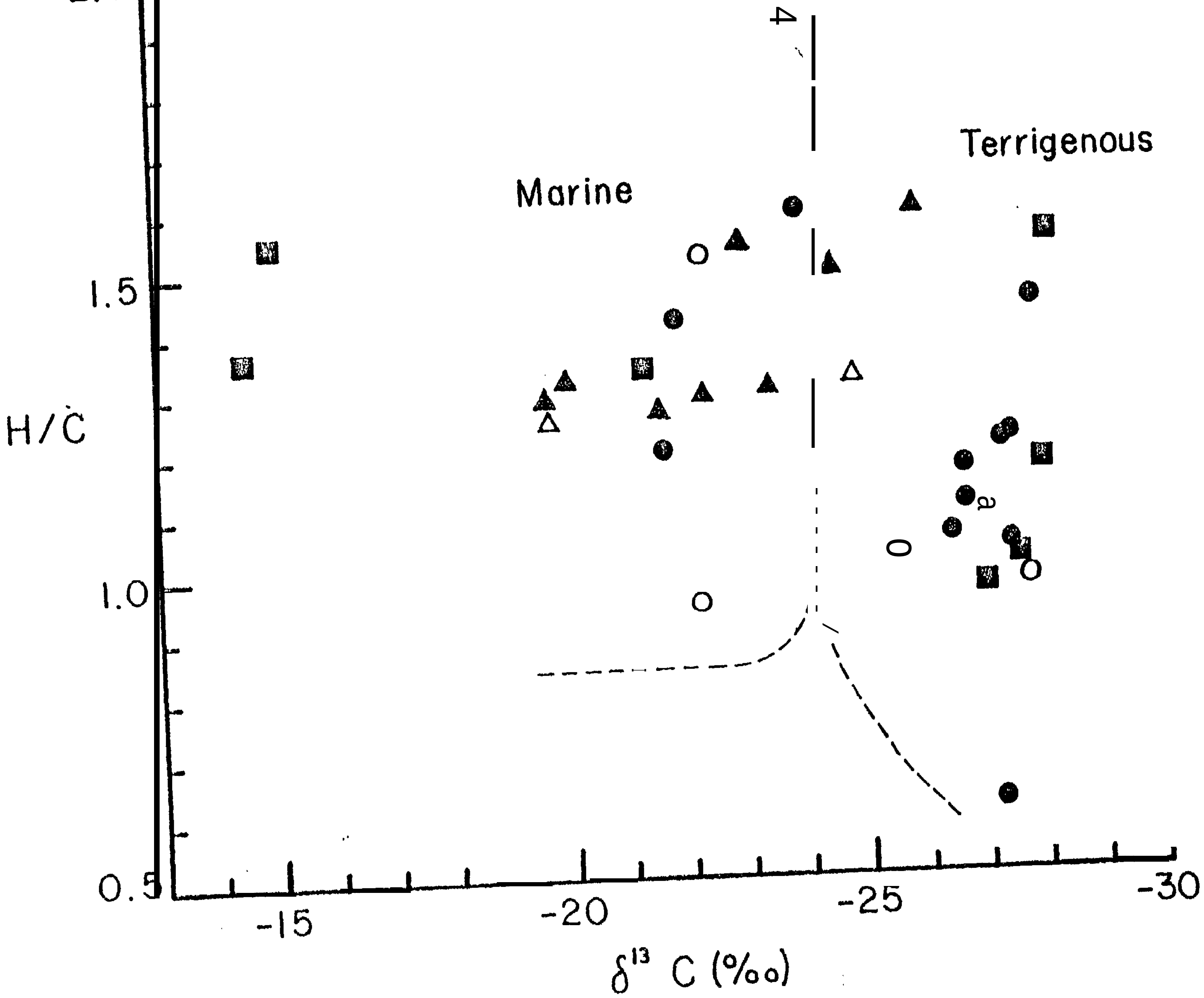


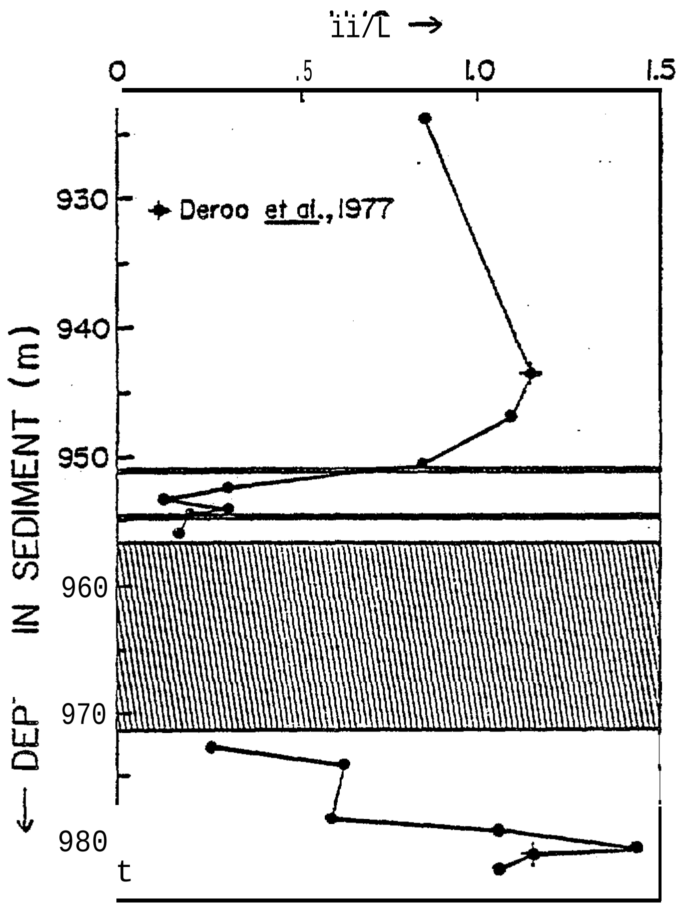
XXVIII. perylene

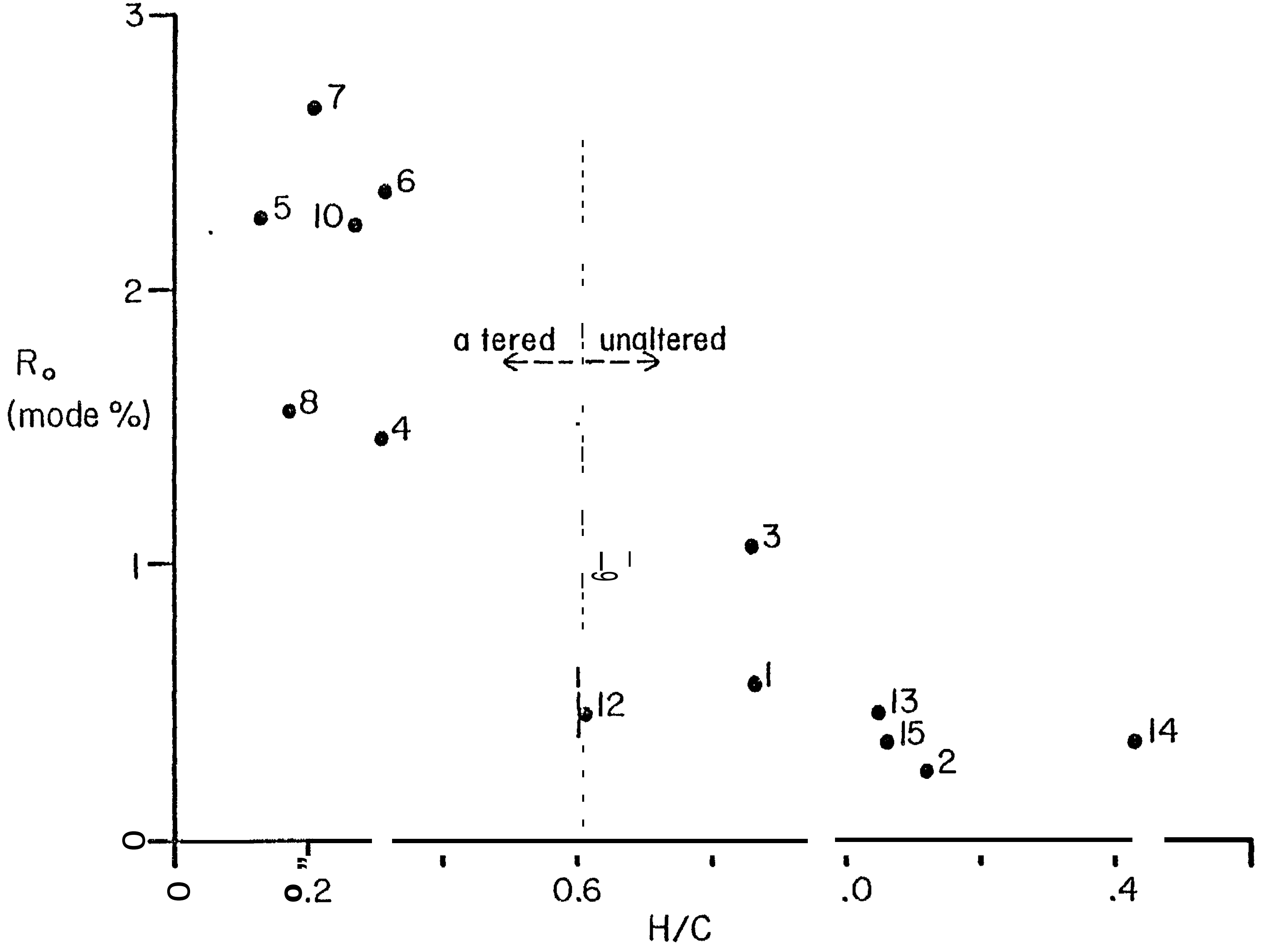


BERND R. T. SIMONEIT


HAC / TOC (%)
0.01
0.1
1.0
10.0
10
0
SEDIMENT DEPTH (m)
200
400
600
800
1000
1200
e


Marine
Terrigenous
4
0
a
H/C
2.0
1.5
1.0
0.5
-15
-20
-25
-30
$\delta^{13}C$ (‰)


ii/L →
0
.5
1.0
1.5
930
940
950
960
970
980
t
✦ Deroo et al., 1977
← DEPT IN SEDIMENT (m)


R₀
(mode %)
3
2
1
0
0
0.2
0.6
.0
.4
H/C
altered
unaltered
7
6
5
10
8
4
3
9
1
12
13
15
2
14

Lines around
drawings will
not be in final
copy."
J. J.
no p. 100

The Composition, Sources and Transport of Organic Matter to Marine Sediments – The Organic Geochemical Approach*

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University of California
Los Angeles, California 90024
U. S. A.

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FEB 3 1981

ABSTRACT

The analytical techniques of organic geochemistry are used to examine organic matter in terms of its structural and compositional makeup. The sources and transport mechanisms to the sedimentary environment of this organic matter can be evaluated from such data.

Organic matter is best examined in three "separated fractions, where (a) lipids (bitumen) are characterized by various molecular markers and homolog distributions in terms of their biogenic precursors and diagenetic alterations, and both (b) humates (and fulvates, in older sediments -- the asphaltenes) and (c) kerogen (and protokerogen) are characterized by their bulk properties (eg., H/C, N/C, stable isotope ratios, ESR) in terms of their biogenic origins and diagenetic and catagenetic evolution. The transport of organic matter to marine sedimentary environments consists of autochthonous production with a varying allochthonous influx of terrigenous detritus by predominantly potamic, eolian and ice-rafting mechanisms and redistribution by turbidite and contour flows. Predation takes place there and throughout the transport, followed by diagenesis and eventually catagenesis.

All of these processes contribute to the ultimate fingerprint of the organic matter in marine sediments. Thus, overall analyses of organic matter (analysis of single compound groups, eg., n-alkanes, PAH, can be misleading) with the effects of its influx on the marine environment, need to be continued. The levels of natural organic matter in recent sediments and the marine environment should be better defined and more work carried out to correlate anthropogenic pollutants in terms of that natural background.

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* *Contribution No. 1932: Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90024.*

INTRODUCTION

The biogenetic and/or geogenetic origin of marine sediments is reflected in the constitution of their organic matter as well as their mineralogy and lithology. Marine sediments are the ultimate depositories of posthumus organic debris. This organic matter is composed of both autochthonous residues and allochthonous organic detritus derived from continental sources (Simoneit, 1975). Recent aquatic sediments receive organic detritus fran natural and anthropogenic sources. Thus the pollutant chemistry is an integral part of the "natural" chemistry and is subject to the same environmental processes (eg., Eglinton et al., 1975).

The preservation of organic matter in marine sediments depends on the initial diagenetic processes involving microbial degradation and chemical conversion, coupled with the environmental conditions of acidity and redox potential (eg., Didyk et al., ,1978). Then, during subsequent sediment maturation and lithification, the organic matter is modified by the effects of temperature, pressure and petrology (eg., Tissot and Welte, 1978; Simoneit, 1978a; Tissot et al., 1971).

The analytical techniques of organic geochemistry are ideally suited to examine the character of such organic matter in terms of its structural and compositional makeup (Simoneit, 1978a) . The sources, the diagenetic and catagenetic histories and the transport mechanisms to the sedimentary environment of this organic matter can then be evaluated from such data. It should be noted that in the following discussion organic matter is comprised of gas, lipids (bitumen) , humic substances (with fulvic substances) and kerogen (with "protokerogen").

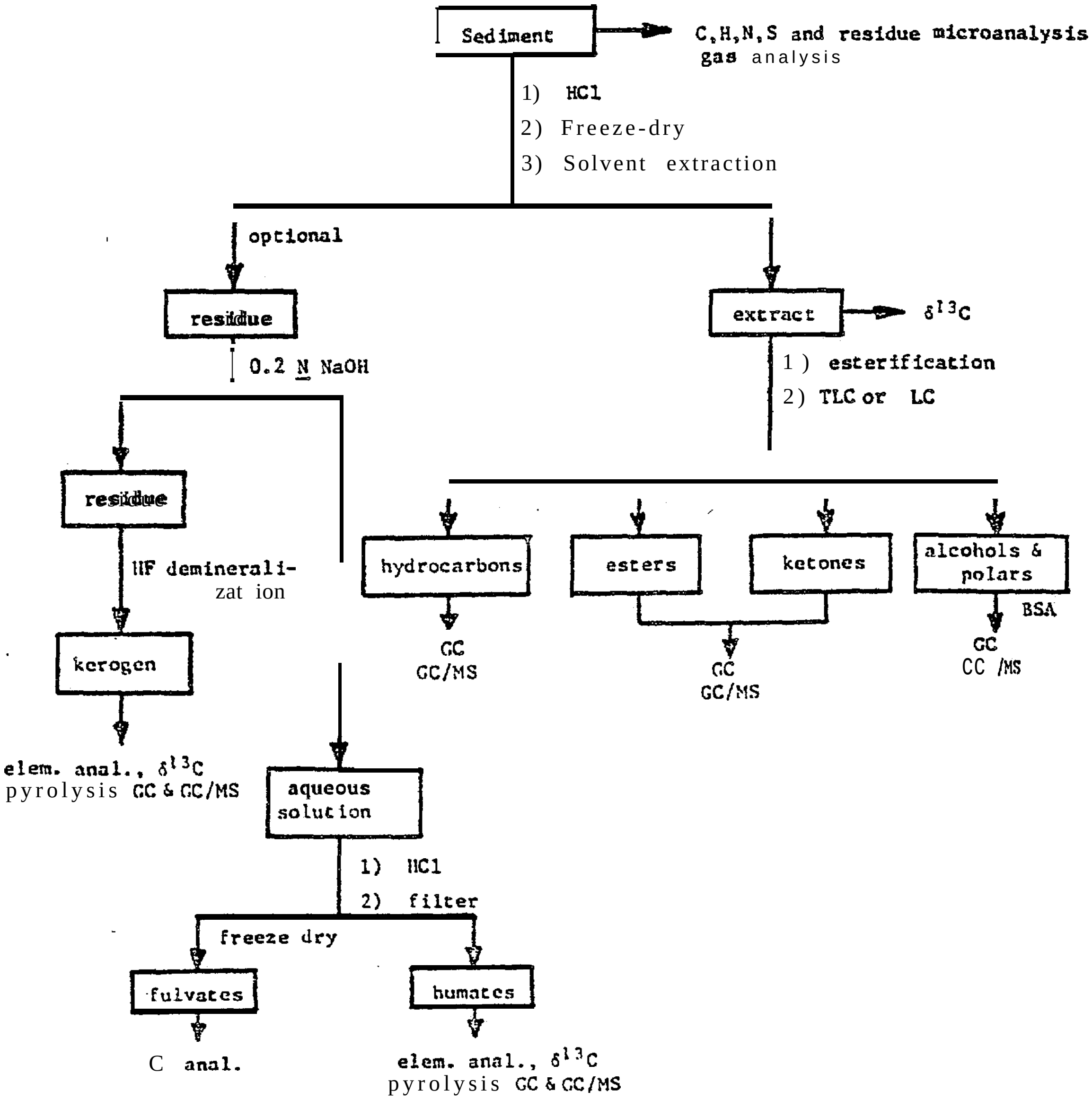


Figure 1: Schematic for the experimental procedures for separating various carbon fractions.

Here I shall illustrate and summarize the analytical techniques and typical data for the various types or organic matter found in marine sediments.

ANALYSES OF ORGANIC MATTER

A typical experimental flow schematic for sample workup is shown in Figure 1. This basic organic geochemical procedure has been in routine use for several years, with only minor modifications tailored to specific problems (eg., Simoneit, 1979a; Simoneit et al., 1979; Boon et al., 1978; Deroo et al., 1978).

Interstitial gas analyses are usually accomplished by gas chromatography (GC) and confirmed by gas chromatography-mass spectrometry (GC/MS) (eg., Hunt, 1975; Simoneit et al., 1979). Stable isotope analyses have also been carried out to delineate sources and genetic origins of gases (eg., Claypool and Kaplan, 1974).

The wet sediments are commonly freeze-dried, powdered and extracted in a Soxhlet apparatus or by ultrasonic or shaker agitation. The extracted lipids or bitumens are separated by column (liquid)-, thin layer- (TLC), gel permeation- or high-pressure liquid chromatography into discrete fractions, which are then analyzed by GC and GC/MS (eg., Simoneit, 1978a). prior to separation, the lipids can also be derivatized (eg., esterification of free fatty acids) to reduce the polarity of some compounds. Saponification of whole sediment or lipids can be employed to deesterify bound lipids (eg., waxes). Argentation-TLC can be utilized to separate saturated from olefinic compounds. Complex fractions can be further separated bimolecular sieving or urea (also thiourea) adduction into normal and branched-cyclic components.

Other ancillary techniques which can be applied to lipid analyses are stable isotope ratios, w-visible spectrophotometry, infrared spectrophotometry and nuclear magnetic resonance spectroscopy.

Humic and fulvic substances are separated from exhaustively extracted sediments (with carbonates removed by HCl treatment) by shaking with aliquots of 0.1-0.3 M sodium hydroxide solution until the extracts are colorless (Stuermer end Simoneit, 1978). The combined extracts are then centrifuged and the supernatant is acidified with hydrochloric acid to pH 1 to precipitate the humic substances. The supernatant, after removal of humic substances, contains the fulvic material. and can be lyophilized after dialysis. The humic substances are washed with 0.01 M HCl and lyophilized to yield the protonated form.

The residual sediment is then treated with hydrofluoric acid to remove silicate minerals yielding a kerogen concentrate. Kerogen with a low ash content can be obtained by density flotation (Stuermer et al., 1978).

130th humates and kerogens are characterized mainly by bulk properties and to a limited extent by chemical degradation (especially kerogen). These analyses consistof elemental composition (eg., H/C, O/C, N/C etc.), stable isotope composition (eg., ^{13}C, ^{34}S, D, etc.), electron spin resonance and nuclear magnetic resonance spectrometry, and for kerogens, a determination of the vitrinite reflectance (Simoneit, 1978a). Pyrolysis GC and pyrolysis GC/MS have also proven to be of utility since they provide a fingerprint pattern and are rapid analytical methods (eg., Van der Meent et al., 1979; Larter and Douglas, 1978; Philp et al., 1978).

RESULTS AND DISCUSSION

The organic matter of sediments can be divided into the following categories based on the limitations imposed by the analytical procedures:

Gas	Lipids (bitumens)	Humates (with fulvates)	Kerogen
(C_1-C_8 , + CO_2 r H_2S, etc.)	(C_8 - C_{40} +)	(macromolecular, M.W. $\sim 10^3$ to > 10^6)	(macromolecular)
minor amount of total C_{org}	minor (max.$\sim$10%)	variable	major

Gas

Interstitial hydrocarbon gases consist primarily of methane with minor amounts of ethane to about C_8 hydrocarbons. Biogenic hydrocarbon gases usually have $CH_4/(C_2H_6 + C_3H_8)$ ratios greater than 1000, while those of petrogenic origin have ratios less than 50 (Bernard et al., 1976). For example, the $C_1/(C_2 + C_3)$ ratios for shallow sediment gases from Guaymas Basin, Gulf of California range from 41-150 and thus indicate a mixed origin of biogenic (CH_4) and petrogenic (C_2 - C_8) hydrocarbons (Simoneit et al., 1979). More detailed analyses of the trace components in interstitial gas can be found in the work of Hun~~d~~t and Whelan (1978) and Thompson {1979).

More data are needed to identify and differentiate the biogenic hydrocarbons other than CH_4 (eg., ethylene, propylene, etc.) from the petrogenic analogs (eg., neopentane, thiophene, etc.].

Lipids

The lipids of sediments, especially the hydrocarbons have been most extensively examined. The compound classes which are commonly analyzed as lipid components and which have reasonable stability over geologic times are: hydrocarbons (n-, iso-, anteiso-, alkenes, aromatic and isoprenoidal), fatty alcohols, ketones, wax esters, steroids, terpenoids (sesqui-, di-, sester-, tri-, and tetra-) , and tetrapyrrole pigments (Simoneit, 1979a). The following additonal compound classes are analyzed in recent sediments only, since their geologic half-lives are short: amino acids and peptides, purines and pyrimidines, and carbohydrates (Simoneit, 1978a). The homolog distributions and molecular markers of the first category of compound classes will be briefly illustrated with some examples and further details can be found elsewhere (Simoneit, 1978a, and references cited therein}.

Distributions of Homologs

Sane typical examples of homologous compound distributions in lipids of sediments are shown in Figures 2 and 3. Sample 36-330-10-1, 95-102 cm, which is of Jurassic age from the South Atlantic," exhibits n-alkanes maximizing at n-C_{17} and n-C_{19} (Fig. 2A) and even carbon numbered n-fatty acids with a maximum at n-C_{16} (Fig 2E) . . Both these distributions are indicative of primary bacterial lipid residues and there are only traces of allochthonous homologs > C_{21}. These lipids areof a marine origin (Simoneit, 1979b). The n-alkanes are superimposed on a minor unresolved hump which maximized in the GC retention region of C_{17}. Such humps were found for bacterial residues in surface sediments at natural gas emanations in Chile (Simoneit and Didyk, 1978) .

Sample ML71-2-23, 8.0m is from Mangrove Lake, Bermuda, of recent origin in a highly productive sapropelic environment (Hatcher et al., 1979) . The n-alkanes (Fig- 2B) show maxima at n-C_{17} from primary algal synthesis, at n-C_{22} from microbial degradation of algal detritus and a minor one at n-C_{29}, with a strong odd carbon number predominance >C_{26}, derived from higher plant wax (Simoneit, 1975).

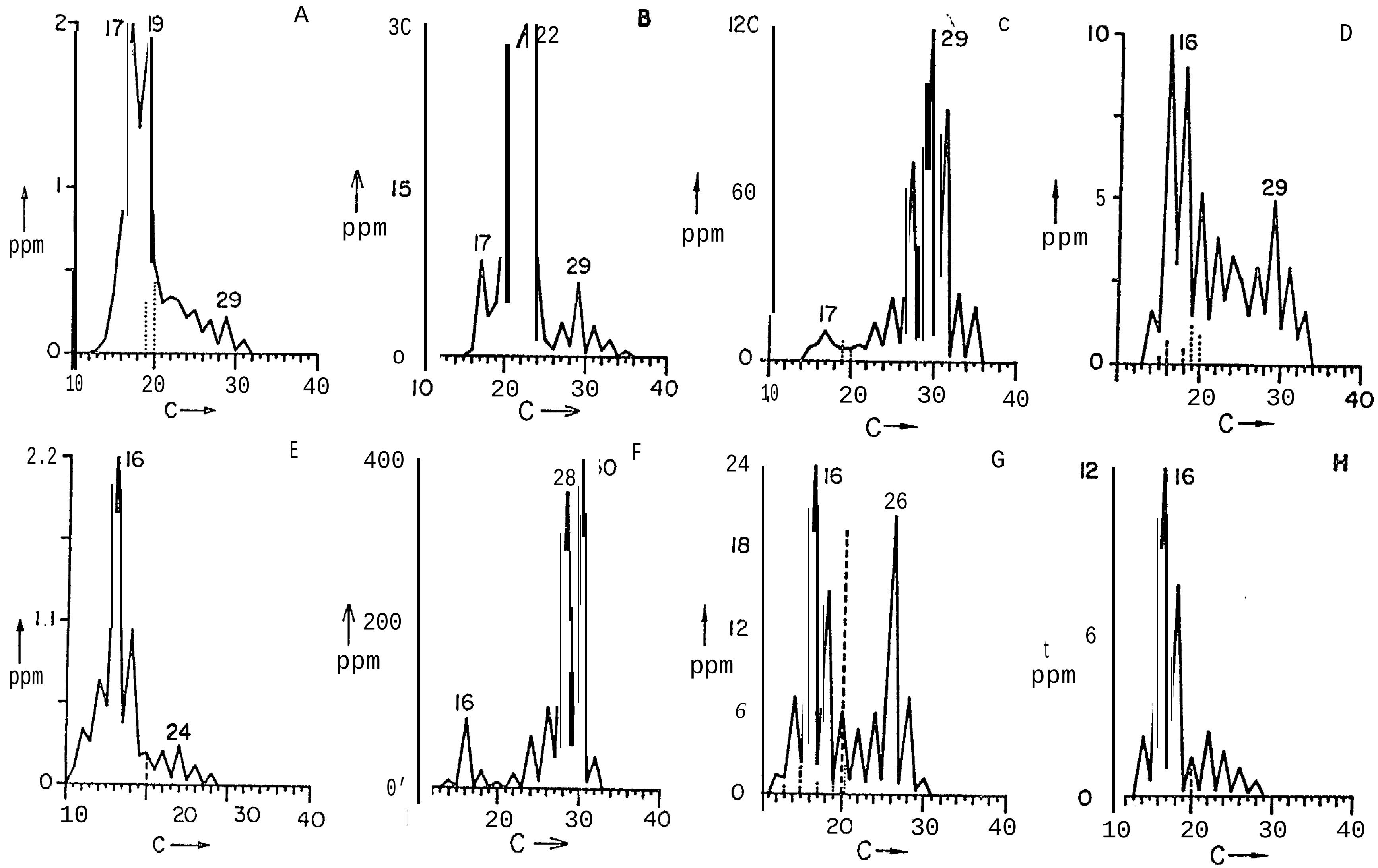


Figure 2: Distribution diagrams of *n*-alkanes (A-D) and *n*-fatty acids (E-H)(...isoprenoids, ---diterpenoids) :

(A,E) Sample 36-330-1.0-1, 95-102 cm, S. Atlantic (Simoneit, 1979b)
(B,F) Sample ML71-2-23, 8.0 m, Mangrove Lake, Bermuda (Hatcher *et al.*,1979)
(C,G) Sample AII49-1462K, 5.0 m, Black Sea (Simoneit 1977b)
(D,H) Sample 18-175-2-2, 45-47 cm, N.E. Pacific (Simoneit, 1979a).

The maximum at n-C_{22} with no carbon number predominance is superimposed on an unresolved hump which also maximizes in that retention region. The n-fatty acids (Fig. 2??} exhibit a bimodal distribution where the predominant maximum at C_{28} and C_{30} is of plant wax origin and the minor homologs < C_{20} are of a marine derivation.

The Black Sea is a sink for terrigenous lipids from plant wax as is indicated by the example (Fig. 2C, G) . The n-alkanes exhibit a maximum at n-C_{29} with a strong odd-to-even carbon number predominance, typical of higher plant wax (Simoneit, 1974, 1977b, 1978b). This is corroborated by the n-fatty acids with their maxima at n-C_{16} and n-C_{26} and strong even carbon number predominance, where the homologs > C_{20} are of an allochthonous terrigenous origin (Simoneit, 1977b, 1978b).

Sample 18-175-2-2, 45-47 cm is an example of a reducing microenvironment, where the n-alkanes (Fig. 2D) exhibit a strong even-to-cold carbon number predominance for the homologs < C_{24} and the distribution follows that of the n-fatty acids < C_{24} (Fig- 2H) . These even n-alkanes < C_{24} may be derived from reduction of fatty acids of olefins from fatty alcohols (Simoneit 1977a; Tiss and Welte, 1977). The n-alkanes > C_{24} with the odd carbon number predominance and maximum at n-C_{29} are derived f rom plant wax.

Strong euxinic conditions of sedimentation are reflected in the saturated hydrocarbons by an excess of phytane > pristane as for example for the Cretaceous black shale from the Cape Verde Basin (Fig. 3A) (Simoneit, 1979a) . Tine n-alkanes exhibit a bimodal distribution with an odd-to-even carbon number predominance and maxima at n-C_{17} and n-C_{31}. The homologs < C_{21} are of an autochthonous origin and those > C_{22} are derived from plant wax. The n-fatty acids (Fig. 3E) also have this same dual. origin, as indicated by the maxima at n-C_{16} and n-C_{24}, with the strong even carbon number predominance. The presence of pristanic and phytanic acids should be noted, as well as the large amount of phytane.

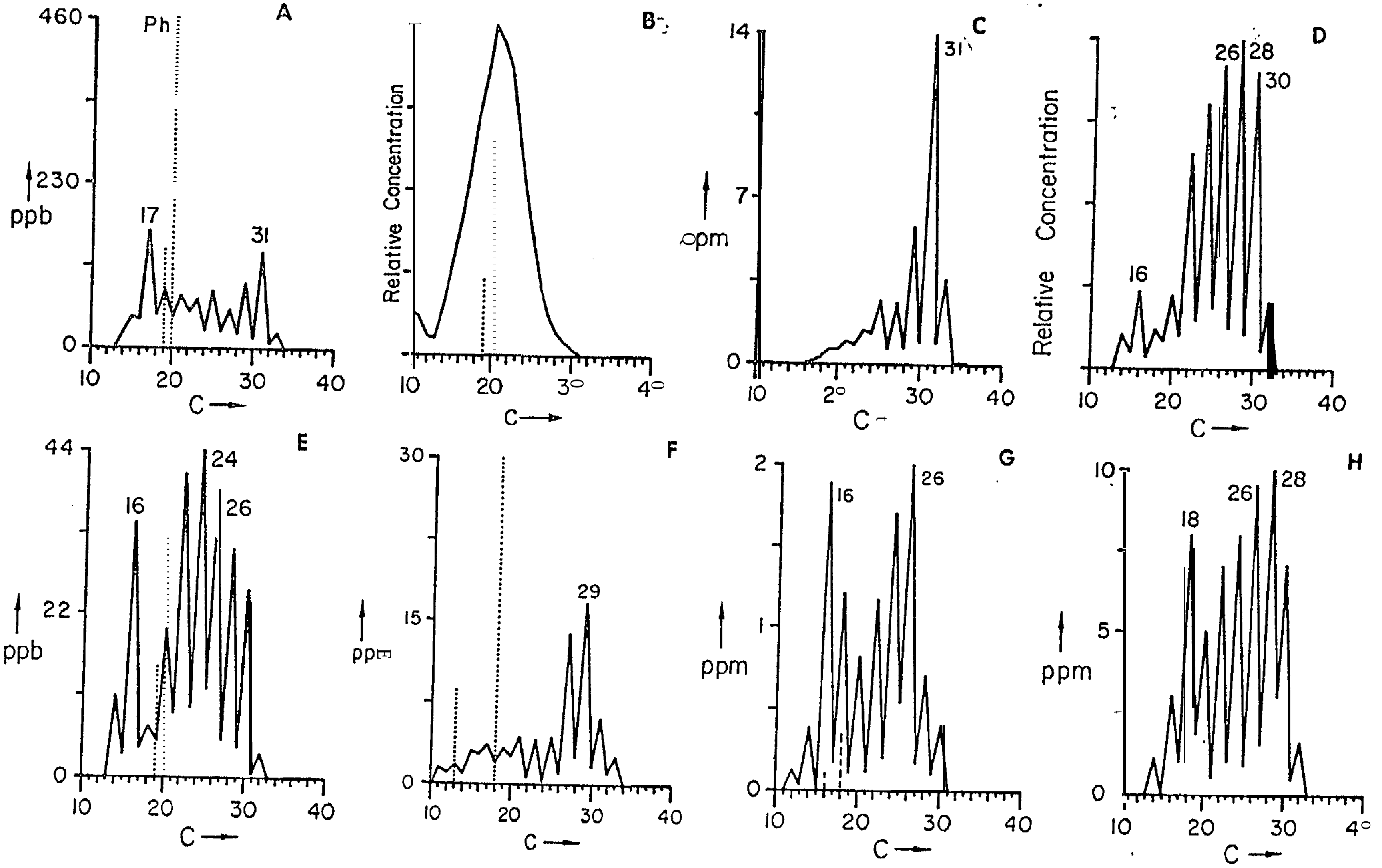


Figure 3: Distribution diagrams of n-alkanes (A-C), n-fatty acids (E,G), n-alkan-2-ones (F) and n-fatty alcohols (D,H)(...isoprenoids,---unsaturated):

(A,E) Sample 41-367-19-4, 10-15 cm, Cape Verde Basin, N. Atlantic (Simoneit,1979a)
(B) Sample 38-345-4-1, 130-140 cm, Norwegian-Greenland Sea, Seepage (Simoneit, 1979a)
(C,G) Eolian dust DC5, North Atlantic (Simoneit, 1977c)
(D) Sample 12-114-5-5, 80-140 cm, N. Atlantic (Simoneit, 1978b)
(F) Sample 42B-381-1-4, 104-115 cm, Black Sea (Simoneit, 1978b)
(H) Eolian dust E2, N. Atlantic (Simoneit, 1977c)

The preservation of the $C_{20} > C_{19}$ isoprenoid skeleton is a consequence of the anoxic depositional environment (Didyk et al., 1978).

The n-alkane distribution of a seep oil from the Norwegian-Greenland Sea is shown in Fig. 3B. It exhibits a maximum at C_{20} and has no carbon number predominance. The n-alkanes are superimposed on the broad unresolved hump which has a maximum at about C_{25} retention and range from C_{12} to C_{31}.

Alkan-2-ones are also found in marine sediments and they are derived from microbial alteration of n-alkanes or n-fatty acids (Arpino, 1973; Simoneit, 1979a). The n-alkan-2-ones of the Pleistocene sample 42B-381-1-4, 104-115 cm from the Black Sea are shown in Fig. 3F. They exhibit a strong odd carbon number predominance with a maximum at C_{29}, reflecting an origin from alkanes of higher plant wax. The 6,10,14-trimethylpentadecan-2-one (Structure I) and 6,10-dimethylundecan-2-one (II) are the predominant isoprenoidal ketones present.

Fatty alcohols are ubiquitous in marine sediments (Sever and Parker, 1969) and an example is shown in Fig. 3D. Sample 12-124-5-5, 80-140 cm is of Oligocene age from the North Atlantic and consists of terrigenous clay (Simoneit, 1979a). The n-fatty alcohols exhibit a bimodal distribution with a major maximum at n-C_{28}, a minor one at n-C_{16} and a strong even carbon number predominance. The homologs > C_{20} are typical of higher plant wax alcohols.

Eolian particulate are carried by trade winds far out to sea and they contain lipids composed of primarily plant wax blown off from continental sources (Simoneit et al., 1977; Simoneit, 1977c). Dust sample DC 5 from over the Atlantic Ocean is shown as an example in Fig. 3C and G for comparison purposes. The n-alkanes show a strong odd carbon number predominance and maximum at n-C_{31} only. The n-fatty acids show a bimodal distribution with a strong even carbon number predominance and maxima at n-C_{16} and n-C_{26}. The n-alkanes > C_{20} and the n-fatty acids > C_{20} are typical of plant wax. The n-fatty acids < C_{20} have a probable dual origin from the sea slick and from desiccated lacustrine muds. The n-fatty alcohols of dust sample E2 from over the Atlantic are shown in Fig. 3H. They exhibit a bimodal distribution with a strong even carbon number predominance and maxima at C_{18} and C_{28}. The homologs > C_{20} are again typical of higher plant wax alcohols.

The distribution patterns of homologous compounds in lipids can be used to make partial assessments of the genetic origins of those compounds. This approach can be further strengthened by coupling it with the analysis and interpretation of the molecular fossils in the lipids.

Molecular Markers

Molecular markers which are characteristic of a biogenic (terrigenous and/or marine] or of a petrogenic origin can be identified in lipid fractions. The n-alkanes, n-fatty acids, n-alkan-2-ones, n-fatty alcohols and isoprenoids can be considered as molecular markers based on their homolog distributions. However, the structurally more complex molecules have a much greater information content. The terpenoids are the compound groups which have had the greatest utility as specific markers.

The sesquiterpenoids that have been identified in the marine environment are primarily cadalene (III), with various tetrahydro analogs. They are of both a marine (algal) and terrigenous origin (Simoneit and Kaplan, 1979).

The diterpenoids that have been characterized fit into two classes, those derived from terrigenous sources (Simoneit, 1977a) and extended diterpanes of a probable marine origin (Simoneit, unpublished data). The terrigenous diterpenoids consist of a large number of compounds and the most abundant analogs are dehydroabietic acid (IV), dehydroabietin (V), dehydroabietane (VI), simonellite (VII), retene (VIII), tetrahydroretene (IX), fichtelite (X), pimanthrene (XI), 17-nordehydroabietane (XII), isoene (XIII), 13-methylpodocarpa-8, 11, 13-triene (XIV), and norsimonellite (XV) (Simoneit, 1979a in preparation). The extended diterpanes were first identified in shale and petroleum (eg., Reed, 1977), where they are ubiquitous, and then in Recent sediments. Most of their occurrences were coupled with the presence of the 17 α(H)-hopane series of triterpanes, which are geologically mature, i.e., old (Simoneit and Kaplan, 1979). These extended tricyclic diterpanes range from $C_{19}H_{34}$ to $C_{26}H_{48}$ and sometimes to $C_{29}H_{54}$ with very similar distributions. The inferred skeleton for the C_{19} - C_{24} homologs is Structure XVI. The $C_{26}H_{48}$ homolog (in some cases to $C_{29}H_{54}$) is resolved on capillary GC into an R and S diastereomeric pair (Simoneit and. Kaplan, 1979). Some distributions are shown as examples in Figure 4. The samples from the Southern California Bight (Fig. 4C, D) are contaminated by petroleum seepage, indicating that the" extended diterpanes are syngenetic with the 17α (H)-hopane series. However, the extended diterpanes in the Recent sample from Walvis Bay (Fig. 4B) must be derived from a marine source since no petroleum contamination is evident.

The triterpenoids found in most marine sediments are of an autochthonous origin and are usually comprised of the hopane and to a lesser extent the moretane series. The homologs consist of trisnorhopane (XVII, R=H), norhopane (XVII, $R=C_2H_5$), hopane (XVII, $R=C_3H_7$) and extended hopanes ranging from C_{31} to C_{35} (XVIII) with minor amounts of the corresponding moretanes (XIX).

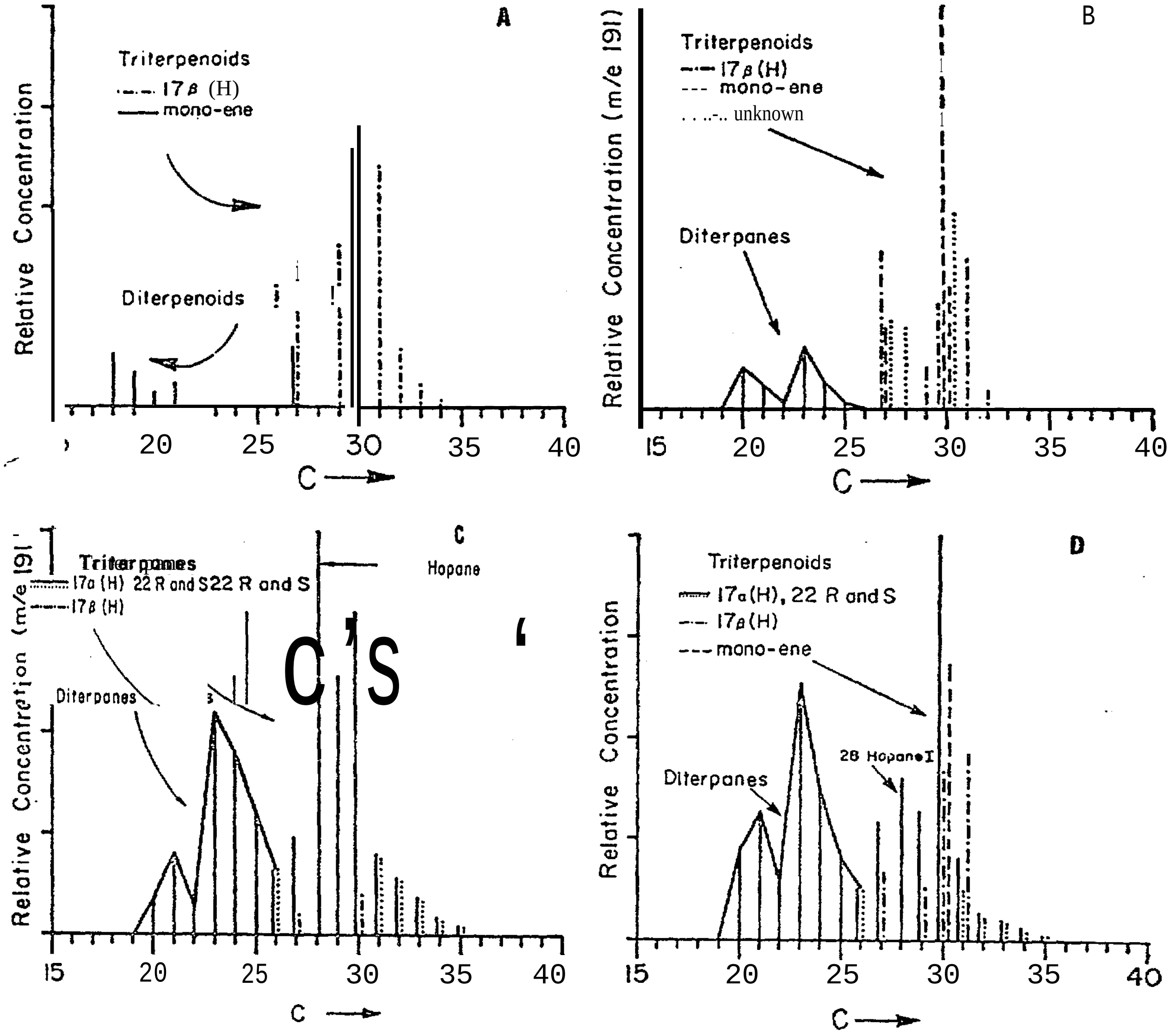


Figure 4: Relative distribution histograms for diterpenoids and triterpenoids (based on the m/e 191 mass chromatograms or gas chromatographic response) of some examples. The R and S diastereomers are also indicated and C_{28} Hopane I is 17α(H),-18α(H),21β(H)-28,30-bisnorhopane.

(A) Sample 30G-I (102-105 cm), Guaymas Basin, Gulf of California (Simoneit et al., 1979).

(B) Sample AII 93/3-18 (197-201 cm), Walvis Bay, SW Africa (Simoneit and Kaplan, 1979)

(C) Sample 193 (25-31 cm), Santa Barbara Coastal Area, Southern California Bight (Simoneit and Kaplan,1979)

(D) Sample 575 (25-31 cm), Tanner Basin, Southern California Bight (Simoneit and Kaplan, 1979).

The $17\overset{\beta}{\cancel{\alpha}}$(H) stereochemistry predominates in Recent, immature sediments (Dastillung and Albrecht, 1976) and various triterpenes such as diploptene (XX), $17\overset{\beta}{\cancel{\alpha}}$(H)-hop-21(22)-ene (XXI) and hop-17(21)-ene (XXII) are also present. The Recent sediments from the Gulf of California and Walvis Bay (Fig. 4A and B) illustrate this point in that only $17\overset{\beta}{\cancel{\alpha}}$(H)-hopanes and hopenes are present. The extended $17\overset{\beta}{\cancel{\alpha}}$(H)-hopanes occur as only the 22S diastereomer in Recent sediments as the direct markers of biosynthesis. In ancient sediments or crude oil, the hopanes occur as the 17α(H) stereomers and the extended 17α(H)-hopanes are found as 22Rand 22S diastereomeric pairs, where full maturity is indicated by an S/R ratio of one (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1979). The samples from the Southern California Bight (Fig. 4C and D) show this type of distribution? where in sample 193 only petroleum residues and matured 17α(H)-hopanes are found and in sample 575, a mixture of Recent and ancient triterpenoids and allied lipids are present. Also a $C_{28}H_{48}$ triterpane is a major analog in the Southern California bight sediments and it has been identified as 17α(H),18α(H),$21\overset{\beta}{\cancel{\alpha}}$(H)-28,30-bisnorhopane (XVIII) (Seifert et al., 1978; Simoneit and Kaplan, 1979). This compound appears to be a specific marker for Southern California petroliferous residues, as it is not found in other areas (Simoneit and Kaplan, 1079).

Steroidal compounds are widespread in marine sediments and they undergo complex diagenetic reactions yielding various series of hydrocarbons, alcohols and ketones (XXIV) (Gaskell, 1974; Lee et al., 1977, 1979; Huang and Meinschein 1979). The saturated hydrocarbons are comprised of the steranes [XXV, eg., cholestane, 5α(H) vs. coprostane, 5β(H)], diasteranes (XXVI) and traces of other isomers. Examples of sterane distributions are shown in Figure 5 for a Cretaceus and a Jurassic sample from the South Atlantic. The 5α stereomers predominante over the 5β (Simoneit, 1979b). Unsaturated hydrocarbons are found mainly as ster-2-enes, ster-4-enes and monoaromatic steranes (XXVII) , and functionalized analogs are found as stan-3-ols and stan-3-ones. Various series of 4-methylsteroids have also been identified in sane environments (eg., Mattern et al., 1970).

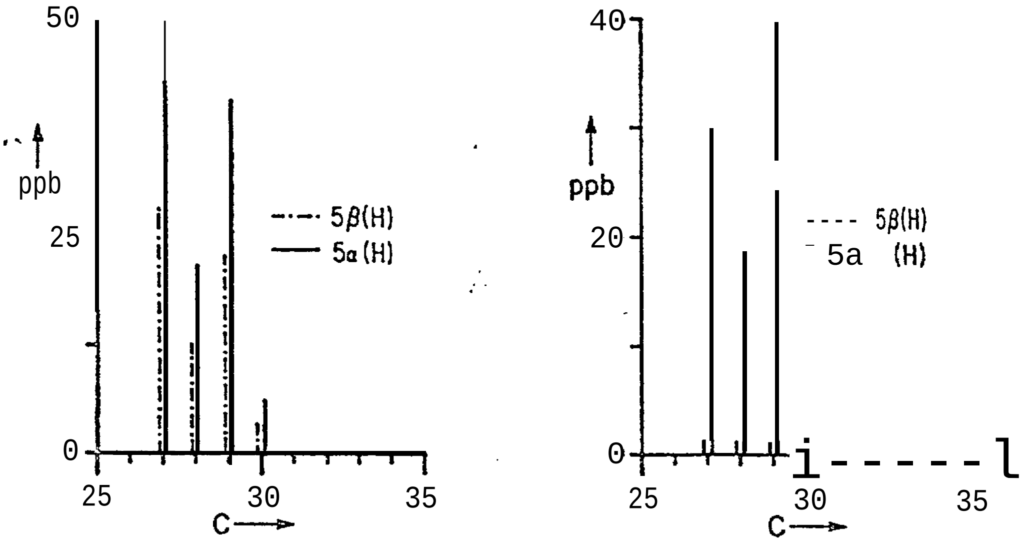


Figure 5. Concentrations of steranes: (A) Sample 36-330-4-2 (120-126 cm) , (B) Sample 36-330-10-1 (95-102 cm) (Simoneit, 1979b).

Other minor components that can be utilized as molecular markers are tetraterpenoids, iso- and anteiso- alkanes or fatty acids, hydroxy fatty acids (eg., Boon et al., 1977), wax esters (Boon and deLeeuw, 1979), tetrapyrrole pigments and aromatic hydrocarbons (eg., Windsor and Hites, 1979). The tetraterpenoids are generally quite labile (eg., carotenoids), but can be preserved in anoxic environments (Watts and Maxwell, 1977). Tetrapyrrole pigments have been extensively studied and they are excellent molecular markers as well as geothermal sensors (eg., Baker and Smith, 1974) .

Aromatic hydrocarbons are found in hemipelagic sediments and are composed mainly of polynuclear aromatic compounds with limited alkyl substitution. These polynuclear aromatic hydrocarbons are proposed as markers of pyrogenic activity (eg., Windsor and Hites, 1979). In anoxic sediments (Recent to Cretaceous), significant amounts of perylene (XXVIII) are found (Didyk et al., 1978; Simoneit, 1978b). This compound appears to be derived from diagenetic alteration of naphthol pigments under reducing conditions. Aromatic hydrocarbons can also be derived from olefinic cyclic precursors of natural origin by disproportionation or hydrogen abstraction reactions. The major examples of such compounds which have been identified in the marine environment are summarized in Figure 6. The compounds in rows a and b are derived from sesquiterpenoids of both marine and terrigenous origins and from diterpenoids of a terrigenous origin (Simoneit, 1977a). The aromatized steranes (XXVII) are derived from diasterenes [ring D olefin of xxvi) (Spyckerelle, 1975). The compounds in row c are derived from the olefins (ring E or side-chain) of the hopane and/or moretane series by successive ring aromatization, which proceeds from ring D to A (Greiner et al., 1977). These compounds can be considered as markers of a predominantly marine (microbial) origin, since their precursors are ubiquitous in these environments (Rohmer, 1975; Rohmer and Ourisson, 1976). They occur as minor components in environments receiving terrigenous detritus. Pentacyclic aromatic hydrocarbons (analogs to those of row C, Fig. 6), where the aromatization occurred from ring A to D, and the series in row D (Fig. 6) have been identified in environments receiving dominantly terrigenous drainage (eg., in Indonesia, P. Albrecht, private communication; Amazon River, Laflamme and Hites, 1979). These compounds can be considered as indicators of terrestrial higher plants.

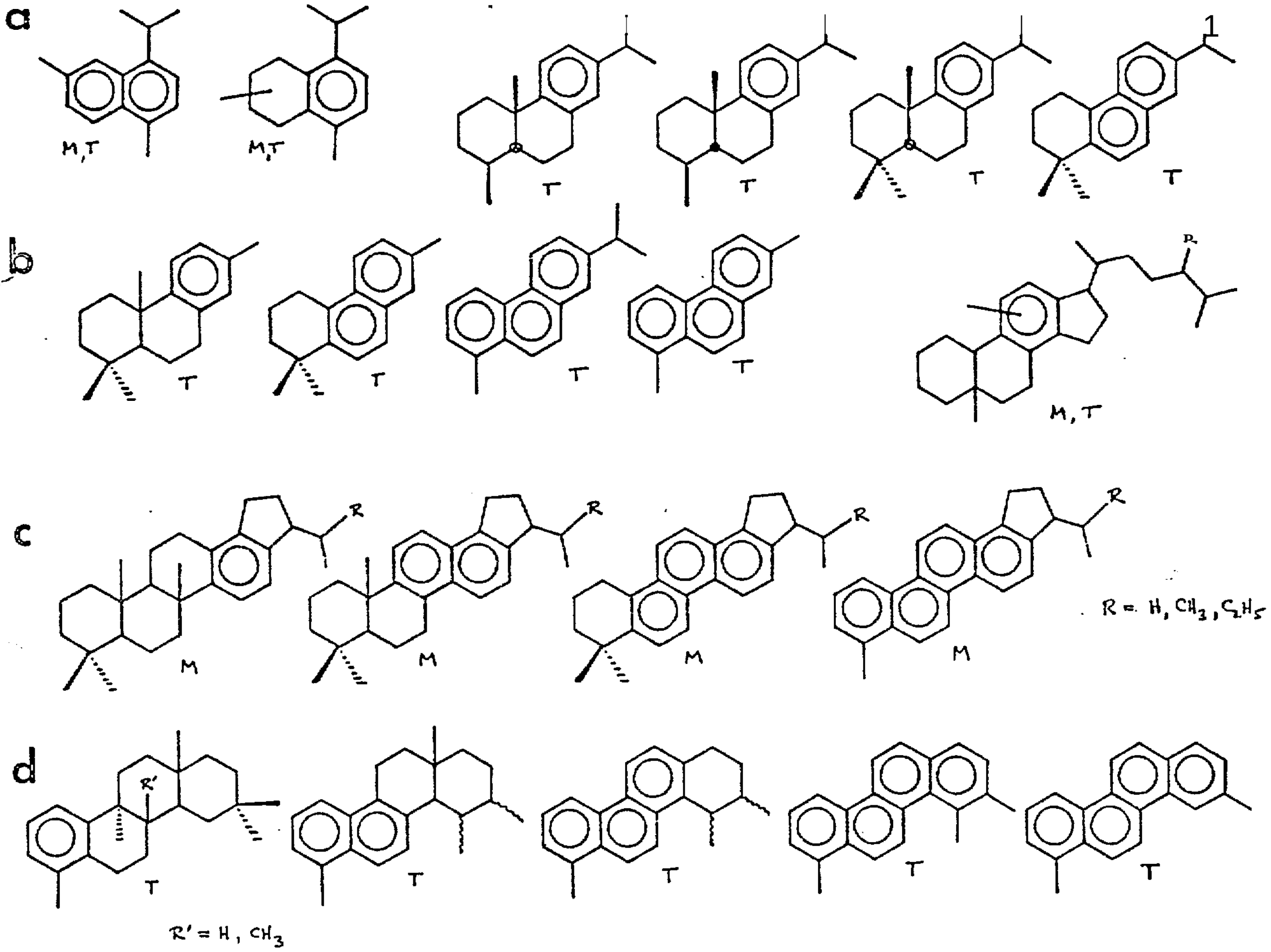


Figure 6: Some aromatic compounds derived from diagenesis of sesqui-, di- and triterpenoids and steroids (T = terrigenous and M = marine origin).

Humates (and fulvates)

Both humic and fulvic substances are mixtures of complex macromolecules, and the latter are of lower molecular weights and thus soluble in dilute HCl. Little is known about the detailed structures of the compounds concerned and the analytical data consist of their various bulk properties (eg., Schnitzer and Khan, 1972; Stuermer, 1975; Huc, 1973, 1978) . It has been shown that humic substances decrease in concentration with depth of burial or geologic age and are probably incorporated into the kerogenous material (eg. , Nissenbaum and Kaplan, 1972; Stuermer and Simoneit, 1978). This trend is illustrated in Fig. 7 showing the decrease of humates with depth to the upper Jurassic for DSDP site 44-391 (Stuermer and Simoneit, 1978). The abundance of humates at this site at depths of 600-1000 m subbottom indicates that a significant contribution of land-derived organic matter had occurred (Deroo _et al._, 1978). Data for fulvates are sparse, although they are being determined in sea waters. Both these carbon fractions should be characterized for more environments to yield better baseline data for the marine realm.

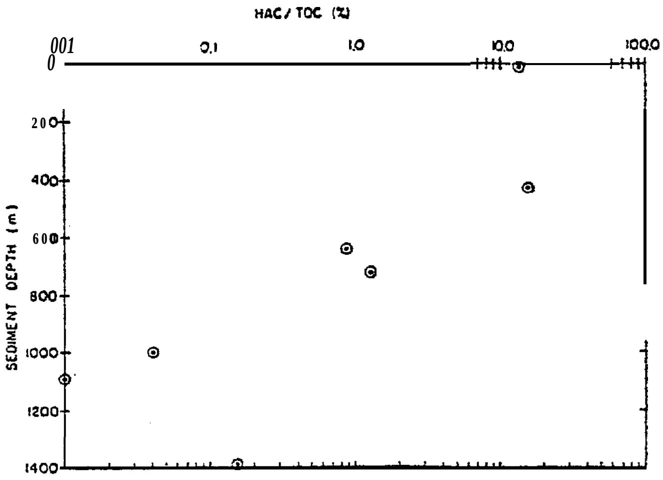


Figure 7: Plot of percent humic acid carbon with respect to total organic carbon versus sediment depth at DSDP site 4.4-391 (Stuermer and Simoneit, 1978).

Kerogen

Kerogens are also complex mixtures of high molecular weight moieties of various, essentially unknown structures. The end members of kerogen sources are coals for terrigenous and alginites for marine origins. Most kerogens of the marine realm are admixtures of all input sources (eg., Tissot et al., 1974). Kerogen is an invaluable endogenous paleoenvironmental marker for the origin of the bulk of the organic matter. This could be enhanced if its bulk structure, and thus its genetic origin, could be characterized. The elemental composition and H/C and O/C ratios of kerogen can be correlated using van Krevelen (1961) diagrams to assess the magnitude of the allochthonous influx and the extent of diagenesis (eg., Deroo et al., 1978) . Using the stable carbon isotope ratios in a correlation versus H/C (eg., Figure 8) of kerogens of Recent to Cretaceus age reveals a clustering which reflects the genetic origin, i.e., terrigenous, marine or a mixture of both. Ancient kerogen can be eroded from continental geologic formations and recycled to marine sediments (eg., Sackett et al., 1974). Recent sediments, eg., algal mats, yield a "protokerogen" which is lipid macromolecular material constitutionally less complex than ancient kerogen but related to it (eg., Philp and Calvin, 1976, 1977).

Kerogen is sensitive to thermal stress from either the normal gradient due to depth of burial (eg., Tissot et al., 1971; Tissot and Welte, 1978) or from transients such as intrusions (Simoneit et al., 1978). This catagenesis results in the generation of bitumen (petroleum) from the kerogen, which in turn becomes more aromatic. This is illustrated in Figure 9, where an igneous sill intrusion into Cretaceus shale resulted in the loss of volatiles and decrease in H/C in the major sill proximity (Simoneit et al., 1978). Thus, the bulk parameters of kerogen can be good indicators of the thermal history of the sediment.

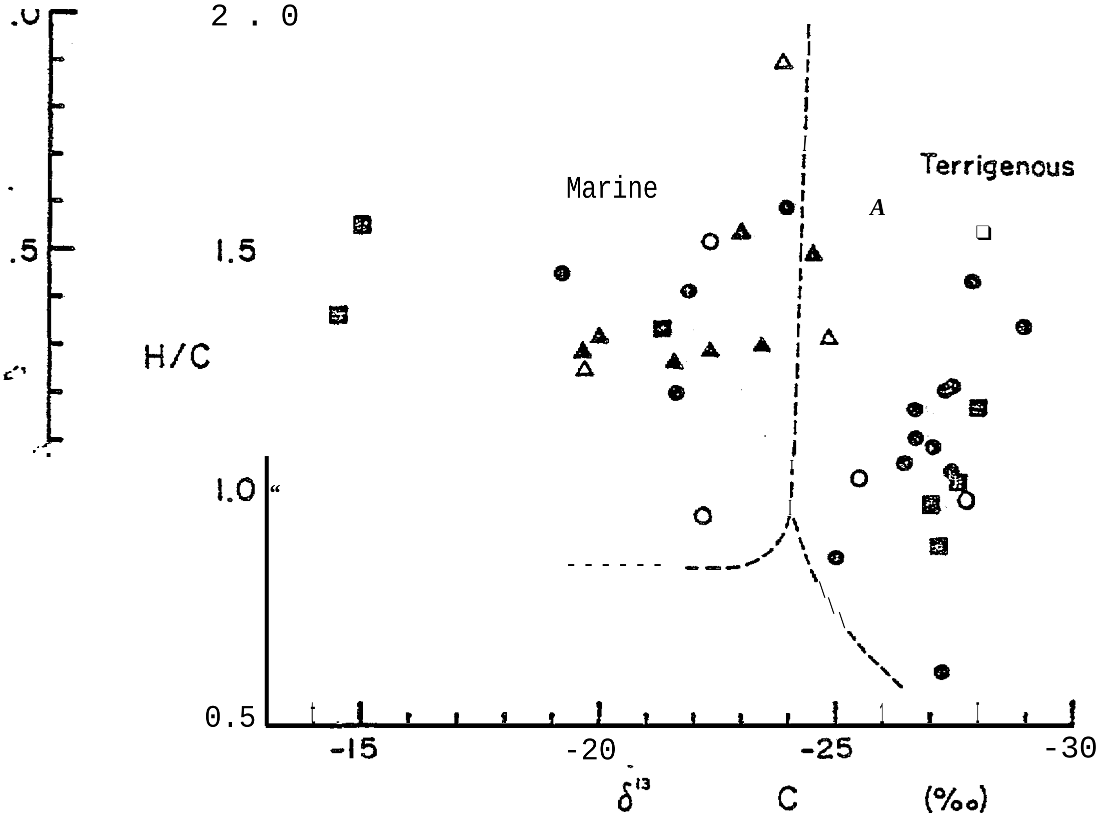


Figure 8: Correlation diagram of H/C versus $\delta^{13}C$ for some kerogens and humates (▲ Recent kerogen; ● Cretaceous kerogen; ■ Recent kerogen from work of Stuermer et al., 1978; △ Recent and ○ Cretaceus humates).

Since kerogen represents the major portion of the sedimentary organic matter, more extensive analyses are needed.

Transit Wales of Organic Matter

Autochthonous organic detritus from the euphotic zone undergoes extensive edification on passing through the feed web down to the sea floor. The residual organic matter from fauna then becomes incorporated into the sediment (Demaison and Moore, 1979; Simoneit, 1975; 1978a).

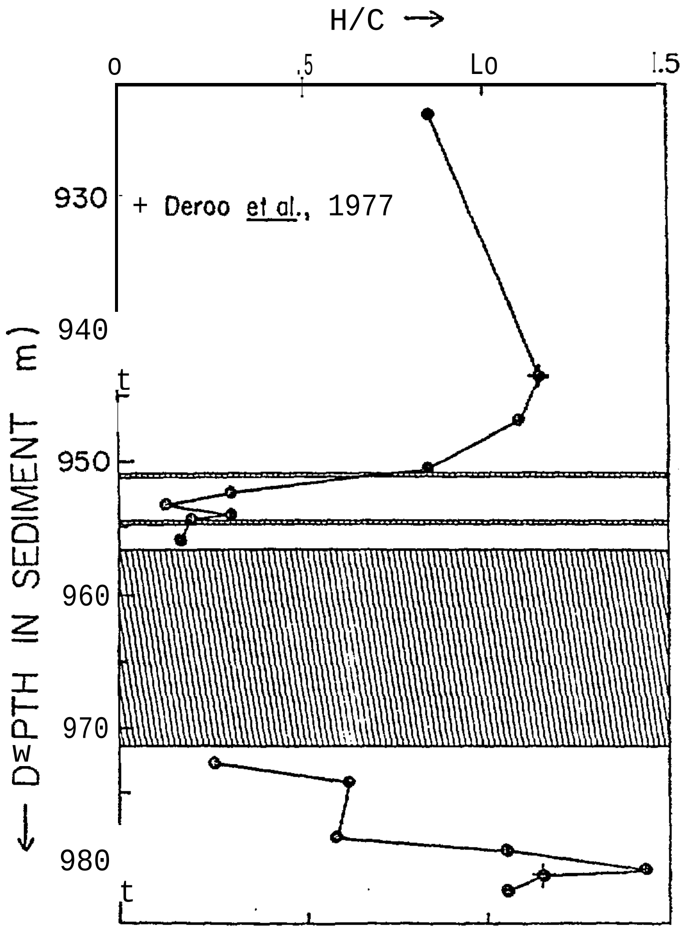


Figure 9: Plot of the atomic H/C of the kerogens at DSDP site 41-368 versus depth in the sediment (Simoneit et al., 1978). The intrusions are indicated by the hatched areas.

The amount of allochthonous organic matter reaching the deep sea is usually small. However, over geological time spans such material makes a significant contribution to hemipelagic sediments. The major transport mechanisms for terrestrial organic detritus are the rivers, wind and ice-rafting (Simoneit, 1975; 1978a; Davies and Gorsline, 1976). Although river transport is obviously the major input mechanism for terrigenous organic matter to the marine environment, little is known about quantities and general makeup of the material. This potamic influence is evident in the Black Sea (Simoneit, 1974, 1977b, 1978a) and in the Amazon outflow (Aizenshtat et al., 1973). Eolian transport carries terrigenous organic detritus far out to sea

Welte, 1978; Simoneit, 1978a) but need more work.

ACKNOWLEDGEMENTS

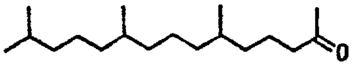
I thank the National Science Foundation (Grants ATM 77-19980 and OCE 76-21506) and the Department of Energy (Grant No. EY76-S-03-0034 , PA134) for partial financial assistance.

DISCUSSION

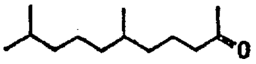
Walton (Fisheries and Oceans Canada, Ottawa): Where was that core taken (Fig.7)?

Simoneit: A deep-sea drilling core from the Western Atlantic. The humic acid has been found in the Cretaceus, where you have the right mild geological conditions.

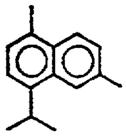
Chemical Structures Cited



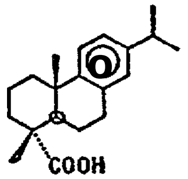
I . 6,10,14-trimethylpentadecan-2-one



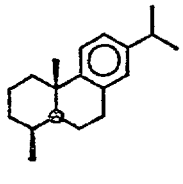
11. 6,10-dimethylundecan-2-one



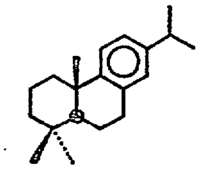
111. cadalene



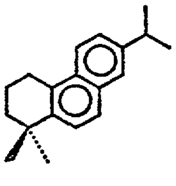
IV. dehydroabietic acid



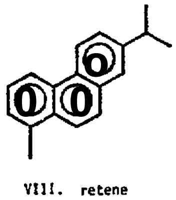
V. dehydroabietin



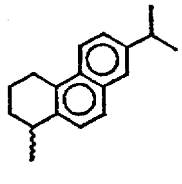
VI. dehydroabietane



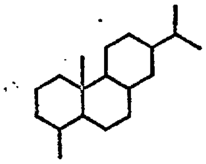
VII. simonellite



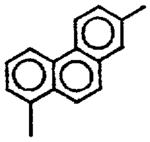
VIII. retene



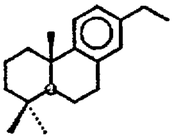
IX. tetrahydroretene



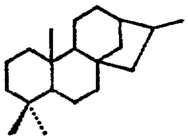
X. fichtelite



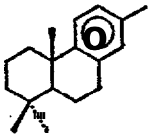
xl. pimanthrene



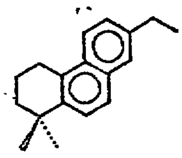
X11. 17-nordehydroabietane



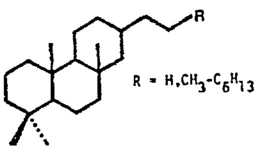
XIII. iosene



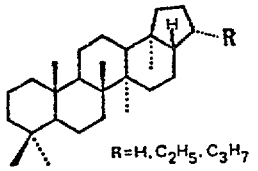
XIV. 13-methylpodocarpa-8,11,13-triene



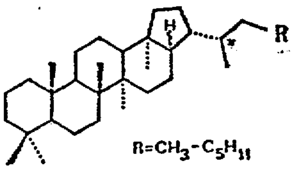
XV. norsimonellite



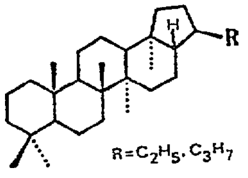
XVI. extended diterpanes



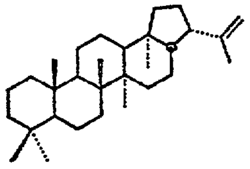
XVII. hopanes



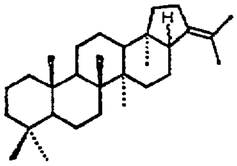
XVIII. extended hopanes



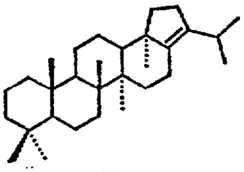
XIX. moretanes



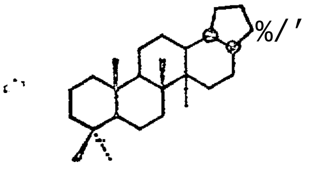
x x. diploptene



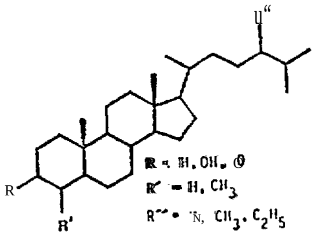
XXI. hop-21 (22)-ene



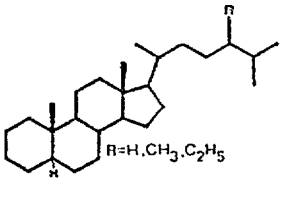
XXII. hop-17(21)-ene



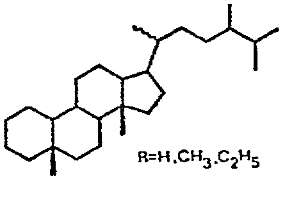
XXIII. $17\alpha(H),18\alpha(H),21\beta(H)$-28,30-bisnorhopane



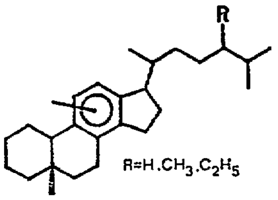
XXIV. steroidal derivatives



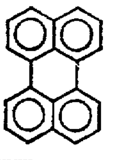
XXV. steranes, $5\alpha/\beta(H)$



XXVI. diasteranes



XXVII. monoaromatic steranes



XXVIII. perylene

REFERENCES

Aizenshtat, A., ?4. J. Baedecker and I. R. Kaplan (1973). Distribution and diagenesis of organic compounds in JOIDES sediment from Gulf of Mexico and Western Atlantic. Geochim. Cosmochim. Acta 37; 1881-1898.

Arpino, P. (19-?3). Les lipides des sediments lacustres eocenes, These, L'Universite Louis Pasteur de Strasbourg, France.

Baker, E. W. and G. D. Smith (1974). Pleistocene changes in chlorophyll pigments, in: Advances in Organic Geochemistry 1973, B. Tissot and F. Bienner, eds., Editions Technid, Paris; pp. 649-660.

Bernard, B. B., J. M. Brooks and W. M. Sackett (1976). Natural gas seepage in the Gulf of Mexico. Earth Planet. Sci. Lett. 31, pp. 48-54.

Boon, J. J., F. W. v. d. Meer, P. J. W. Schuyl, J. W. de Leeuw, P.A. Schenck, and "A. L. Burlingame (1978). Organic geochemical analyses of core samples from site 362, Walvis Ridge, DSDP Leg 40, in Initial Reports of the Deep Sea Drilling Project, Vol. 40, Suppl., U. S. Govt. Printing Office, Washington, D. C., pp. 627-637.

Boon, J. J., R. deLange, P. J. W. Schuyl, J. W. deLeeuw and P. A. Schenck (1977). Organic geochemistry of Walvis Bay diatomaceous ooze-II. Occurrence and significance of the hydroxy fatty acids, in: Advances in Organic Geochemistry 1975, R. Campos and J. Goni (eds.), ENADIMSA, Madrid; pp. 255-272.

Claypool, G. E. and I. R. Kaplan (1974). The origin and distribution of methane in marine sediments, in Natural Gases in *Marine* Sediments, I.R. Kaplan, cd., Plenum Publishing Corp., New York, pp. 99-3.39.

Dastillung, M. and P. Albrecht {1976}. Molecular test for oil pollution in surface sediments. Mar. Poll. Bull. 7; 13-15.

Davies, T. A. and D. S. Gorsline (1976). Oceanic sediments and sedimentary processes, in Chemical Oceanography, J. P. Riley and R. Chester, eds., Vol. 5, Academic Press, pp. 1-80.

Demaison, G. J. and G. T. Moore *(1979)*. Anoxic environments and oil source bed genesis, Org. Geochem. (in press).

Deroo, G., J. P. Herbin, J. Roucache, B. Tissot, P. Albrecht and J. Schaeffle (1977). Organic geochemistry of some Cretaceous black shales from sites 367 and 368, Leg 41, Eastern North Atlantic, in Initial Report of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., U. S. Gov. Print. Office, Washington, D. C., 865-873.

Deroo, G., J. P. Herbin, J. R. Roucache, B. Tissot, P. Albrecht and M. Dastillung (1978). Organic geochemistry of some Cretaceus claystones from site 391, Leg 44, Western North Atlantic, in Initial Reports of the Deep Sea Drilling 44, W. E. Benson, R. E. Sheridan, et al., U. S. Govt. Printing Office, Washington D. C., pp. 593-598.

Didyk, B. M., B. R. T. Simoneit, S. C. Brassell, and G. Eglinton (1978) Organic geochemical indicators of paleoenvironmental conditions of sedimentation. Nature 272; 216-222.

Eglinton, G., B. R. T. Simoneit and J. A. Zero (197S). The recognition of organic pollutants in aquatic sediments. Proc. Roy. Sot. Lond. B189, pp. 415-442.

Gaskell, S. J. (1974). The environmental geochemistry of sterols, Ph.D. Thesis, University of Bristol, England; 321 pp.

Greiner, A. C., C. Spyckerelle, P. Albrecht and G. Ourisson (1977). Aromatic hydrocarbons from geological sources. Part V. Mono- and di-aromatic hopane derivatives. J. Chem. Res. (S) 1977; p. 334.

Hatcher, P. G., B. R. T. Simoneit, F. T. Mackenzie, A. C. Neumann, D. C. Thorstenson and S. M. Gerchako~~w~~v (1979). Organic geochemistry of Mangrove Lake Bermuda. Org. Geochem., in preparation.

Huang, W. Y. and W. G. Meinschein (1979). Sterols as ecological indicators. Geochim. Cosmochim. Acts 43; 739-745.

Hue, A. Y. (1973). Contribution a l'etude de l'humus marin et de ses relations avec les kerogenes, These Docteur-ingenieur, University de Nancy, France.

Huc, A. Y. (1978). Geochimie organique des schistes bitumineux du Toarcien du bassin de Paris, These Docteur es-Sciences, l'University Louis Pasteur de Strasbourg, France, 137 pp.

Hunt, J. M. (1975). Origin of gasoline range alkanes in the deep sea. Nature 254, 411-413.

Hunt, J. M. and J. K. Whelan (1978). Dissolved gases in Black Sea sediments, in Initial Reports of the Deep Sea Drilling Project, Vol. 42B, D. A. Ross, Y. Neprochnov, et al., U. S. Govt. Printing Office, Washington, D. C., pp. 661-665.

Laflamme, R. E. and R. A. Hites [1979). Tetra and pentacyclic naturally-occurring, aromatic hydrocarbons in recent sediments. Geochim. Cosmochim. Acts 43; 1687-1691.

Larter, S. and A. G. Douglas (1978). Low molecular weight aromatic hydrocarbons in coal maceral pyrolysates as indicators of diagenesis and organic matter type in Environmental Biogeochemistry and Geomicrogeology, W. E. Krumbein, cd., Ann Arbor, Vol. 1, pp. 373-386.

Lee, C., R. B. Gagosian and J. W. Barrington (1977). Sterol diagenesis in Recent sediments from Buzzard's Bay, Massachusetts. Geochim. Cosmochim. Acta 41; 985-992.

Lee, C., J. W. Barrington and R. B. Gagosian (1979). Sterol geochemistry of sediments from the western North Atlantic Ocean and adjacent coastal areas. Geochim. Cosmochim. Acts 43; 35-46.

Mattern, G., P. Albrecht and G. Ourisson (1970). 4-Methyl-sterols and sterols in Messel shale (Eocene). Chem. Comm. 1970; 1570-1571.

Philp, R. P. and M. Calvin (1976). Kerogen structures in recently-deposited algal mats at Laguna Mormona, Baja California: A Model system for the determination of kerogen structures in ancient sediments. in Environmental Biogeochemistry, J. O. Nriagu, cd., Ann Arbor, Vol. 1, pp. 1.31-148.

Philp, R. P. and M. Calvin (1977). Kerogenous material in Recent algal *mats* at Laguna Mormona, Baja California, in Advances in Organic Geochemistry 1975, R. Campos and J. Goni, eds., ENADIMSA, Madrid, pp. 735-752.

Philp, R. P., M. Calvin, S. Brown and E. Yang (1978). Organic geochemical studies on kerogen precursors in recently-deposited algal mats and oozes, Chem. Geol. 22; 207-231.

Reed, W. E. (1977). Molecular compositions of weathered petroleum and comparison with its possible source. Geochim. Cosmochim. Acts 41; 237-247.

Reed, W. E. and I. R. Kaplan (1977). The chemistry of marine petroleum seeps, J. Geochem. Explor. 7, 255-293.

Rohmer, M. (1975). Triterpenoides de procaryotes, Ph.D. Thesis, University Louis Pasteur de Strasbourg, France: 100 pp.

Rohmer, M. and G. Ourisson (1976). "Derives du bacteriohopane: Variations structurales et repartition. Tetr. Lett. 1976; 3637-3640.

Sackett, W. M., C. W. Poag and B. J. Eadie (1974). Kerogen recycling in the Ross Sea, Antarctica. Science 185, 1045-1047.

Sever, J. and P. L. Parker (1969). Fatty alcohols (normal and Isoprenoid) in sediments. Science 164; 1052-1054.

Schnitzer, M. and S. U. Khan (1972). Humic Substances in the Environment, Marcel Dekker, New York, 327 pp.

Simoneit, B. R. (1974). Organic analyses of Black Sea cores, in The Black Sea-Geology, Chemistry and Biology, E. T. Degens and D. A. Ross, eds., Memoir 20, Amer. Assoc. Petrol. Geol., Tulsa, pp. 477-498.

Simoneit, B. R. T. (1975). Sources of organic matter in oceanic sediments, Ph.D. Thesis, University of Bristol, England, 300 pp.

Simoneit, B. R. T. (1977a). Diterpenoid compounds and other lipids in deep-sea. sediments and their geochemical significance. Geochim. Cosmochim. Acts 41, 463-476.

Simoneit, B. R. T. (1977b). The Black Sea, A sink for terrigenous lipids. Deep-Sea Res. 24, 813-830.

Simoneit, B. R. T. (1977c). Organic matter in eolian dusts over the Atlantic Ocean. Proc. of Symp. on concepts in Marine Chemistry, Mar. Chem. 5; 443-464.

Simoneit, B. R. T. (1978a). The organic chemistry of marine sediments in Chemical Oceanography, 2nd Edition, J. P. Riley and R. Chester, eds., Academic

Press, New York, Vol. 7, Chap. 39; pp. 233-311.

Simoneit, B. R. T. (1978b). Organic geochemistry of terrigenous muds and various shales from the Black Sea, DSDP Leg 42B, in Initial. Reports of the Deep Sea Drilling Project, 42, Part 2, D.. Ross, Y. Neprochnov et al., U. S. Govt. Printing Office, Washington, D. C.; pp. 749-753.

Simoneit, B. R. T. (1979a). Terrigenous and marine organic markers and their input to marine sediments in Proceedings of Symp. on Organic Geochemistry of Deep Sea Drilling Project Sediments, E. W. Baker, ed., Science Press, Princeton, N. J., in press.

Simoneit, B. R. T. (1979b). Organic geochemistry of Mesozoic sediments from the Falkland Plateau, DSDP Leg 36 Site 330, in Initial Reports of the Deep Sea Drilling Project, Vol. 50, Y. Lancelot, E. Winterer, et al., U. S. Government Printing Office, Washington, D. C., in press.

Simoneit, B. R. T. and B. M. Didyk (1978). Organic geochemistry of a Chilean paraffin dirt. Chem. Geol. 23; 21-40.

Simoneit, B. R. T. and I. R. Kaplan (1979). Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern California Bight. Mar. Environ. Res., in press.

Simoneit, B. R. T., R. Chester and G. Eglinton (1977). Biogenic lipids in particulate from the lower atmosphere over the Eastern Atlantic. Nature 267; 682-685.

Simoneit, B. R. T., S. Brenner, K. E. Peters and I. R. Kaplan (1978). Thermal. alteration of Cretaceus black shale by basaltic intrusions in the Eastern Atlantic. Nature 273; 501-504.

Simoneit, B. R. T., M. A. Mazurek, S. Brenner, P. T. Crisp and I. R. Kaplan (1979). Organic geochemistry of Recent sediment from Guaymas Basin, Gulf of California. Deep-Sea Res., in press.

Spyckerelle, C. (1975). Constituents aromatiques de sediments, Ph.D. Thesis, University Louis Pasteur de Strasbourg, France; 108 pp.

Stuermer, D. H. (1975). The characterization of humic substances in seawater, Ph.D. Thesis, Massachusetts Institute of Technology and Weds Hole Oceanographic Institution, Woods Hole, 188 pp.

Stuermer, D. H. and B. R. T. Simoneit (1978). Varying sources for the lipids and humic substances at site 391, Blake-Bahama Basin, DSDP Leg 44, in Initial Reports of the Deep Sea Drilling Project, Vol. 44, W. E. Benson, R. E. Sheridan, et al., U. S. Government Printing Office, Washington, D. C., pp. 587-591.

Stuermer, D. H., K. E. Peters and I. R. Kaplan (1978). Source indicators of humic substances and protokerogen: Stable isotope ratios, elemental compositions and electron spin resonance spectra, Geochim. Cosmochim. Acta 42; 989-997.

Thompson, K. F. M. (1979). Light hydrocarbons in subsurface sediments. Geochim.

Comsochim. Acts 43; 657-672.

Tissot, B. P. and D. H. Welte (1978). Petroleum Formation and Occurrence, A New Approach to Oil and Gas Exploration, Springer-Verlag, Berlin; 538 pp.

Tissot, B., Y. Califet-Debyser, G. Deroo and J. L. Oudin (1971). Origin and evolution of hydrocarbons in Early Toarcian shales. Amer. Assoc. Petrol. Geol. Bull. 55; pp. 2177-2193.

Tissot, B., B. Durand, J. Espitalie and A. Combaz (1974). Influence of nature and diagenesis Of organic matter information of petroleum, Amer. Assoc. Petrol. Geol.Bull. 58; pp. 499-506.

van de Meent, D., R. P. Philp and B. R. T. Simoneit (1979). Pyrolysis high resolution gas chromatography of kerogens and kerogen precursors. Geochim. Cosmochim. Acta, submitted for publication.

van Krevelen, D. W. (1961). Coal, Typology, Chemistry, Physics and Constitution, Elsevier Publishing Company, Amsterdam; 514 pp.

Watts, C.D. and J. R. Maxwell (1977). Carotenoid diagenesis in a marine sediment. Geochim. Cosmochim. Acta 41; 493-497.

Wilson, R. D., P. H. Monaghan, A. Osanik, L. C. Price and M. A. Rogers (1974). Natural. marine oil seepage, Science 184; pp. 857-865.

Windsor, J. G., Jr. and R. A. Hites {19?9). Polycyclic aromatic hydrocarbons in Gulf of Maine sediments and Nova Scotia soils. Geochim. Cosmochim. Acts 43; 27-33.

Initial Reports of DSDP, Vol. 64

ORGANIC GEOCHEMISTRY OF LIPIDS AND KEROGEN AND EFFECTS OF BASALT INTRUSIONS ON UNCONSOLIDATED OCEANIC SEDIMENTS, SITES 477, 478 AND 481 IN GUAYMAS BASIN, GULF OF CALIFORNIA*

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ABSTRACT

Pleistocene sediments in Guaymas Basin, Gulf of California have been intruded by sills and their organic matter was thus subjected to thermal stress. This was the case for DSDP/IPOD Sites 477, 478 and 481. Sediment samples from these sites and of thermally unaltered materials from Site 474 and 479were analyzed to characterize the lipids and kerogens and to evaluate the effects of the intrusive thermal stresses.

The lipids of the thermally unaltered samples are derived from microbial and terrestrial higher plant detritus. The samples from the sill proximities contain the distillates and those adjacent to the sills contain essentially no lipids. The pyrograms of the kerogens from the unaltered samples reflect their predominantly autochthonous microbial origin. The pyrograms of the kerogens of the altered samples reflect the thermal effects by a reduction in the complexity of the products, when compared with the unaltered samples. Kerogens adjacent to the sills produced little or no pyrolysis products.

The effects of intrusions into unconsolidated, wet sediments resulted in *in situ* pyrolysis of the organic matter as confirmed by these data.

INTRODUCTION

The drilling in the central Gulf of California concentrated on the Guaymas Basin and the Continental Slope east of that basin. The Guaymas Basin is an actively-spreading oceanic basin, part of the system of spreading axes and transform faults that extends from the East Pacific Rise to the San Andreas fault system (Curray *et* al., 1979). It is therefore tectonically very active and consists of two rift valleys separated by a 20 km transform fault area. The basin is characterized by a high sedimentation rate, which keeps its floor and rifts covered, while a complex ocean crust and intrusions are forming (Curray *et al.*, 1979).

Site 477 is in the southern rift and 481 in the north (the locations of all drill sites of Leg 64 are found on the map of the area in the Introduction to the shorebased geochemistry). The sediments were all diatomaceous oozes and turbidites intruded by various sills and of late Quaternary age (Curray *et al.*, 1979). Site 477 showed extensive hydrothermal alteration and high *in situ* heat flow. Site 478 was located on the basin floor in the transform fault zone and consisted of similar sediments with intrusive (Curray *et al.*, 1979). All these sites showed biogenic gas and thermogenic hydrocarbons ranging to C_7 derived from the endogenous organic matter were also detected at Sites 477 and 481 (Curray *et al.*, 1979).

Site 479 was situated on the Guaymas Slope and consisted of primarily diatomaceous ooze, which was laminated below 250 m subbottom (Curray *et al.*, 1979).

It was therefore of interest to examine the organic matter in samples from these sites to evaluate two major questions: (1) The sources and characteristics of the organic matter and (2) the effects of the thermal stress on that organic matter. The sources and characteristics of the organic matter can be determined by the analysis of the lipid fractions in terms of the homologous compound distributions, the structural types of molecular markers and the nature of the unresolvable mixtures (Simoneit, 1975; 1978b; 1981), and by the analyses of the kerogens in terms of their bulk compositional properties and by pyrolysis-GC and pyrolysis-GC/MS (eg., van de Meent et al., 1980). The effects of thermal stress on the organic matter can also be evaluated by these same lipid and kerogen analyses. Such data can then be correlated with the results of the interstitial hydrocarbon gas (C_1-C_7) compositions.

Here we present the data of the lipid analyses of the hydrocarbon and the fatty acid (as methyl esters) with ketone fractions for selected samples listed in Table 1. All the samples that were analyzed are listed sequentially by sites in Table 1 and their locations are indicated to the left of each lithologic column by the numerals in Fig. 1 (supplemental samples are indicated by A-F).

Curie point pyrolysis (Cupy) of the kerogens from the Leg 64 sampling sites was chosen as the method for examining the effects of sills on the organic matter for a variety of reasons.

Pyrolysis has become a powerful analytical tool in the past few years, especially in-the study of macromolecular materials. This rapid expansion in the use of pyrolysis has been due to the development of fast micro-scale flash pyrolysis techniques which appear to yield predominantly primary degradation products (Jones and Cramers, 1977). Pyrograms, obtained by either Cupy-GC or Cupy-MS, are found to be sufficiently reproducible and specific to be used for the characterization of synthetic polymers, biopolymers and geopolymers. In order to relate the thermal degradation products to the original macromolecule, it is necessary to identify the products, and try to understand how they are formed. Cupy-GC-MS (Simmonds et al., 1969) and Py-high resolution MS, using both field ionization and field resorption techniques (Schulten et al., 1973; 1978), have been used successfully to obtain a great deal of information on the structure of thermal degradation products from various types of macromolecular materials. The general reaction mechanisms by which pyrolysis products are formed are only poorly understood at the present time, although recently substantial advances have been made in this area (Posthumus et al., 1974; Posthumus and Nibbering, 1977a; De Jongh, 1977). Despite this shortcoming, pyrolysis techniques have been successfully employed in the study of biopolymers (Meuzelaar etal., 1977), humic substances (Bracewell et al., 1976) and kerogens (Maters et al., 1977; Larter and Douglas, 1978). More recently, Cupy combined with both GC and GC-MS has been used to characterize a series of protokerogens from Recent algal mats and kerogens from DSDP core samples and ancient sediments (van de Meent et al., 1980).

Here we discuss the results obtained from the pyrolysis of the kerogens of some of the samples listed in Table 1. In addition, we illustrate how these results show the effects of thermal stress on the kerogens in the sill vicinities.

EXPERIMENTAL METHODS

Lipids

The small *core* samples were dried *in* an oven at 45°C and extracted after C, H, N analysis (onboard) with methylene chloride (CH_2Cl_2). The larger samples were freeze-dried and then extracted with chloroform and methanol (1:1) using ultrasonication. The extracts were concentrated on a rotary evaporator and treated with BF_3 in methanol to derivative free fatty acids. The extracts were then subjected to thin-layer chromatography (TLC) on silica gel and using hexane and diethyl ether (9:1) as eluent. The bands (after development with iodine vapor) corresponding to hydrocarbons, esters and ketones were' scraped off the TLC plates and eluted with methylene chloride. The hydrocarbon and combined ester and ketone fractions were analyzed by gas chromatography (GC) and GC-mass spectrometry (MS).'

The GC analyses were carried out on a Hewlett-Packard Model 5830 gas chromatograph using-a 25 m x 0.20 mm fused silica capillary column coated with SP-2100, programmed from 35-280°C at 4°C per minute and using He carrier gas.

The GC/MS analyses were carried out on a Finnigan Model 4000 quadruple mass spectrometer interfaced directly to a Finnigan Model 9610 gas chromatography, equipped with a 30 m x 0.25 mm fused silica capillary column coated with SE-54. The GC conditions for the GC/MS analyses were as those for the analytical GC system. The mass spectrometric data was acquired and processed using a Finnigan-Incos Model 2300 data system.

Kerogen

The exhaustively extracted samples were treated with 3M HCl and warmed to approximately 60°C for 1 hour. The acid was removed and the residue washed with water and dried. After weighing, the sample was treated with aliquots of

3M HCl and 50% HF in a 1:1 ratio until no further weight loss of the residue was recorded. Finally, the kerogen concentrate was re-extracted with CH_2Cl_2 to remove the entrapped lipids. The extracts obtained after the acid treatment were evaporated to dryness and the weights of each fraction are recorded in Table 1. The entrapped lipid fractions were not analyzed further.

Curie point pyrolysis combined with gas chromatography (Cupy-GC) and Cupy-GC/MS

The exhaustively extracted kerogens were used for pyrolytic analyses, but were further purified for subsequent analyses (Jenden *et al*., this volume). Cupy-GC of the kerogens was performed using a Pye Curie-point pyrolyzer coupled to a Hewlett-Packard Model 5710 GC. Ni/Fe alloy wires were used in the pyrolyzer to produce a pyrolysis temperature of 610°C for 12.5 sees. The GC was equipped with a fused silica capillary column (50 m x 0.3 mm o.d.), coated with SE-30. Temperature conditions were: ambient for 2 reins; 70°C for 2 reins; temperature programmed at 4°C/min to 260°C.

Cupy-GC/MS of the kerogens were performed using a Pye Curie-point pyrolyzer coupled to a Finnigan Model 4023 GC/MS system equipped with an INCOS data system. Ni/Fe alloy wires were used with the pyrolyzer to give a pyrolysis temperature of 610"C for 12.5 sees. A 30m SP-2100 WCOT column was used in the GC/MS system and temperature programmed from 100 to 270°C at 4°C/minute. The separator temperature was 250°C; ion source temperature 260°C; filament current 250 μA, electron energy 70 eV and scan speed 0.95 seconds/decade.

RESULTS AND DISCUSSION

The results of the carbon and lipid analyses and kerogen yields are found in Table 1. The total lipid contents, including the entrapped lipids which are liberated after demineralization, are both high and consist of dominantly polar materials. The kerogen yields are also high and they reflect a significant inorganic content.

Lipids

The lipid data will be discussed in two aspects, namely the nature and sources of the lipids in the surface sediments and some unaltered deeper sediments and then the effects of the various intrusions on those lipids.

1) Surface samples from Sites 474, 477 to 479 and 481

The distributions of the n-alkanes and fatty acids are given in Fig. 2.

The lipids of the surface samples from the mouth of the Gulf of California are of a primarily marine autochthonous origin (Simoneit, this volume). This can be discerned in the example from Site 474 shown in Fig. 2a and h, where the n-alkanes and the n-fatty acids are derived mainly from microbial sources, coupled with a minor higher plant wax component.

The shallow samples from Sites 477 and 478 reflect a lipid composition from marine and terrestrial sources in about equal proportions. The n-alkanes (eg., Fig. 2b-d) range from C_{12}. to C_{35}, with maxima at C_{19}, C_{22} and C_{29} and a strong odd-to-even carbon number predominance > C_{24}. The lower molecular weight homologs (<C_{25}), with the associated unresolved complex mixture (hump) represent primary and degraded detritus from microbiota and the higher homologs are from vascular plant wax (Simoneit, 1975; 1980a,b). The dominance of n-nonadecane (Fig. 2b,d) may indicate a primary bacterial residue. Phytane is the dominant isoprenoid hydrocarbon (Pr/Ph < 1) and varying amounts of both sulfur and perylene are also present, indicating partially euxinic paleoenvironmental conditions of sedimentation (Didyk et al., 1978). Perylene is commonly found in Recent sediments and probably indicates deposition under anoxic conditions, where it may derive from possible biogenic precursors of either a marine or terrigenous origin (Simoneit et al., this volume}. The presence of organic and/or elemental sulfur is, however, less definitive in terms of paleoenvironmental conditions, but does indicate a low level of oxygen (i.e., euxinic). This is in agreement with the lithologic interpretation of a high influx of sedimentary detritus to the Guaymas Basin (Curray et al., 1979), leading to euxinic conditions where all the organic matter cannot be fully degraded. The high phytane content of sample 477-7-1, 124-126 cm (Fig. 2c) is characteristic of a more sapropelic sediment deposited under strong euxinic conditions (eg., Simoneit, 1977a; 1980a; Simoneit et al., 1979).

Sample 479-29-5, 114-116 cm is from 267 m subbottom and its lipids are as immature as those of the surface samples. Approximately equal proportions of autochthonous marine ($< C_{24}$, Fig. 2e) and allochthonous terrigenous n-alkanes are present. The Pr/Ph is less than one and both perylene and sulfur are present, again indicating partially euxinic paleoenvironmental conditions.

At Site 481 the lipids are derived from primarily terrestrial sources. The n-alkanes (eg., Fig. 2f,g) range from C_{11} to C_{35}, with maxima at C_{17} and C_{29} and a strong odd-to-even carbon number predominance $> C_{23}$. The minor components $< C_{21}$ are derived from degraded microbial detritus and the significant odd carbon n-alkanes ($> C_{23}$) are derived from vascular plant wax (Simoneit, 1975; 1980a,b). These distributions correlate with some of the surface samples analyzed from Site 30G (about 8 km to the northeast)(Simoneit, et al., 1979) and the terrestrial wax component may originate from primarily grassland with forest vegetation. The Pr/Ph is about one {some sulfur is present, but no perylene) and indicates partially euxinic conditions, again as a result of the high and varying influx of sedimentary detritus by turbidite transport, which leads to a greater preservation of the organic matter.

The n-fatty acids exhibit bimodal distributions, ranging from C_{10} to C_{32}, a strong even-to-odd carbon number predominance and maxima at C_{16} and C_{24} or C_{26} or C_{30} (eg., Fig. 2i-l). The n-fatty acids of the samples from the mouth of the Gulf are primarily marine in origin (Simoneit, this volume) and in the southern trench of the Guaymas Basin (Site 477, also 478 and 479) their origin is both marine and allochthonous terrigenous. In the northern trench (Site 481, also 30G--Simoneit et al., 1979) the distributions (eg., Fig. 2k,l) reflect a primarily terrigenous origin from plant wax, with a lesser component derived from marine microbial sources (Simoneit, 1975). Unsaturated fatty acids were not detectable.

The aliphatic ketones consisted of only traces of n-alkan-2-ones (C_{10} to C_{21}), with primarily 6,10,14-trimethylpentadecan-2-one and a minor amount of 6,10-dimethylundecan-2-one for most of the shallow samples. The isoprenoidal ketones reflect an origin from phytol by microbial degradation.

Dehydroabietic acid (Structure I), the dominant molecular marker of resinous higher plants (Simoneit, 1977b), is present in all the shallow samples and also in 30G (Simoneit et al., 1979). Its concentration is indicated on the plots of the fatty acids (eg., Fig. 2i-l). Dehydroabietic acid was not detected in the samples from the mouth of the Gulf (Simoneit, this volume). This confirms the influx of a terrestrial component from resinous plants to the Guaymas Basin and Slope.

The distributions of the major triterpenoids are given in Fig. 3. The shallow samples at Site 477 (eg., Fig. 3a) contain triterpanes ranging from C_{27} to C_{32}, consisting of the hopane series (II) with primarily the 17α(H) stereochemistry and lesser amounts of 17β(H)-hopanes, neo-hopanes (III), hop-17(21)-ene (IV) and moretanes (V). The dominant homolog is 17α(H)-hopane and the 22S to 22R stereomer ratio for the C_{31} to C_{34} 17α(H)-hopanes is about 0.8 for the shallow samples and about 1.2 for sample 477-7-2, 14-16 cm closer to the sill. These triterpenoids are probably of an autochthonous syngenetic origin and the dominance of the 17α(H) stereochemistry with the 22S/R of ∿ 1 indicates geologic maturity, probably due to the high geothermal gradient at this site (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Simoneit, this volume).

This can be compared with the triterpenoids of sample 479-29-5, 114-116 cm from 267 m subbottom and the shallow samples from Site 481 (eg., Fig. 3h-j). In these cases the major series are the 17β(H)-hopanes (II) and the *neo*-hopanes (III)(also termed *iso*-hopanes), with significant amounts of various triterpenes and 17α(H)-hopanes. The major olefins are hop-17(21)-ene (IV) and iso-hop-13(18)-ene (VI) and 17α,18α,21β(H)-28,30-bisnorhopane (VII) is present in sample 481A-6-5, 118-120 cm only, where it is the major analog (Fig. 3i). These triterpenoid distributions correlate with those at Site 30G (Simoneit *et al.*, 1979) and they reflect an origin primarily from autochthonous microbiota. The preponderance of the 17β(H) stereochemistry of the hopanes with the presence of olefins confirms the Recent origin of these molecular markers. *Iso*-hop-13(18)-ene appears to be a primary residue from microbiota (Howard, 1980), rather than allochthonous sources (eg., ferns--Ageta *et al.*, 1968).

The fatty acid fractions of all shallow samples contain various amounts of extended 17β(H)-hopanoic acids (VIII), ranging from C_{31} to C_{33} and with 17β(H)-bishomohopanoic acid as the major homolog. The source of these markers is probably the bacteriohopanepolyols of autochthonous microbiota (Ourisson *et al.*, 1979). Triterpenoidal ketones are present as trace components only.

Minor amounts of sesquiterpenoid and diterpenoid hydrocarbon residues are present in all samples analyzed. Their concentrations are highest in the shallow and geothermally unaltered samples. They consist of primarily cadalene (IX), dehydroabietane (X), dehydroabietin (XI), retene (XII, $R-CH_3$), simonellite (XIII, $R-CH_3$), 1-methyl -7-ethylphenanthrene (XII, R=H) and norsimonellite (XIII, R=H). These molecular markers are derived primarily from terrestrial resinous plants

(Simoneit, 1977b), however, cadalene may also have an autochthonous origin from algae. Extended diterpanes (XIV) were detected only in a few thermally altered samples (477-A-5-1, 477A-9-1, 481A-14-3) and they appear to be syngenetic with the 17α(H)-hopane series.

Steroidal residues are present and were characterized mainly in the hydrocarbon fractions as steranes and sterenes (Fig. 4). The steranes present in the shallow samples of Site 477 (eg., Fig. 4a) consist primarily of the 5a and 5β,8β,14α(H)-homologs (XV,R=H) ranging from C_{26} to C_{30}, with minor amounts of the 5α and 5β,8β,14β(H)-steranes. Sterenes were not detectable. The presence of the high concentrations of the 5β(H)-steranes in these shallow samples indicates a significant maturation, probably due to the very high thermal gradient at this site. The dominance of the C_{27} steranes is consistent with an origin from marine planktonic detritus (Huang and Meinschein, 1979) and the presence of varying amounts of norcholestane (XVI) is a further indicator of such a source (eg., Djerassi *et al.*, 1979). Lesser amounts of 4-methylsitostane (XV, $R=CH_3$, $R'=C_2H_5$) and diasterenes (XVII) ranging from C_{27} to C_{29} are also present.

The steroidal compounds in the shallow or unaltered samples from Sites 478, 479 and 481 consist of steranes with primarily the 5α(H)-stereochemistry (XV, R=H), diasterenes (XVII′), 5α(H)-ster-2-enes (XVIII) and ster-4-enes (XIX) (eg., Fig. 4f,g). Trace amounts of various steradienes are also present in some of the samples. Some of the samples from Sites 479 and 481 exhibit a dominance of the C_{29} sterane, which reflects the more pronounced influx of terrigenous detritus (Huang and Meinschein, 1979), which was also indicated by other lipid data.

2) Hydrothermal effects of intrusive on lipids

The distributions of the *n*-alkanes and *n*-fatty acids of the deeper samples from Sites 477, 478 and 481 are given in Figs. 5 and 6.

Site 477

Sample 477-7-1, 124-126 cm is situated from 1.2 to 8 m above the sill (depending upon how depths are assigned, cf., Table 1], whereas sample 477-7-2, 14-16 cm is only 40 cm closer to that sill. The differences in the hydrocarbon distributions are quite dramatic (Fig. 2c vs. 5a). A definite thermogenic component with no carbon number predominance ranging from C_{20} to C_{33} and a maximum at C_{25} has appeared and the wax alkanes have disappeared. Phytane is still dominant and the C_{17} and C_{19} reflect microbial remnants. A broad unresolved mixture (hump) of hydrocarbons. is also evident in the GC traces of this and the following samples, further evidence of a thermogenic component. Similar hydrocarbon distributions are observed below the sill in the high heat flow zones (eg., Fig. 5b-e) of both Holes 477 and 477A. As the subbottom depth increases, the *in situ* temperature rises and these hydrocarbon distributions reflect primarily the effects of very high (> 350-400°C) hydrothermal activity. These hydrocarbon distributions do not compare directly with similar data for an intrusive event into semi-lithified Cretaceus black shale (DSDP Site 368--Simoneit *et al.*, 1978; 1981). In that case the hydrocarbon distributionsin close sill proximity were narrower (C_{12} to C_{20} only).

The molecular markers also exhibit the effects of thermal stress. The triterpenoids of sample 477-7-2, 14-16 cm (Fig. 3b) are more mature or thermodynamically equilibrated than those of sample 477-7-1, 124-126 cm (Fig. 3a). They consist primarily of the $17\alpha(H)$-hopanes (II) and the extended homologs are present at a 22S to R ratio of about 1.2, very mature for such a Recent sediment. Similar triterpenoid distributions are observed for the samples below the sills (Fig. 3c-g) in both holes 477 and 477A.

The sesquiterpenoid and diterpenoid residues present in the shallow samples are found in these samples as traces or as more aromatized minor components only. The extended diterpanes (XIV) are present as trace components only and they appear to be syngenetic with the triterpanes. Steroidal residues are found mainly as steranes (XV, R=H) with the 5α(H) and a significant amount of the 5β(H) stereomers (Fig. 4b-e). The predominance of the C_{27} steranes and the presence of norcholestane (XVI) still reflect their primarily marine origin (Djerassi et al., 1979; Huang and Meinschein, 1979).

One major group of compounds, namely various olefins and di-olefins, are found only in samples 477-7-2, 14-16 cm; 477-17-3, 44-46 cm; and 477A-5-1, 44-46 cm; and 481A-14-4, 52-53 cm. They range from C_{14} to C_{26}, with the major homologs of $C_{18}H_{36}$ and $C_{20}H_{40}$ and an even carbon number predominance. The mass spectra of the two major olefins are shown in Fig. 7. The molecular ion of $C_{18}H_{36}$ is at m/z 252 and the loss of ethylene is observed to yield the even ion at m/z 224 (.Fig. 7a). Various other even rearrangement ions are present (eg., m/z 68, 168, 182, 196, 210) and the base peak at m/z 55. These data indicate that the molecular is probably. the terminal olefin octadec-1-ene. The analogous fragmentation is observed for eicos-1-ene (Fig. 7b). An additional minor series of mono-olefins with a base peak at m/z. 70 and no carbon number predominance is also present. In view of the location of these samples in the proximity of a high temperature environment it can be concluded that these olefins are thermogenic products derived from the protokerogen of the sediments.

It should also be noted that these lipid fractions contain large amounts of probably polysulfide moieties, eg., S_8, S_7 and S_6. This sulfur was probably generated by the hydrothermal activity from organic sulfur and/or H_2S. Such polysulfide moieties are also observed in euxinic sedimentary environments (eg., the shallow sediments in Guaymas Basin and the Southern California Borderland--Simoneit and Mazurek, 1981).

Site 478

The lipids of samples 478-13-12, 138-140 and 116-118 cm; 478-29-1, 57-59 and 124-126 cm (below the upper sill and about 1.5 to 4.0 m above the small sill) and 478-35-2, 77-79 cm (below small sill and about 40 m above major sill) are immature and unaltered, reflecting the primary biogenic residues (Fig. 5f,g,j and Fig. 6b). The n-alkanes , C_{23} are derived from terrestrial plant wax as discussed above and the homologs < C_{23} are of an autochthonous marine origin. The n-fatty acids also reflect a mixed origin from autochthonous microbiota and allochthonous plant wax (eg., Fig. 6h).

Sample 478-29-2, 108-110 cm is located 1.8 m below the previous sample (478-29-1) and about 0.6 to 2.9 m above a small sill (∿ 1.5 m thick]. The n-alkanes appear typically altered (> C_{21}), with a remnant microbiological imprint < C_{20} (Fig. 5h). Sample 478-29-2, 129-131 cm is about 5 cm from the contact of the small sill and is in the hydrothermally altered zone. The n-alkanes confirm this (Fig. 5i) in that their low concentration has a very narrow distribution similar to those observed for the intruded Cretaceus shales (Simoneit et al., 1978; 1981). Sample 478-40-2, 61-63 cm is located about 80 cm above the lower major intrusion. The n-alkanes again appear typically altered (Fig. 5k) as is the case for sample 478-29-2, 108-110 cm.

These hydrothermally altered samples do not contain any significant amounts of molecular markers (eg., triterpanes), but do have high concentrations of sulfur (S_8, etc.) and some minor polycyclic aromatic hydrocarbon series. The triterpanes and other lipids may have been removed by the hydrothermal circulation.

Site 481

The lipids of all the samples examined from Hole 481A with depth across two basalt layers are essentially unaltered and reflect primarily their biogenic origin.

Sample 481A-12-1, 107-109 cm is located about 25 m above the first sill and the n-alkanes (Fig. 6a) are essentially the same as for the shallow samples (eg., Fig. 2g). Phytane is dominant and this may be the result of minor differences in paleoenvironmental conditions. Sample 481A-12-4, 55-65 cm is located about 22 m above the first sill and it has a different composition of the n-alkanes and n-fatty acids (Fig. 6b,i). The even carbon number alkanes represent a significant proportion of the homologous series and also the odd carbon number fatty acids are quite high. Pristane is the dominant isoprenoid hydrocarbon. This may represent some contribution of a thermogenic component to the natural background lipids. This distribution closely resembles some observed for the Intruded Cretaceus shale (Simoneit et al., 1978; 1981). This interpretation is further strengthened by the next two lower samples, which contain essentially no thermogenic lipids.

Sample 481A-14-3, 50-52 cm is located about 1.5-5.0 m above the sill and the n-alkane and n-fatty acid distributions (Fig. 6c,f) are the same biogenic fingerprints as observed in the shallow samples. The same is the case for sample 481A-14-4, 2-4 cm (eg., Fig. 6d) located about 50 cm to 4 m above the sill (depths are dependent on convention of assignment, cf., Table 1). "The n-alkanes are dominated by terrestrial plant wax (> C_{23}) with a minor autochthonous microbial constituents and the n-fatty acids also contain both of these source components. Two explanations for the presence of these immature, unaltered 'lipids close to the sill are proposed. First, the true in situ distance of the samples to the sill contact may be greater due to sediment loss during drilling. Second, the section above the sill described as a megaturbidite (Fig. 1), which includes these samples, may have been emplaced on a flow of basalt after cooling. This second suggestion, however, is not supported by the samples analyzed below the sill, as they too are essentially unaltered.

Sample 481A-14-4, 52-54 cm is located about 5 cm to 3.5 m (depending upon depth assignment, Table 1) above the sill and it is heavily altered. The n-alkanes range from C_{13}-C_{29}, with a maximum at C_{18} and essentially no carbon number predominance. This distribution reflects the effects of thermal stress, which is further confirmed by the presence of various olefins, found in only this sample from Site 481, and a large amount of sulfur. The major olefins are the n-alk-1-enes (cf., Fig. 7) ranging from C_{14} to C_{26}, with a strong even carbon number predominance and maximum at C_{18}.

Sample 481A-18-1, 27-29 cm is located about 80 cm to 7.8 m below the sill complex and this large depth discrepancy is due to poor core recovery and the depth assignment (Table 1). The n-alkanes (Fig. 6e) are dominated by terrestrial plant wax (> C_{23}), a lesser microbial residue and major isoprenoid hydrocarbons (Ph >> Pr). This distribution can be correlated with a sapropelic algal sediment that received a large terrigenous influx (eg., Simoneit, 1977a; 1978a,b; Simoneit et al., 1979). Thermogenic lipids are not evident.

Samples 481A-20-1, 60-62 cm and 481A-25-cc are located about 23 to 34m and " 77 m, respectively, below the sill complex and in excess of 50 m above the minor sills at depth. The n-alkanes (Fig. 6f,g) exhibit essentially identical distributions, with a dominance of the terrestrial plant wax components and a minor residue of autochthonous marine lipids. These distributions are also very similar to those just above the sill complex and in the shallow samples. Thermogenic lipids are not evident. The n-fatty acids (Fig. 6k,l) exhibit bimodal distributions comprised of both a terrigenous influx from plant wax and autochthonous marine component, again similar to the other samples reported.

The molecular markers of the lipids in the samples from Hole 481A show limited effects of thermal maturation, most are immature. The diterpenoid and sesquiterpenoid residues are still present and consist primarily of dehydroabietic acid (I), cadalene (IX), dehydroabietin (XI), retene (XII, R=CH_3), simonellite (XIII, R=CH_3), 1-methyl-7-ethylphenanthrene (XII,R=H), and norsimonellite (XIII , R=H).

The triterpenoids of the deepest sample (481A-25-cc) consist mainly of 17β(H)-hopanes (II), hop-17(21)-ene (IV), other olefins and moretanes (Fig. 3n). This distribution is very similar to that of the shallow sample 481A-8-7 (Fig. 3j) and represents immature markers in the early stages of diagenesis. The triterpenoids of the other samples are more mature, with a dominance of 17α(H)-hopanes (II) and 17β(H)-moretanes (V) and essentially no triterPenes (eg., Fig. 3k-m). These distributions approach the fully matured patterns at Site 477 (eg., Fig. 3b-g) and coupled with the immature pattern below these samples, this data indicates a lesser but definite thermal effect on the molecular markers in the lipids of the sediments around the upper sill complex.

The steroidal hydrocarbon residues are present primarily as ster-2-enes (XVIII}, ster-4-enes (XIX) and various steradienes in the deepest sample {Fig. 4j). These markers are immature and are the same as encountered in shallow samples. Samples- 471A-12-4 and 481A-14-4, 2-4 cm (Fig. 4h,i) contain the more mature 5α(H) and 5β(H)-steranes (XV, R=H), with 4-methylsteranes (XV, R=CH_3) and" only traces of sterenes. These distributions lend further-support to the lipid. alterations caused by the thermal effects around the upper sill complex as discussed above.

Kerogen

This section of the paper will be divided into two major portions. First, a comparison will be made between the pyrolysis products of kerogens from surface samples at each site; second the pyrograms from the kerogens isolated from each dawn-hole sample will be discussed in some detail, with emphasis on the effects of the intrusions on these kerogens. The yields of kerogen are found in Table 1.

1. Surface samples from Sites 474, 477, 478 and 479

The pyrograms of the kerogens from unaltered (near) surface samples from Sites 474 and 477 to 479 are shown in Fig. 8. For the sake of comparison, a pyrogram of kerogen isolated from a diatomaceous ooze of Walvis Bay (Namibian Shelf, SW Africa) is also shown. This kerogen represents the organic residue from diatoms in an upwelling area similar to parts of the Gulf of California. It should be noted that the kerogen from sample 479-29-5 (114-116 cm) at a subbottom depth of about 266 m is essentially unaltered (immature), even though it is of Pliocene age.

A comparison of the four pyrograms (Fig. 8) shows a significant similarity. This provides a strong basis for the theory that the organic material currently being deposited at all four sites is very similar. A further comparison of these four pyrograms with the Walvis Bay pyrogram (Fig. 7e) again shows a very strong similarity between them. Thus, the bulk organic matter currently being deposited at the Gulf of California sites is of a predominantly marine origin similar to the Walvis Bay diatomaceous ooze and is lacking in any significant contribution from higher plants.

The major features of the pyrograms in Fig. 8 can be summarized:

(i) Predominance of n-alkane/alkane doublets in the range C_{10} to C_{21} or C_{22}, with relatively minor amounts of higher homologs above C_{22}. The alkene in each doublet generally predominantes over the corresponding alkane. The complex "humps" of unresolved components make it difficult to determine whether or not there is any marked even/odd predominance of these doublets.

In contrast to the isoprenoids, normal paraffins and olefins can have their origin in all kinds of lipids and hence these products are commonly considered to be uncharacteristic (van de Meent et al., 1980). However, the relatively low concentration of aliphatic products in the higher carbon number range is probably a reflection of the relatively low abundance of long chain structures generally encountered in the macromolecular organic matter (kerogen) of aquatic ecosystems.

(ii) Prist-1-ene is a prominent component of each pyrogram and generally is two or three times the concentration of the C_{17}-doublet. The mass spectrum of the prist-1-ene detected in these samples was found to be identical with that of prist-1-ene, recently identified by Larter et al. (1979) as the major pyrolysis product of Messel shale kerogen. Pristene is one of the most abundant products in nearly all kerogens studied here. This observation is consistent with findings of other investigators (Larter, 1978 and references therein). The ubiquitous occurrence of pristene in kerogen pyrolysates suggests that its source is widespread. The most commonly-proposed source is chlorophyll. Chlorophyll itself, on pyrolysis, does not yield any significant quantity of prist-1-ene but phytadienes instead. However, prist-1-ene was observed in the pyrolysate of surface sediments from environments extremely rich in phytoplankton, which indicates a rapid biotransformation of chlorophyll into the pristene precursor (van de Meent et al., 1980). The one exception is the surface sample from Site 474, where pristene is present at a much lower concentration.

Each pyrogram has a second peak, present in varying amounts, which is just resolved from prist-1-ene. It is proposed that this peak corresponds. to the prist-2-ene isomer. In the pyrogram of the 474 sample (Fig. 8a), prist-1-ene and prist-2-ene are present in approximately a 1:1 ratio. Prist-1-ene is a common component in pyrograms of almost all geological samples reported in the literature. The presence of prist-2-ene is not so widely reported and only appears in samples of relatively recent geological age. This introduces the possibility of using the prist-1-ene/prist-2-ene ratio as a possible early maturation indicator for samples of similar source material.

(iii) The pyrograms of these kerogens (Fig. 8) exhibit a complex hump of unresolved components underlying the alkene/alkane doublets described above. The "humps" actually have two maxima, one in the C_{18}-C_{20} region appears to consist of polar material (possibly phenolic) and another in the C_{28}-C_{30} region may consist of a complex sterane/triterpane mixture. This complexity is clearly visible in the pyrogram of the samples from Site478 and Walvis Bay (Fig. 8d,e). These peaks presumably represent sterane and triterpane derivatives as observed by Gallegos (1975) and Philp *et al.* (1978), and differences in relative concentrations probably reflect differences in source material and/or the environmental conditions under which it was deposited.

(iv) Comparison of these pyrograms with previously published pyrograms obtained from immature terrestrial type kerogens or lignite (van de Meent *et al.*, 1980) confirm the essential absence of a higher plant contribution to these kerogens. Kerogens derived from terrestrial higher plants produced alkylphenols and methoxyphenols in significantly higher amounts than from other kerogens. Higher plant wax residues are found in the pyrolysates as long chain alkanes and alkenes with odd and even carbon number predominances, respectively. Both phenol humps and long-chain alkane/alkanes are found, however, in very minor amounts in some of these kerogens.

In summary, the pyrograms of all the near-surface samples are similar to each other and to the Walvis Bay diatomaceous ooze. The pyrograms are characterized by alkene/alkane doublets predominantly $< C_{20}$ and the presence of prist-1-ene and prist-2-ene. Each pyrogram also has a complex hump of unresolved components underlying the alkene/alkane doublets.

2. Effect of burial and sill intrusions on kerogen.

Site 474

Only two near-surface samples were analyzed from Site 474. The pyrograms of kerogens isolated from 474-5-3 (105-107 cm) and 474-6-5 (32-34)(Fig. 8a) are very similar to each other and to the Walvis Bay diatomaceous ooze as described above.

Site 477 and Hole 477A

The pyrogram of the kerogen from composite sample 477-5-1 (89-91; 94-96 cm) (Fig. 9a) is virtually identical to that for 474-6-5 (32-34 cm) shown in Fig. 8a. The pyrogram of 474-6-5 (32-34 cm has been discussed above and is typical of an unaltered marine kerogen, as is the case for these samples.

The pyrogram of the kerogen from 477-5-CC is shown in Fig. 8b and is very similar to that obtained for the kerogen from 477-5-1 (89-91, 94-96 cm) and the other surface samples. The major difference between the pyrograms of 477-5-CCand 477-5-1 is the enhanced intensity of the alkene/alkane doublets below C_{20} for the former. Whether or not this represents a possible variation in the composition of the organic matter of the two samples is unclear at this time.

Sample 477-7-1 (124-126 cm) is the first kerogen examined in this study that shows any effect due to a dolerite intrusion. Major differences between the pyrograms of this kerogen and that of 477-5-cC are immediately apparent (cf., Fig. 9b). It is proposed that the differences observed between these pyrograms are mainly a result of the close proximity of the sill to 477-7-1 and not natural diagenesis of the organic matter. The reasons for this will become apparent in the following discussion of pyrograms from the other samples at this site.

The most characteristic feature in the pyrograms of all the kerogens thought to have been affected by sill intrusions is the presence of a complex multiplet of components in the n-C_{12} region of their pyrograms. The overall abundance of the alkene/alkane doublets has decreased. Prist-1-ene is still present in the pyrograms and the relative abundance of the unresolved complex hump has been reduced. It is proposed that the effect of the sill intrusions has been to cause partial but natural pyrolysis of the organic material in the samples. This has removed much of easily pyrolyzable material responsible for the complex pyrograms of the near-surface samples. In addition it has caused a certain amount of alteration to the kerogen structure such that subsequent Cupy-GC produces the complex, but characteristic, multiplet in the n-C_{12} region.

The effects of the sill intrusion are more distinct in the pyrogram of the kerogenof 477-7-2 (14-16 cm)(Fig. 9c). The multiplet of peaks in the n-C_{12} region is now the most abundant feature of the pyrogram. Components observed in the C_{18}-C_{20} regions of previous pyrograms are still visible but present only in relatively minor quantities. None of the other features described above for the other pyrograms are present. The alkene/alkane doublets are absent; prist-1-ene and prist-2-ene are absent and the pyrogram is devoid of any complex hump of unresolved components. The source of these traces of volatilizable compounds is unknown.

Sample 477-17-3 (44-46 cm) was collected from approximately 25 m below the bottom of the sill. The pyrogram of the kerogen is virtually identical to that obtained from 477-7-2 (14-16 cm) (Fig. 9c) which was 0.8-7.6 m from the top of the sill. If a comparison is made of pyrograms of kerogens from similar distances above the below the sill, it appears that kerogens below the sill have been affected slightly more by the heat than those above the sill. Two explanations are available to explain this observation. Either heat transfer through the underlying sediments from the sill is more efficient or the underlying sediments are affected by both the heat from the sill plus a greater heat flow from depth. It is not possible to draw a firm conclusion on this matter from the available evidence.

Sample 477-20-2 (61-63 cm) was collected from 50m below the sill. The pyrogram shows that the kerogen has been altered most probably by the effect of the sill plus a small contribution of heat flow from depth. The only feature of the pyrogram is the multiplet of components in the n-C_{12} region. Apart from this no additional pyrolysis products could be detected.

The pyrogram of kerogen (Fig. 9d) isolated from sample 477-22-1 (26-26 cm), collected 75m below the sill, shows signs of being less altered than the kerogens of samples 477-17-3 (44-46 cm) and 477-20-2 (61-63 cm). The multiplet in the n-C_{12} region is present in this pyrogram, but in addition prist-1-ene, alkene/ alkane doublets and indications of a sterane/triterpane mixture in the C_{30} region are all present. It is proposed that at this depth slight alteration of the kerogen has occurred by the natural heat-flow phenomena and the kerogen has not been affected by the sill intrusion.

The pyrogram also has four relatively intense peaks in the C_{19}-C_{22} region. Two of these have been identified by GC-MS as the C_{16} and C_{18} saturated fatty acid methyl esters. Their presence in the pyrogram is puzzling. The possibility that they are contaminants from the pyrolysis wire cannot be eliminated. However, all the wires were cleaned and handled in the same fashion, but these compounds are only present in certain pyrograms. By analogy it is unlikely that they are contaminants in the kerogen simply because of the isolation procedure. If these compounds are not artifacts, it is proposed that they were trapped in the kerogen and released by pyrolysis at 600°C.

The major peaks of the pyrogram of sample 477A-5-I (.44-46 cm) (Fig. 9e) are to be found in the multiples in the n-C_{12} region. In addition, relatively small amounts of alkene/alkane doublets, and broad peaks, probably phenolic type compounds, are also present in the region above C_{20}. These phenolic-type compounds may be present in previous pyrograms but not easily observable due to much higher abundance of the alkene/alkane doublets.

Sample 477A-9-I (39-41 cm) was the deepest material analyzed from this site. The pyrogram obtained for this kerogen (Fig. 9f) does not differ significantly from that described above for 477A-5-I (44-46 cm)(Fig. 9e). Again, it is proposed that it is the effect on the organic matter of the high heat flow from depth and not from the sill which has caused the alteration of the kerogen.

Site 478

Cores recovered from this site span the depth range of 0-464m subbottom. Dolerite sills intruded into the section at 230 and 255m. Samples for this study were obtained from the surface, between the sills, below the lower and smaller sill at about 260m, and another at about 340m, just above the major dolerite. Various samples were composite to increase their overall amounts.

Composite sample 478-2-2 (2-5 cm), 2-6 (102-104 cm), and 3-1 (19-21 cm) has a pyrogram of the kerogen which is virtually identical to the other surface samples (Fig. 8). It is dominated by alkene/alkane doublets in the range C_{10} to C_{30}, which predominance in the region below C_{20}. Prist-1-ene and prist-2-ene are present in a ratio of approximately 3:1. Two prominent peaks in the C_{18} and C_{20} region of the pyrograms have been tentatively identified as the C_{16} and C_{18} fatty acid methyl esters as previously described in the GC-MS analysis of 477-22-1 (26-28 cm). A complex mixture of steranes and triterpanes is also present 'n the C_{30} region"

The composite sample 478-12-2 (81-83 cm), 13-1 (138-140 cm) and 13-2 (116-118 cm) is derived from approximately 110m subbottom and the pyrogram of the resulting kerogen is not dominated by the characteristic signs of thermal alteration previously observed in the pyrograms discussed above. Although the multiplet in the n-C_{12} region, common to the other pyrograms of thermally-altered kerogens, is present in this pyrogram; the major components are still the alkene/alkane doublets. Prist-1-ene and prist-2-ene are present in a 1:1 ratio. There appears to be a slight even/odd predominance of the alkene/alkane doublets, but since the doublets are superimposed over the complex hump, it is unrealistic to attach any great significance to this observation.

The composite sample 478-29-1 (57-59 cm), 29-1 (124-126 cm) and 29-2 (34-36 cm) is derived from about 5-7m above the minor sill (254m subbottom) and the pyrogram of the kerogen (Fig. 10a) shows a remarkable absence of any signs of thermal alteration. The pyrogram is dominated by alkene/alkane doublets with carbon numbers primarily < C_{20} and extending to C_{30}; prist-1-ene and prist-2-ene are present in a 1:1 ratio, steranes and triterpanes are present in the C_{30} region and the underlying complex hump of unresolved components is also present. It must be speculated that the heat flow resulting from this narrow intrusion was not large enough to have caused any significant alteration to this sample.

Sample 478-29-2 (108-110 cm), which is approximately 0.4-3m from the sill, shows some effects of thermal alteration due to the intrusion. In the pyrogram {Fig. 10b) the unresolved complex humps are absent; prist-1-ene predominates over prist-2-ene and the relative intensity of the alkene/alkane doublets is reduced. In addition, a fairly well resolved complex mixture of components is now present in the C_{17}-C_{21} region.

Sample 478-29-2 (129-131 cm) is about 0.2-2.8m -From the sill contact and the pyrogram of the kerogen confirms more extensive thermal alteration than for sample 478-29-2 (108-110 cm). The dominance of the multiplet in the n-C_{12} region of the pyrogram is a good indication of the extensive alteration incurred by this sample as a result of the intrusion. The relative intensity of the alkene/alkane doublets has been further reduced. The complex mixture in the C_{17}-C22 region is still evident and similar to that observed in the pyrogram of 478-29-2 (108-110 cm). Although not confirmed by GC-MS, the major peaks in this region are probably the C_{16} and C_{18} fatty acid methyl esters as described for 477-22-1 (26-28 cm)(Fig. 9d).

The carbonaceous slick of sample 478-30-1 also reflects the thermal stress of that sill as indicated by the pyrogram in Fig. toe. The amount of pyrolyzable material in the sample is reduced but the characteristics of a thermally altered sample are still visible in the pyrogram. The alkene/alkane doublets are absent and the appearance of a series of well defined humps of polar material can now be observed in the C_{17}-C_{22} region of the pyrogram.

Sample 478-40-2 (61-63 cm) is from a depth of about 340m subbottom, which eliminates any possibility of alteration of the organic material by the lower sill at 255m. However, the major cause of alteration is probably the major dolerite present immediately below the sample. The pyrogram (Fig. 10d) is very similar to that for the slick described above (Fig. 10c). The multiplet in the n-C_{12} region is present, the alkene/alkane doublets and prist-1-ene are absent. The phenolic-type humps are present in the C_{17}-C_{22} region.

Site 481

The shallowest sample analyzed from this hole was at a depth of 147.5m, therefore, no direct comparison has been made with the surface samples from the other sites. However, changes observed in the pyrograms of these samples with increasing sample depth clearly show that alteration has occurred as a result of the intrusions and not the natural geothermal gradient.

Sample ,481A-12-1 (107-109 cm) is derived from about 25m above the sill complex (170.5 to 203m) and the pyrogram of the kerogen is already showing certain signs of thermal alteration (Fig. ha). The multiplet has partially developed in the n-C_{12} region and the complex humps observed in pyrograms of surface samples from other sites are essentially absent. The pyrogram is dominated by alkene/alkane doublets ranging from C_{10} to C_{30} maximizing between C_{18} and C_{20}. The presence of both prist-1-ene and prist-2-ene in a ratio of about 1:1 suggests that the sample has only undergone limited alteration. Previous pyrograms obtained in this study indicate that prist-2-ene tends to be absent if the sample has been substantially altered. Steranes and triterpanes are present in the C_{30} region of the pyrogram.

Sample 481A-14-3 (50-52 cm) is the first of three samples analyzed from the immediate vicinity of the sill complex. The pyrogram (Fig. 11b) has many of the characteristics observed in the pyrograms of previous samples which were extensively altered. The amount of pyrolyzable material appears to be low and its source is unknown. The multiplet in the n-C_{12} region is the dominant feature and the pyrogram generally lacks any other interpretable information.

Sample 481A-14-4 (2-4 cm) was derived from only a slightly greater depth (Ire) than 481 A-14-3 (50-52 cm) and the pyrogram of the kerogen (Fig. 1 1c) lacks any evidence of alkene/alkane doublets. Instead, seven or eight broad humps in the C_{17}-C_{30} region are the major characteristic features of the pyrogram. On top of each hump is a triplet of peaks which appear to form three homologous series. This pyrogram has only a small contribution from the multiplet in the n-C_{12} region.

Sample 4818-14-4 (52-54 cm) is 50 cm lower than sample 481A-14-4 (2-4 cm) and its kerogen has a very similar program. The series of broad humps and associated triplets are present. In addition, this sample has a significant contribution from the multiplet in the C_{12} region, plus a complex distribution of other components in this lower molecular weight region.

The appearance of these two pyrograms is quite different from any of the other pyrograms produced by thermally altered kerogens in this study. The multiple emplacement of the sill complex in this hole indicates that these two samples may represent "bituminized kerogens" (Peters et al., 1979). The "pressure cooking" effect on the trapped kerogen and liquids produced by thermal degradation of the organic material, could cause them to recombine to form a coke-like material, similar to mesophase formation in coal (Durand, 1980; van Krevelen, 1961).

Sample 481A-18-1 (27-29 cm) was derived from directly beneath the sill and the pyrogram of this kerogen shows no indication of any extensive alteration.

The extract from the sample shows no fluorescence, also indicative of the absence of any major thermal alteration. The dominant features of the pyrogram are the alkene/alkane doublets ranging from C_9 to C_{31}, with no odd/even carbon predominance and maximizing at C_{20}. Prist-1-ene and prist-2-ene are also observed to be present in approximately equal amounts. The pyrogram is very similar in appearance to that of sample 481A-20-1 (60-62 cm) shown in Fig. 11d.

Examination of the pyrogram of the kerogen from sample 481A-20-1 (60-62 cm) showed it to be virtually identical to the surface sample and Walvis Bay diatomaceous ooze pyrograms (Fig. 8). Alkene/alkane doublets are present throughout the pyrogram predominating below C_{20}; prist-1-ene and prist-2-ene are present in a 1:1 ratio and more abundant than the C_{17} doublet. Steranes and triterpanes are present in the C_{30} region and the complex unresolved humps are also a prominent feature of the pyrogram.

It would appear, therefore, that the two samples beneath the sill are virtually unaffected by the thermal effects of the sill. Likewise, very little alteration of the samples has occurred from the natural geothermal gradient and by diagenesis.

SUMMARY AND CONCLUSIONS

The lipids and kerogens from representative samples at shallow and increasing depths and across sill contacts have been analyzed from Sites 474, 477-479 and 481. The lipids have been characterized in terms of their homolog distributions, molecular markers and the unresolvable components to assess their genetic sources and the resultant thermal alteration effects due to the intrusions into the sediments. The kerogens have been analyzed in terms of their capability of generating pyrolysis products, which is utilized as a measure of both the geologic maturity (i.e., the degree of thermal stress accumulated in situ) and the sources of that kerogen.

Site 474

The lipids of the shallow samples at the mouth of the Gulf are of an autochthonous marine origin deposited under oxic conditions (Simoneit, this volume). The kerogen analyzed from Site 474 is unaltered and comparable to shallow samples from the other sites. .

Site 477

The lipids of the shallow samples from Site 477 are primarily of an autochthonous marine origin, with a minor influx of terrestrial plant wax. The paleoenvironmental conditions of sedimentation were partially euxinic, probably as a result of the high deposition rates. Close to and below the sill the lipids are thermally altered. This is indicated by the loss of the carbon number predominance, the appearance of a broad hump and the thermodynamic equilibration of certain stereomers of molecular markers. Also large amounts of olefins, only in the altered 477 samples, and elemental sulfur are present. This thermal alteration of lipids is most severe at this site.

Kerogens from 477-5-1 and 477-5-CC are virtually identical to surface samples from all the other sites examined and are representative of unaltered material. Sample 477-7-1, a few meters above the sill, shows signs of being altered presumably as a result of the intrusion. Sample 477-7-2 shows an even more dramatic effect of the alteration resulting from its proximity to the sill. A characteristic feature of these thermally altered samples is a multiplet of peaks in the n-C_{12} region of the pyrogram. Samples 477-17-3 and 477-20-2 produce pyrograms very similar in appearance to 477-7-2, which indicates a high degree of thermal alteration resulting from the intrusion. Sample 477-22-1, 75m below the bottom of the sill, produces a pyrogram showing some signs of alteration indicated by the multiplet in the n-C_{12} region, and in addition, it also has some characteristics of the unaltered samples. It is proposed that this sample has not been affected as much by the sill as by the high heat flow from depth. Finally, the two deepest samples, 477A-5-1 and 477A-9-1 have similar pyrograms and appear to be more altered than 477-22-1. It is proposed that the high heat flow from greater depth has played a greater role in the alteration of these two deep samples than the sill intrusion.

Site 478

In the shallow samples, the lipids derived from mainly autochthonous marine and allochthonous terrigenous sources in about equal proportions. They were deposited under partially euxinic conditions, again due to the high sedimentation rates. The lipids of the samples from greater depths are essentially unaltered (eg., 478-35-2) unless they are in closer proximity to sills. The unaltered samples reflect the same sources and depositional conditions as observed for the shallow samples. The lipids of the altered samples indicate a lower thermal stress than at Site 477 based on the distributions of the homologous compounds, the hump and the degree of isomerization of the molecular markers (eg., triterpanes).

For the kerogens, as observed at Site 477, increasing sample depth shows an increase in the thermal alteration. The effect of alteration is first noticeable in the pyrogram of" sample 478-29-2 (108-110 cm) collected in the vicinity of the sill (around 255m). There is no evidence for a "pressure cooker" effect on the organic matter trapped between the sills as was the case at Site 477. It is evident that the presence of the sills is responsible for the majority of the thermal alteration observed in these samples. The presence of intrusions in the vicinity of all the samples examined virtually eliminates the chance of distinguishing any effect of natural heat flow on the samples.

Site 481

The lipids of the shallow samples in the northern rift are derived from primarily terrigenous sources with a minor component of autochthonous marine detritus. On"the slope (Site 479) these two sources are about equivalent, due to the high marine productivity. The paleoenvironmental conditions were partially euxinic, as in the other areas due to the high sedimentation rates. The lipids of the thermally altered samples indicate a similar stress as was the case for the samples from Site 478. The carbon number predominance is lost, a broad hump is present, and molecular markers have undergone isomerization, but lesser amounts of sulfur are present and olefins are found only in sample 481A-14-4, 52-54 cm close to the sill complex.

The kerogens of the threes samples from above the sill complex show definite signs of thermal alteration. Two of them (481-14-4, 2-4 cm and 14-4, 52-54 cm) are particularly unique within the set of samples studied in this work. The presence of a series of phenolic-type humps in their pyrograms has led to the suggestion of recombination of kerogens and liquids in a "pressure cooker" type environment. Below the sill complex , the samples have not been affected by the sill or the natural geothermal gradient to any extent and the pyrograms are very similar to those of the surface samples and the Walvis Bay diatomaceous ooze.

In conclusion, both lipids and kerogen are two ideal carbonaceous fractions that complement each other in their information content regarding the origins and thermal history of the sedimentary organic matter. Kerogen is a very sensitive _in situ_ marker for thermal stress and the lipids can represent the products from that stress which have moved a distance away by hydrothermal circulation.

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REFERENCES

Ageta, H., K. Shioima, and Y. Arai (1968). Fern constituents: Neohopane, hopene-II, neohopadiene and fernadiene isolated from Adiantum species, Chem. Comm. 1968; 1105-1107.

Bracewell, J.M., G.W. Robertson and K.R. Tate (1976). Pyrolysis gas chromatography studies on a climosequence of soils in Tussock Grasslands, New Zealand. Geoderma 15; 209-215.

Curray, J.R., D.G. Moore, J.E. Aguayo, M.P. Aubry, G. Einsele, D.J. Fornari, J. Gieskes, J.C. Guerrero, M. Kastner, K. Kelts, M. Lyle, Y. Matoba, A. Molino-Cruz, J. Niemitz, J. Rueda, A.D. Saunders, H. Schrader, B.R.T. Simoneit and V. Vacquier (1979). Leg 64 seeks evidence on development of basin in the Gulf of California. Geotimes 24 (7); 18-20.

Dastillung, M. and P. Albrecht (1976). Molecular test for oil pollution in surface sediments. Mar. Poll. Bull. 7; 13-15.

DeJongh, D.C. (1977). Pyrolytic reaction mechanisms. In: Analytical Pyrolysis, Proc. Third Int. Symp. on Anal. Pyrol. Amsterdam 1976, C.E.R. Jones and C.A. Cramers, eds., Elsevier, Amsterdam; 261-275.

Didyk, B.M., B.R.T. Simoneit, S.C. Brassell and G. Eglinton (1978). Geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 272; 216-222.

Djerassi, C., N. Theobald, W.C. Kokke, C.S. Pak and R.M.K. Carlson (1979). Recent progress in the marine sterol field. Pure Appl. Chem. 51; 1815-1828.

Durand, B., ed. (1980). Kerogen, Insoluble Organic Matter from Sedimentary Rocks, Editions Technip, Paris; 519 pp.

Gallegos, E.J. (1975). Terpane-sterane release from kerogen by pyrolysis GC-MS. Anal. Chem. 47; 1524-1528.

Howard, D.L. (1980). Polycyclic triterpenes of the anaerobic photosynthetic bacterium Rhodomicrobium vanniellii, Ph.D. Thesis, University of California, Los Angeles; 272 pp.

Huang, W.-Y. and W.G. Meinschein (1979). Sterols as ecological indicators. Geochim. Cosmochim. Acts 43; 739-745.

Jones, C.E. R. and C.A. Cramers (eds.)(1977). Analytical pyrolysis, Proc. Third Int. Symp. on Anal. Pyrolysis, Amsterdam 1976, Elsevier.

Larter, S.R. (1978). A geochemical study of kerogen and related materials. Ph.D. Thesis, University of Newcastle-Upon-Tyne, England.

Larter, S. and A.G. Douglas (1978). Low molecular weight aromatic hydrocarbons in coal maceral pyrolysates as indicators of diagenesis and organic matter type. In: Environmental Biogeochemistry and Geomicrobiology, (W.E. Krumbein, ed.), Ann Arbor, Vol. 1; 373-386.

Larter, S.R., H. Solli, A.G. Douglas, F. de Lange, and J.W. de Leeuw (1979). The occurrence and significance of prist-1-ene in kerogen pyrolysates. Nature 279; 405-407.

Maters, W.L., D. van de Meent, P.J.W. Schuyl, J.W. deLeeuw, P.A. Schenck and H.L.C. Meuzelaar (1977). Curie point pyrolysis in organic geochemistry. In: Analytical Pyrolysis, Proc. Third Int. Symp Anal. Pyrol., Amsterdam, 1976, (C.E.R. Jones and C.A. Cramers, eds.), Elsevier, Amsterdam; 203-216.

Meuzelaar, H.L.C., K. Haider, B.R. Nagar and A.J.P. Martin (1977). Comparative studies on pyrolysis mass spectra of melanins, model phenolic polymers and humic acids. Geoderma 17; 239-252.

Ourisson, G., P. Albrecht and M. Rohmer (1979). The hopanoids. Palaeochemistry and biochemistry of a group of natural products. Pure Appl. Chem. 51; 709-729.

Peters, K.E., B.R.T. Simoneit, S. Brenner and I.R. Kaplan (1979). Vitrinite reflectance-temperature determinations for intruded Cretaceus black shale in the Eastern Atlantic. Symp. Low Temperature Metamorphism: Kerogen and Clay Minerals, (D.F. Oltz, ed.), Pacific Section, SEPM, Los Angeles; 53-58.

Philp, R.P., M. Calvin, S. Brown, and E. Yang (1978). Organic geochemical studies on kerogen precursors in recently-deposited algal mats and oozes. Chem. Geol. 22; 207-231.

Posthumus, M.A., N.M.M. Nibbering, A.J. H. Boerboom, and H.R. Schulten (1974). Pyrolysis mass spectrometric studies on nucleic acids. Biomed. Mass Spectrometry 1; 352-367.

Posthumus, M.A., N.M.M. Nibbering (1977a). Pyrolysis mass spectrometry of methionine. Org. Mass Spectrom. 12; 334-337.

Posthumus, M.A., N.M.M. Nibbering (1977b). Pyrolysis mass spectrometry of model compounds labelled with stable isotopes. In: Analytical Pyrolysis, Proc. Third Int. Symp. Anal. Pyrol., Amsterdam, 1976, (C.E.R. Jones and C.A. Cramers, eds.), Elsevier, Amsterdam; 277-288.

Schulten, H.R., H.D. Beckey, H.L.C. Meuzelaar, and A.J.H. Boerboom (1973). High resolution field ionization mass spectrometryof bacterial pyrolysis products. Anal. Chem. 45; 191-195.

Schulten, H.R., W. Görtz and C.H. Stembridge (1978). Curie-point pyrolysis and field ionization mass spectrometry of polysaccharides. Anal. Chem. 50; 428-433.

Simmonds, P. G., G.P. Schulman, and C.H. Stembridge (1969). Organic analysis by pyrolysis gas chromatography-mass spectrometry. A candidate experiment for the biological exploration of Mars. J. Chrom. Sci. 7; 36-41.

Simoneit, B.R.T. (1975). Sources of organic matter in oceanic sediments. Ph.D. Thesis, University of Bristol, England; 300 pp.

Simoneit, B.R.T. (1977a). Leg 41 sediment lipids--Search for eolian organic matter in Recent samples and examination of a black shale. In: Intital Reports of the Deep Sea Drilling Project, Vol. 41, (Y. Lancelot, E. Seibold et al., eds.), U.S. Government Printing Office, Washington, D.C.: 855-858.

Simoneit, B.R.T. (1977b). Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acts 41; 463-476.

Simoneit, B.R.T. (1978a). Organic geochemistry of terrigenous muds and various shales from the Black Sea, DSDP Leg 42B. In: Initial Reports of the Deep Sea Drilling Project, Vol. 42, Part 2, (D. Ross, Y. Neprochnov et al., eds.), U.S. Government Printing Office, Washington, D.C.; 749-753.

Simoneit, B.R.T. (1978b). The organic chemistry of marine sediments. In: Chemical Oceanography, 2nd Ed ., (J.P. Riley and R. Chester, eds.), Academic Press, New York, Vol. 7; pp. 233-311.

Simoneit, B.R.T. (1980a). Organic geochemistry of the shales and sapropels of the Cretaceus Atlantic. In: Proc. 8th Int'l. Meeting Organic Geochemistry, USSR Acad. Sci., Moscow, in press.

Simoneit, B.R.T. (1980b). The composition, sources and transport of organic matter to marine sediments--The organic geochemical approach. In: Proc. Symp. Marine Chem. into the Eighties, (J.A.J. Thompson, cd.), Natl. Research Bd., Canada, in press.

Simoneit, B.R.T. (1981). Mass spectrometry and ancillary techniques in fossil energy research--an overview. In: Atomic and Nuclear Methods in Fossil Energy Research, R.H. Filby, ed., Plenum Press, New York, in press.

Simoneit, B.R.T. and I.R. Kaplan (1980). Triterpenoids as molecular markers of paleoseepage in Recent sediments of the Southern California Bight. Mar. Environ. Res. 3; 113-128.

Simoneit, B.R.T. and M.A. Mazurek (1981). Organic geochemistry of sediments from the Southern California Borderland, DSDP/IPOD Leg 63. In: Initial Reports of the DSDP, Vol. 63, (B. Haq, R.S. Yeats et al, eds.), U.S. Government Printing Office, Washington, D.C., in press.

Simoneit, B.R.T., S. Brenner, K.E. Peters and I.R. Kaplan (1978). Thermal alteration of Cretaceus black shale by basaltic intrusions in the Eastern Atlantic. Nature 273; 501-504.

Simoneit, B. R. T., M.A. Mazurek, S. Brenner, P.T. Crisp and I.R. Kaplan (1979). Organic geochemistry of Recent sediments from Guaymas Basin, Gulf of California, Deep-Sea Res. 26A; 879-891.

Simoneit, B.R.T., S. Brenner, K.E. Peters and I.R. Kaplan (1981). Thermal alteration of Cretaceus black shale by diabase intrusions in the Eastern Atlantic: II. Effects on bitumen and kerogen. Geochim. Cosmochim. Acts, in press.

van de Meent, D., S.C. Brown, R.P. Philp and B.R.T. Simoneit (1980). Pyrolysis-high resolution gas chromatography and pyrolysis gas chromatography-mass spectrometry of kerogens and kerogen precursors. Geochim. Cosmochim. Acts 44; 999-1013.

Van Krevelen, D.W. (1961). Coal, Elsevier, Amsterdam; 514 pp.

TABLE 1. SAMPLE DESCRIPTIONS AND RESULTS OF THE CARBON, LIPID AND KEROGEN ANALYSES FOR THE SAMPLES FROM THE CENTRAL GULF OF CALIFORNIA LEO 64

Sample		Subbotom	Lithology	Carbon[1]		CaCO$_3$[1]	C/N	Lipids[2]		n-Alkanes			Pr/Ph[5]	~-Fatty Acids			Kerogen[6]
Number (cf. Fig 1)	Designation	Depth (m)	and Age	Total (%)	Organic (%)	(%)		Free (µg/g)	Entrapped (µg/g)	Total NC (µg/g)	CPI[3]	Max[4]		Total µg/g)	CPI[3]	Max[4]	Yield (%)
1	477-5-1 (81-91, 94-96 cm)	30..4 (36.7)[9]	Diatom. ooze, Late Pleist.	3,6	2.6	8	13	1040	1120	7a	1.87	19,29	0.61	n.d.	--	--	4.2
2	.477 -5-CC	32.6 (39.0)	Diatom. ooze; Late Pleist.	3.9	2.6	10	16	3600	3200	n.d.	--	--	--	n.d.	--	--	9.1
3	477-7-1 (124-126 cm)	.%9.7 (56.8)	Diatom. ooze, Late Pleist.	2.8	1,8	8	21	860	930	3ao	1.10	18,Ph,22, 29	0.24	260	8.06	36,24	to. ?
4	477-7-2 (14-16 cm)	50.1 (57.2)	Sandy silt, debris flow, Late Pleist.	1.3	0.7	4	27	4ao	750	1s0	1.03	19,Ph,26	0.42	n.d.	--	--	8.7
5	417-17-3 (44-46 cm)	127.9 (133.4)	Silty clay-stone, ?	1.0	018	0	12	1000	230	430	1.03	18,25	1.2	n.d.	--	--	8 . 3
6	4?7-20-2 (61-63 cm)	155.1 (161.8)	Silty clay-atone, ?	1.6	1.0	4	28	720	470	50	1.23	39, 25	0.83	n.d.	--	--	7.2
7	411-22-1 (26-28 cm)	172.3 (179.3)	silty clay* altered, ?	1.6	0.8	7	47	410	1200	34	1.14	17,25	1.1	n.d.	--	--	10.1
A	477-23-1 slick	185.0	Carbonaceous click, ?	14.0	14.0	0	86	20	n.d.	n.d.	--	none present	--	--	none present	--	--
8	471 A-5-1 (44-46 cm)	191.4 (199.6)	Friable silt-atone, ?	1.2	0.6	6	69	3500	1600	400	--	none	--	n.d.	--	--	15.6
9	477A-9-1 (39-41 cm)	229.4 (237,6)	Sandstone, ?	0.5	0.4	3	8633	180	2200	14	1.02	19,25	‘ 1.11	n.d.	--	--	13.2
10	418-2,3-2,3,6,1 Composite	8.0	Diatom. ❑ud ooze, Late Pleistocene	3.9	2.9	9	12	500	1350	20	1.73	19, 29	0.s0	n.d.	--	--	8.8

Table 1 (Cont. p. 2)

Sample Number (cf. Fig 1)	Sample Designation	Subbotom Depth (m)	Lithology and Age	Carbon[1] Total (%)	Carbon[1] Organic (%)	CaCO$_3$[2] (%)	C/N	Lipids* Free (µg/g)	Lipids* Entrapped (µg/g)	n-Alkanes Total HC (µg/g)	n-Alkanes CPI[3]	n-Alkanes Max[4]	Pr/Ph[5]	n-Fatty Acids Total (µg/g)	n-Fatty Acids CPI[3]	n-Fatty Acids Max[4]	Kerogen[6] Yield (%)
11	478-12/13-1,2 (138-140,116-118 cm)	I 10.0 (114.0)	Diatom. mud ooze, Late Pleist.	3.9	2.4	6	14	2050	1480	18	2.65	17,29	1.17	n.d.			11.5
12	478-29-1 (57-59, 124-126cm)	251.4 (254.4)	Diatom. mud, Late Pleist.	3.4	2.2	11	16	2100	1500	12	3,44	17,29	0.5	n.d			12.6
13	478-29-2 (108-110cm)	253.1 (255.9)	Dolomitic clay-stone, Late Pleist.	2.1	1.7	3	17	240	1260	10	1.07	17,25	1.14	n.d.		-	7.2
14	.478 -29-2 (129 -131cm)	253.3 (2 S6.7)	Dolomite clay-atone, Baked, Late Pleist.	1.4	1.4	0	26	170	400	8	1.01	21,24	3.00	n.d.			9.8.
15	478-30-1	257.3	Slick, Late Pleist.	-	2.1		22	500		n.d.				n.d.			9.8
%	478-35-2 (77-79 cm)	300.0 (302.3)	Muddy diato-mite, Late Pleist.	4,2	2.7	13	17	380	n.d	28	1.77	17,22,22,31	0.91	40	7.47	16,26	n.d.
16	478-40-2 (61-63 cm)	338.1 (343.3)	Dolomitic clay-atone, Late Pleist.	1.1	1.1	0	13	680	500	42	1.07	18,25	1..14	n.d.			7.2
17	479-29-5 (114-116 cm)	266.6	Diatom. Mud. Pleist.	3.0	2.6	3	15	490	730	64	1.60	17,29,31	0.88	80	8.ss	36,26	11.5
C	481-11-2 (140-145 cm)	50.4	Wood, Late Pleist.			n.d	n.d	n.d	n.d	8				n.d			

Table 1 (cont. p. 3)

Sample		Subbotom	Lithology	Carbon[1]		$CaCO_3$[1]	C/N	Lipids[2]		n-Alkanes			Pr/Ph[5]	n-Fatty Acids			Kerogen[6]
Number (cf. Fig 1)	Designation	Depth (m)	and Age	Total (%)	Organic (%)	(%)		Free (µg/g)	Entrapped (µg/g)	Total HC (µg/g)	CPI[3]	Max[4]		Total (µg/g)	CPI[3]	Max[4]	~ (%)
D	481A-6-5 (118-120cm)	96.7	Sand turbidite, Late Pleist.	1.5	1.3	2	14	1060	n.d.	18	3.96	17,29	1.60	12	5.38	16,30	σ. #.,
E	481A-8-7 (0-5cm)	117.5	Diatom. Mud, Late Pleist.	1,6	1.4	2	n.d.	1410	n.d.	36	2.51	17,29	0.78	45	3.93	16,30	n. d.
18	481 A-12-1 (107-109cm)	147.6 (148.8)	Silty Clay, Late Pleist.	1.5	1.3	2	13	2700	380	74	4.10	16,29,31	0.38	n.d.	--	--	8.2
18	481A-12-4 (55-65 cm)	151.6 (152.8)	silty Clay, Turbidite, L. Pleist.	1.4	1.0	4'	n.d.	735	n.d.	120	1.55	15, Pr, 23, 29	1.47	70	1.88	16,24	n.d.
19	481 A-14-3 (50-52 cm)	169.0 (172.5)	silt, Pleist.	1.1	0.8	2	19	1010	870	60	3.23	17,Pr,29	1.07	62	3.82	16,24	6.5
20	481 A-14-4 (2-4cm)	170.0 (173.5)	Cemented silt, Pleist.	1.2	0.6	5	n.d.	490	9700 (s)	36	3.34	16,29,31	0.40	n.d.	--	--	6.1
21	481A-14-4 (52-54cm)	170.5 (174.0)	Siltstone, Pleist.	0.6	0.4	2	14	350	1030	n.d.	--	---	--	n.d.	--	--	7.5
22	481 A-18-1 (27-29 cm)	203.8 (212.4)	Sandy clay, Late Pleist.	1.1	0.9	2	14	800	530	40	2.44	19,Ph,29	0.26	n.d.	--	--	9.2
23	481A-20-1 (60-62 cm)	223.1 (230.4)	Diatom. mudst., Late Pleist.	3.5	1.8	14	n.d.	1740	1000	64	2.82	19,Ph,29	0.50	46	3.29	16,24	10.0
F	481A-25-cc	279.5	Silty clayst., Late Pleist.	1.8	1.1	6	n.d.	560	n.d.	26	3.38	17,Ph,31	0.45	80	4.80	16,22,28	n.d.
	30G-I[7]	1.0	500 Yr bp	2.8	2.5	3	n.d.		n.d.	24	1.5	17,19,29	0.6	30	7.5	16,24	n.d.
	30G-II[7]	1.8	900 yr bp	2.8	1.8	9	n.d.		n.d.	1	3.0	17,29	1.2	90	7.8	16,26	n.d.
	Walvis Bay[8]																
	AII93-3-various	0.0-0.2	Diatom. . . A, Holocene	5.0	5,0	2	n.d.	10,000	n.d.	50	1.1	17,19,22,31		1500	10.0	14,16,24	n.d.

---

[1] Data supplied by shipboard party and Microanalytical Laboratory, Chemistry Dept., University of California at Berkeley; [2] Based on dry weight of sediment; entrapped lipids are liberated from mineral matrix after demineralization; [3] Carbon preference index, summed from C_{12} to C_{35}, odd-to-even for alkanes and even-to-odd for fatty acids; [4] The dominant homolog is underscored; [5] Pristane-to-phytane ratio (Didyk et al., 1978); [6] Curie point pyrolysis of kerogen, yield is percent of total dry sediment; [7] Data from Simoneit et al., 1979; [8] Data from unpublished results (Simoneit et al., 1981); [9] The depth according to the DSDP convention is given and the depth calculated upward from the core catcher is given in parentheses if that is different.

FIGURE LEGENDS

Figure 1: Lithologic columns for Sites 477 to 479 and 481 showing the positions of the samples analyzed here (samples 1-23 and A-F *in* Table 1).

Figure 2: Distribution diagrams for the n-alkanes (a-g) and n-fatty acids (h-l) of the shallow samples from Sites 474, 477 to 479and 481. . .(. . . indicates isoprenoids, --- dehydroabietic acid).

a,h: Sample 474-5-3
b: Sample 477-5-1, 81-91, 94-96 cm ,
c,i: Sample 477-7-1, 124-126 cm
d: Sample 478-2/3-composite
e,j: Sample 479-29-5, 114-116 cm
f,k: Sample 481A-6-5, 118-120 cm
g,l: Sample 481A-8-7, 0-5 cm

Figure 3: Distribution diagrams for triterpenoids of samples from all sites (the concentrations are based on the relative intensity of m/z 191 correlated to the GC response). The R and S diastereomers of the extended homologs are also indicated and the C28 compound is $17\alpha,18\alpha,21\beta(H)$-28,30-bisnorhopane (VII).

a) 477-7-1, 124-126 cm
b) 477-7-2, 14-16 cm
c) 477-17-3, 44-46 cm
d) 477-20-2, 61-63 cm
e) 477-22-1, 26-28 cm
f) 477A-5-1, 44-46 cm
g) 477A-9-1, 39-41 cm
h) 479-29-5, 114-116 cm
i) 481A-6-5, 118-120 cm
j) 481A-8-7, 0-5 cm
k) 481A-12-4, 55-65 cm
l) 481A-14-3, 50-52 cm
m) 481A-14-4, 2-4 cm
n) 481A-25-cc

Figure 4: Distribution diagrams for steranes and sterenes of the samples analyzed.

a) 477-7-1, 124-126 cm
b) 477-7-2, 14-16 cm
c) 477-20-2, 61-63 cm
d) 477A-5-1, 44-46 cm
e) 477A-9-1, 39-41 cm
f) 481A-6-5, 118-120 cm
g) 481A-8-7, 0-5 cm
h) 481A-12-4, 55-65 cm
i) 481A-14-4, 2-4 cm
j) 481A-25-cc

Figure 5: Distribution diagrams for the n-alkanes of samples from Sites 477 and 478 (..... indicates isoprenoids).

a) 477-7-2, 14-16 cm
b) 477-17-3, 44-46 cm
c) 477-20-2, 61-63 cm
d) 477-22-1, 26-28 cm
e) 477A-9-1, 39-41 cm
f) 478-13-1/2, 131-140, 116-118 cm
g) 478-29-1, 57-59, 124-126 cm
h) 478-29-2, 108-110 cm
i) 478-29-2, 129-131 cm
j) 478-35-2, 77-79 cm
k) 478-40-2, 61-63 cm

Figure 6: Distribution diagrams for the n-alkanes (a-g) and the n-fatty acids (h-l) of samples from Sites 478 and 481 (.... indicates isoprenoids, ---- dehydroabietic acid).

a) 481A-12-1, 107-109 cm
b) 481A-12-4, 55-65 cm
c) 481A-14-3, 50-52 cm
d) 481A-14-4, 2-4 cm
e) 481A-18-I, 27-29 cm
f) 481A-20-1, 60-62 cm
g) 481A-25-cc
h) 478-35-2, 77-79 cm
i) 481A-12--4, 55-65 cm
j) 481A-14-3, 50-52 cm
k) 481A-20-1, 60-62 cm
l) 481A-25-cc

Figure 7: Mass spectra of major olefins present in sample 477-17-3, 44-46 cm.

a) n-Octadec-1-ene, $C_{18}H_{36}$
b) @ices-1-ene, $C_{20}H_{40}$

Figure 8: Examples of Curie-point pyrolysis gas chromatograms (Cupy-GC) of kerogen concentrates from shallow and unaltered samples (subbottom depths are given in parentheses].

a) 474-6-5, 32-34cm (46 m)
b) 477-5-cc (39 m)
c) 479-29-5, 115-116 cm (266 m) .
d) 478-2/3-composite (8 m)
e) Walvis Bay, S.W. Africa (0.5 m)

Figure 9: Examples of Cupy-GC traces of kerogen concentrates from Site 477 versus depth (subbottom depths are given in parentheses):

a) 477-5-1, 89-91 and 94-96 cm (30 m)
b) 477-7-1, 124-126 cm (50 m)
c) 477-7-2, ?4-16 cm (50+ m) (* designates the C_{12} retention region)
d) 477-22-1, 26-28 cm (172 m)
e) 477A-5-1, 44-46 cm (191 m)
f) ,477A-9-1,39-41 cm (240 m)

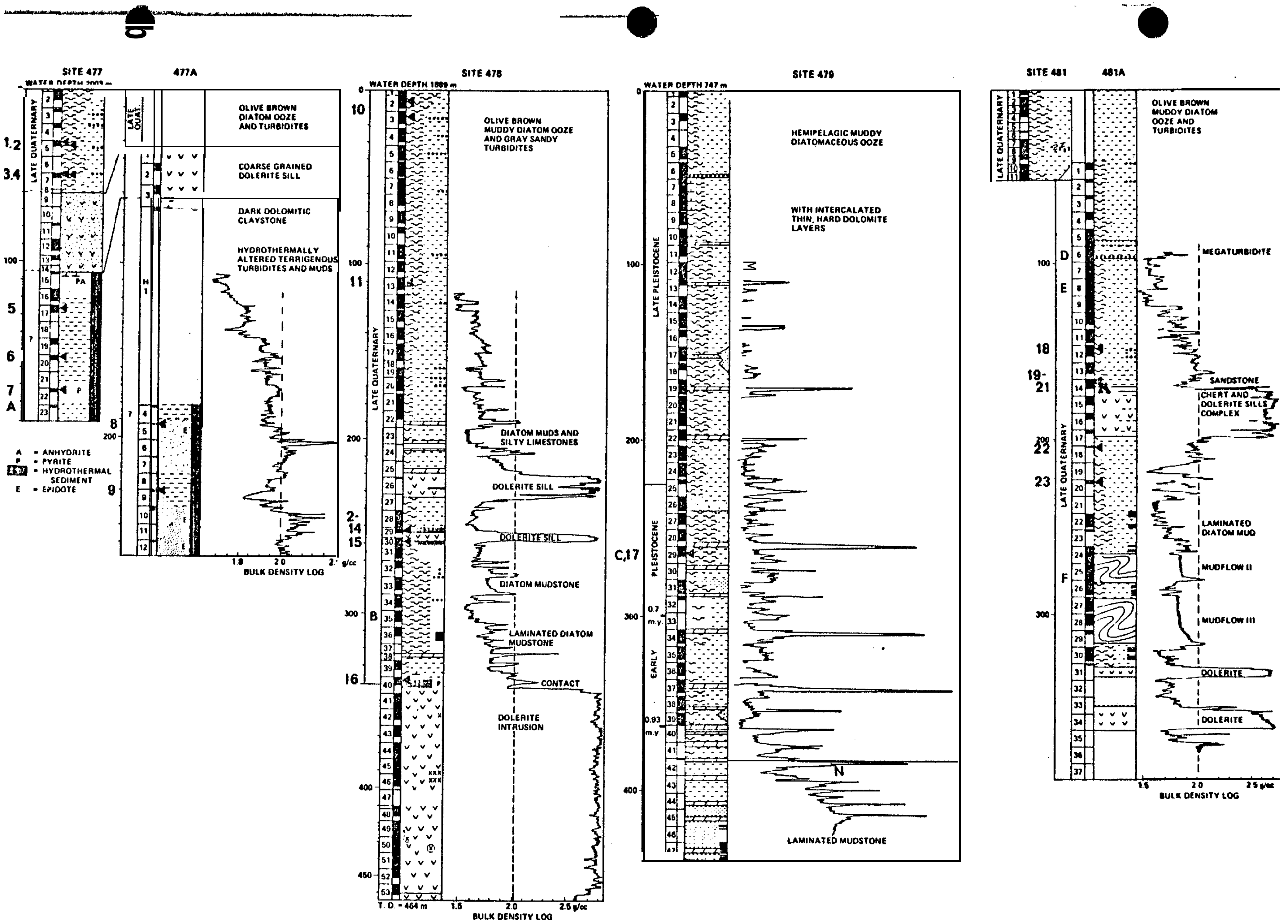
Figure 10: Examples of Cupy-GC traces of kerogen concentrates from Site 478 (subbottom depths are given in parentheses):

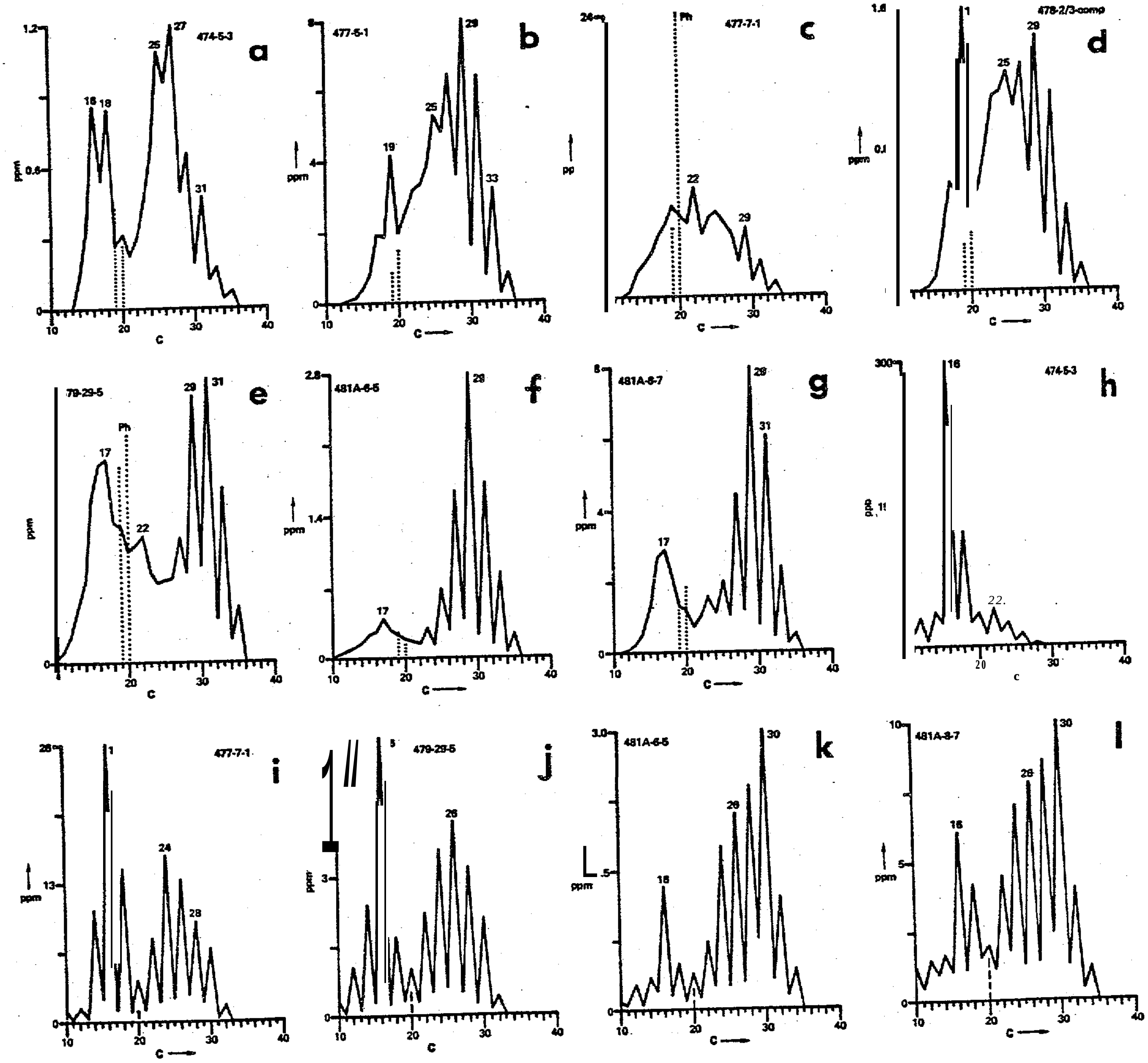
a) 478-29-1, composite (250 m)
b) 478-29-2, 108-110 cm (253 m)
c) 478-30-1 slick (257 m)
d) 478-40-2, 61-63 cm (378 m)

Figure 11: Examples of Cupy-GC traces of kerogen concentrates from Site 481 (subbottom depths are given in parentheses).

a) 481A-12-I, 107-109 cm (148cm) "
b) 481A-14-3, 50-52 cm (169 m)
c) 481A-14-4, 2-4 cm (170 m)
d]. 481A-20-1, 60-62 cm (223 m)

Appendix I. Chemical Structures Cited.


b
SITE 477
WATER DEPTH 2003 m
477A
SITE 478
WATER DEPTH 1889 m
SITE 479
WATER DEPTH 747 m
SITE 481
481A
LATE QUATERNARY
LATE QUAT.
LATE PLEISTOCENE
PLEISTOCENE
EARLY
0.7 m.y.
0.93 m.y.
OLIVE BROWN DIATOM OOZE AND TURBIDITES
COARSE GRAINED DOLERITE SILL
DARK DOLOMITIC CLAYSTONE
HYDROTHERMALLY ALTERED TERRIGENOUS TURBIDITES AND MUDS
OLIVE BROWN MUDDY DIATOM OOZE AND GRAY SANDY TURBIDITES
DIATOM MUDS AND SILTY LIMESTONES
DOLERITE SILL
DOLERITE SILL
DIATOM MUDSTONE
LAMINATED DIATOM MUDSTONE
CONTACT
DOLERITE INTRUSION
T. D. = 464 m
HEMIPELAGIC MUDDY DIATOMACEOUS OOZE
WITH INTERCALATED THIN, HARD DOLOMITE LAYERS
LAMINATED MUDSTONE
OLIVE BROWN MUDDY DIATOM OOZE AND TURBIDITES
MEGATURBIDITE
SANDSTONE
CHERT AND DOLERITE SILLS COMPLEX
LAMINATED DIATOM MUD
MUDFLOW II
MUDFLOW III
DOLERITE
DOLERITE
A = ANHYDRITE
P = PYRITE
= HYDROTHERMAL SEDIMENT
E = EPIDOTE
PA
BULK DENSITY LOG
1.8
2.0
2. g/cc
1.5
2.0
2.5 g/cc
100
200
300
400
450
1,2
3,4
5
6
7
A
8
9
10
11
2-14
15
16
B
M
N
C,17
18
19-21
22
23
D
E
F



474-5-3
a
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0.6
ppm
16
18
25
27
31
C
477-5-1
b
8
4
ppm
19
25
29
33
C
477-7-1
c
24
pp
Ph
22
29
C
478-2/3-comp
d
1.6
0.1
ppm
25
29
C
79-29-5
e
ppm
Ph
17
22
29
31
C
481A-6-5
f
2.8
1.4
ppm
17
29
C
481A-8-7
g
8
4
ppm
17
29
31
C
474-5-3
h
300
ppb
16
22.
C
477-7-1
i
26
13
ppm
24
28
C
479-29-5
j
3
ppm
26
C
481A-6-5
k
3.0
.5
ppm
16
26
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C
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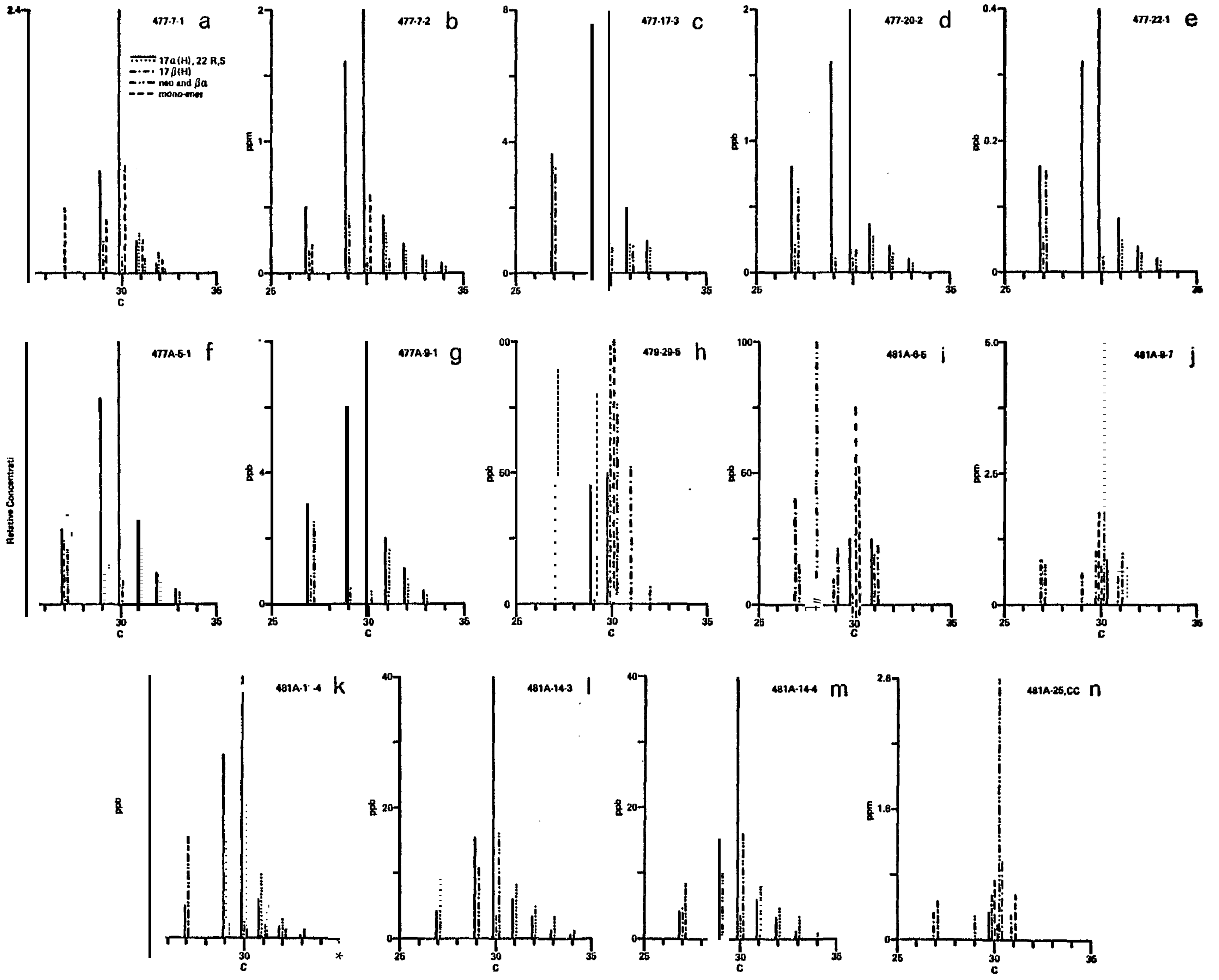
l
10
5
ppm
16
26
30
C
10
20
30
40



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17α(H), 22 R,S
17β(H)
neo and βα
mono-enes
2.4
30
35
c
477-7-2 b
ppm
2
1
0
25
30
35
477-17-3 c
8
4
0
25
35
477-20-2 d
ppb
2
1
0
25
35
477-22-1 e
ppb
0.4
0.2
0
25
35
Relative Concentrati
477A-5-1 f
30
35
c
477A-9-1 g
ppb
4
0
25
30
35
c
479-29-5 h
ppb
00
50
0
25
30
35
c
481A-6-5 i
ppb
100
60
0
25
30
35
c
481A-8-7 j
ppm
5.0
2.5
0
25
30
35
c
481A-1-4 k
ppb
30
c
*
481A-14-3 l
ppb
40
20
0
25
30
35
c
481A-14-4 m
ppb
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35
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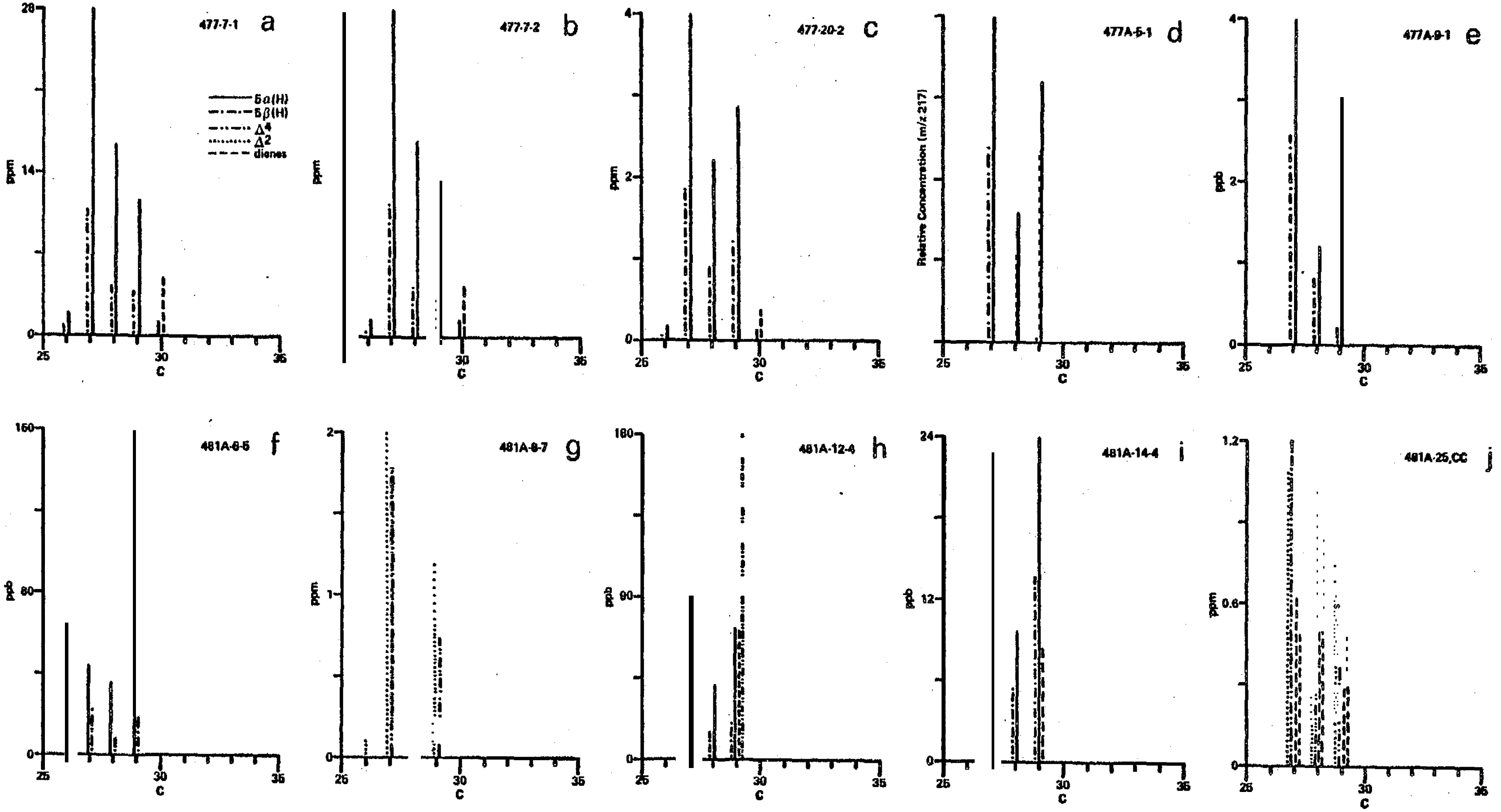
25
30
35
c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477-20-2 c
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481A-14-4 i
481A-25,CC j
5α(H)
5β(H)
Δ4
Δ2
dienes
ppm
ppb
Relative Concentration (m/z 217)
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1
90
12
24
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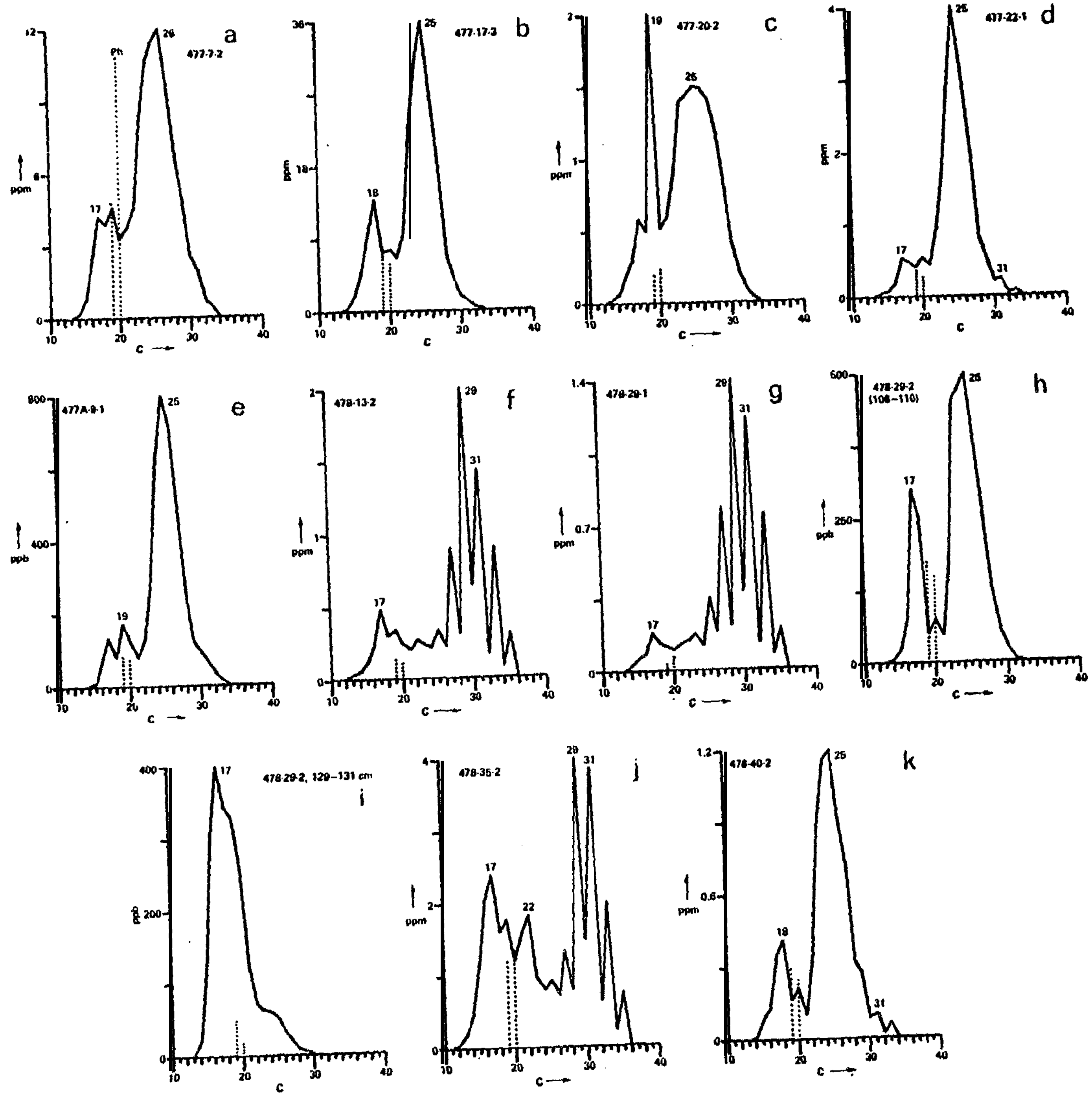
1.2
25
30
35
C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e
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f
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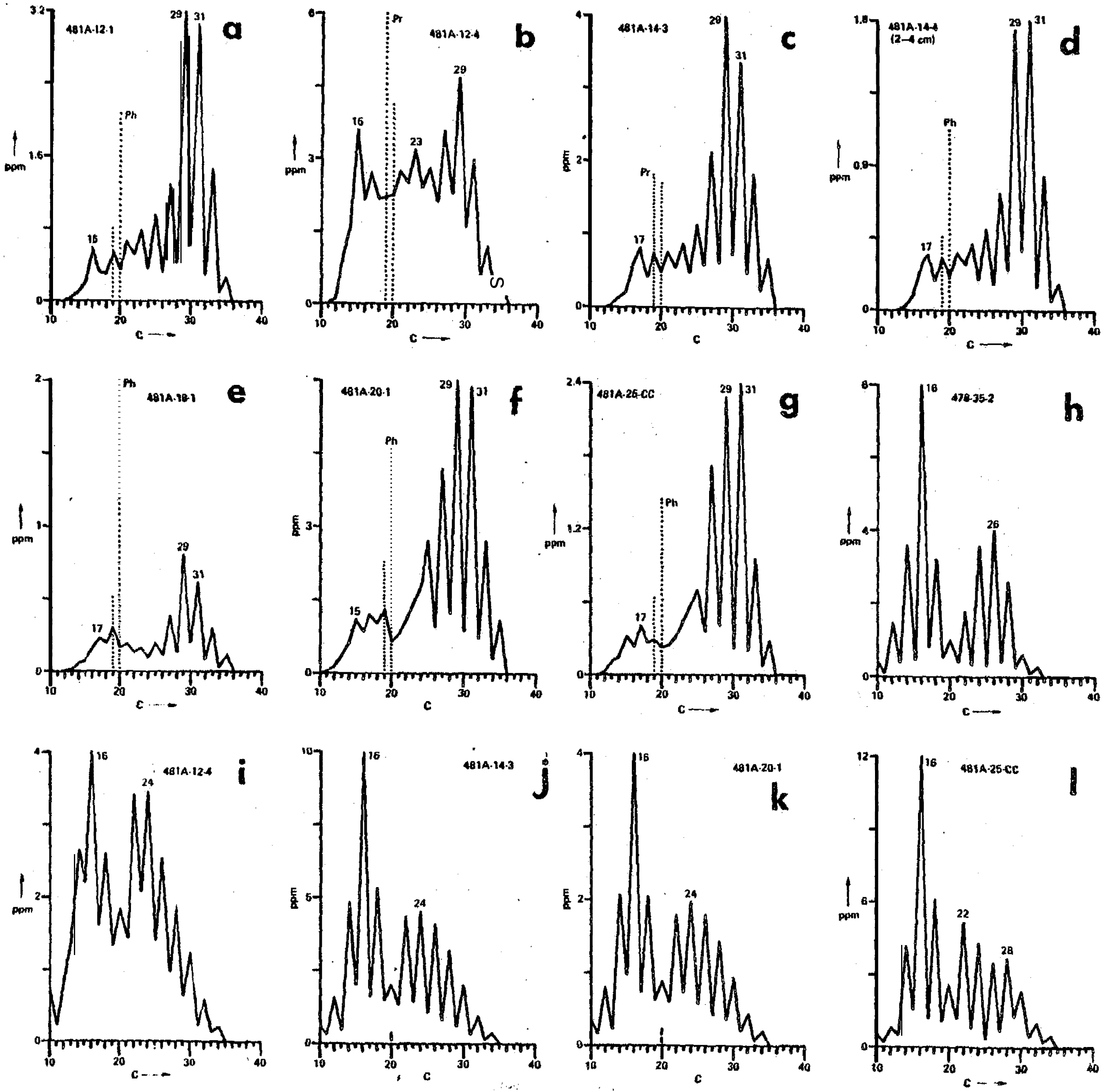
g
478-29-1
h
478-29-2
(106–110)
i
478-29-2, 129–131 cm
j
478-35-2
k
478-40-2
ppm
ppb
Ph
C



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16
Ph
29
31
b
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Pr
16
23
29
S
c
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Pr
17
29
31
d
481A-14-4 (2–4 cm)
Ph
17
29
31
e
481A-18-1
Ph
17
29
31
f
481A-20-1
Ph
15
29
31
g
481A-25-CC
Ph
17
29
31
h
478-35-2
16
26
i
481A-12-4
16
24
j
481A-14-3
16
24
k
481A-20-1
16
24
l
481A-25-CC
16
22
28
ppm
C →
10
20
30
40
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1.6
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1.8
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1
2.4
1.2
8
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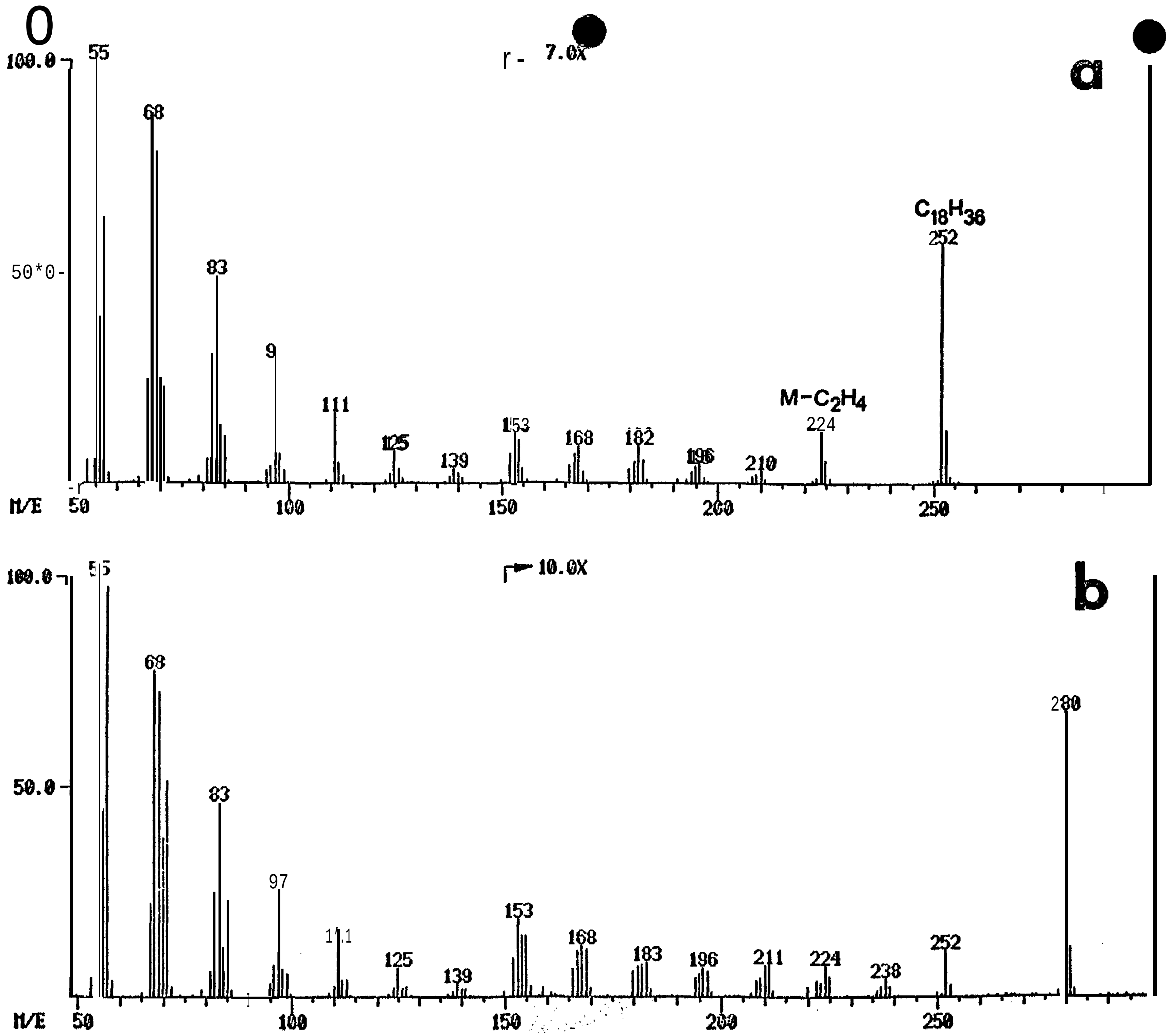
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M-C_2H_4
224
$C_{18}H_{36}$
252
M/E
50
100
150
200
250
100.0
55
10.0X
b
68
50.0
83
97
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153
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224
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M/E
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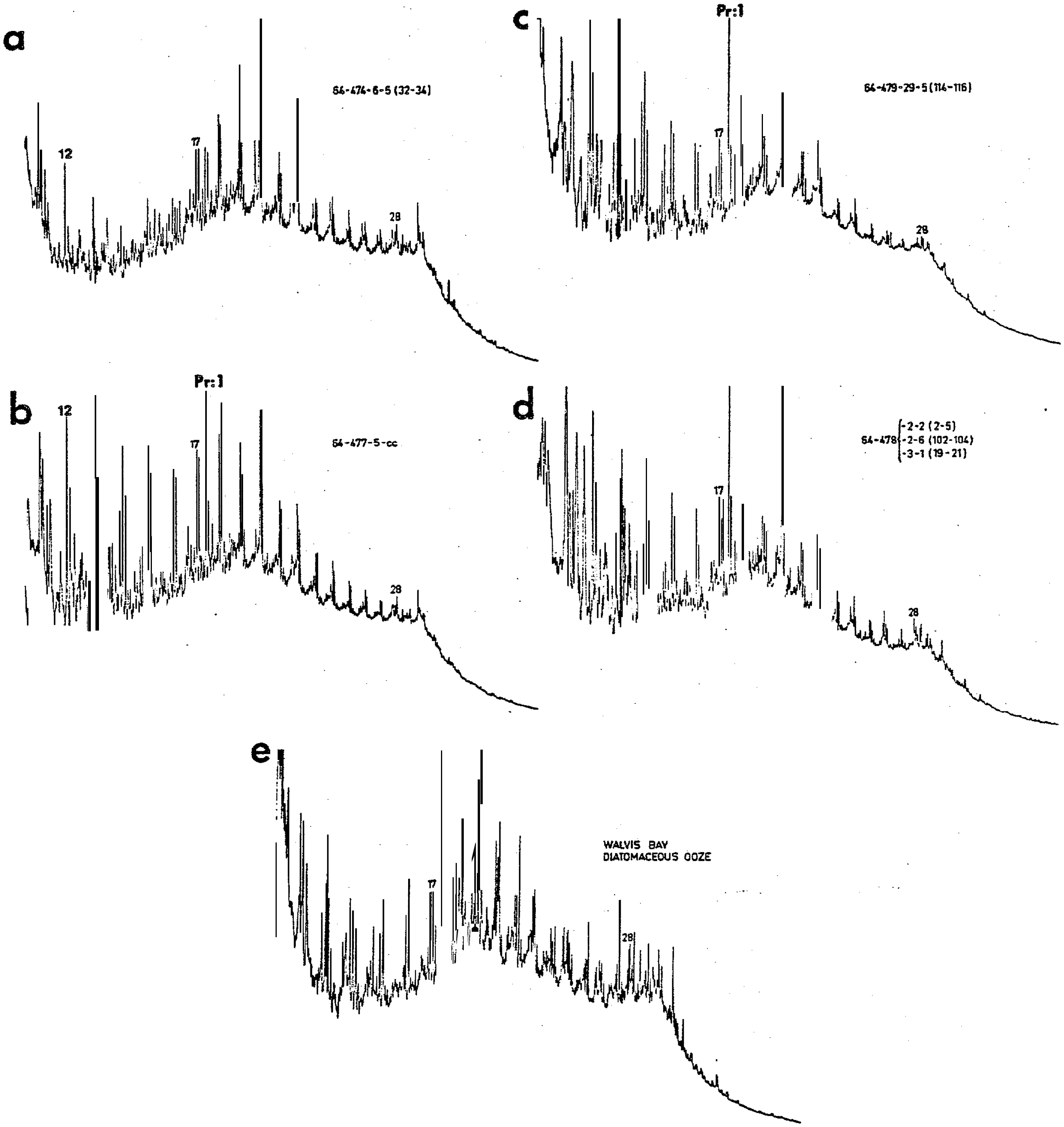
150
200
250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Pr:1
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b
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Pr:1
17
28
64-477-5-cc
d
17
28
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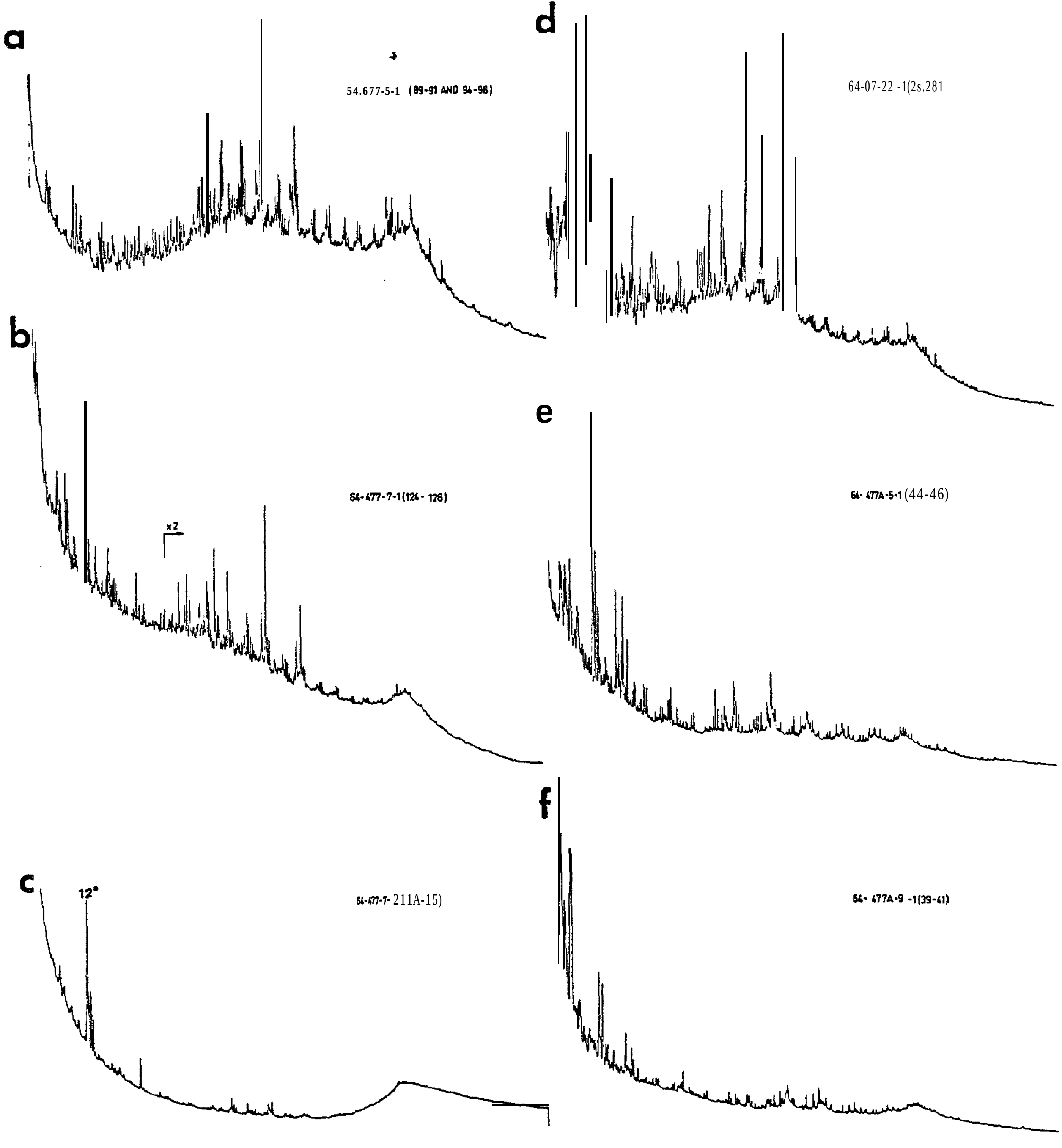
-2-6 (102-104)
-3-1 (19-21)
e
17
28
WALVIS BAY
DIATOMACEOUS OOZE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b
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x2
e
64- 477A-5-1(44-46)
c
12°
64-477-7- 211A-15)
f
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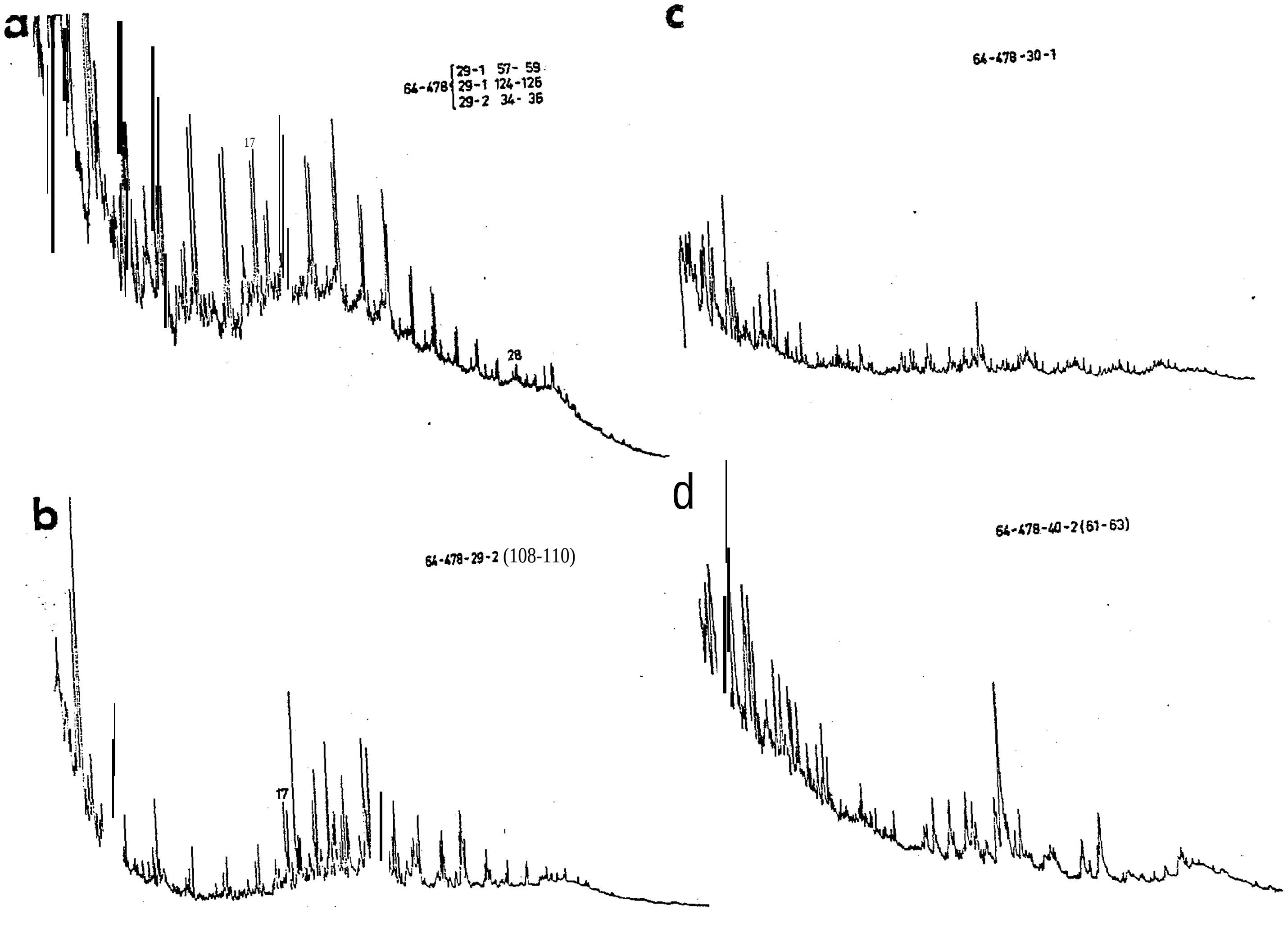
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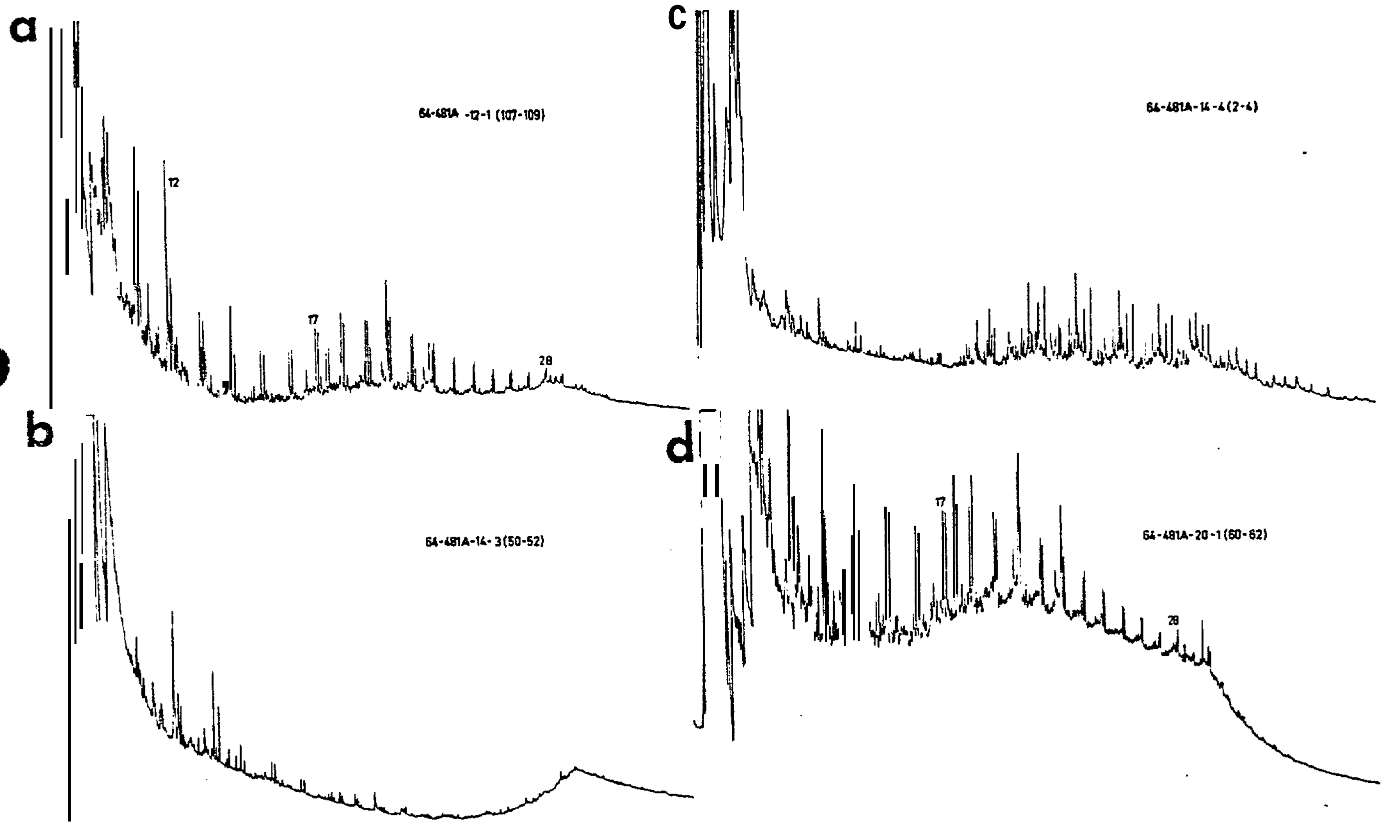
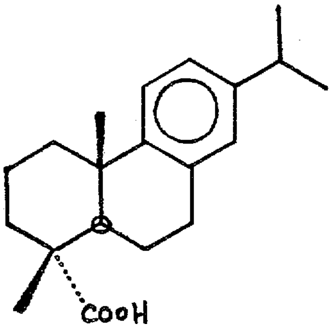
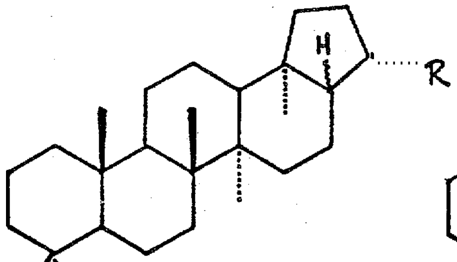
17
28
b
64-478-29-2 (108-110)
17
c
64-478-30-1
d
64-478-40-2(61-63)


a
64-481A -12-1 (107-109)
12
17
28
b
64-481A-14-3(50-52)
c
64-481A-14-4(2-4)
d
17
64-481A-20-1(60-62)
28

APPENDIX 1. Chemical Structures Cited

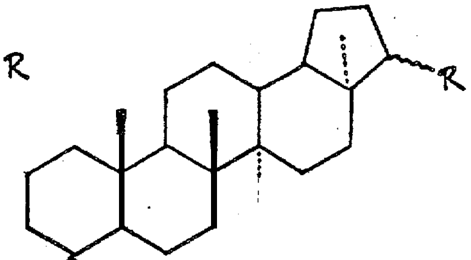


1. Dehydroabietic Acid



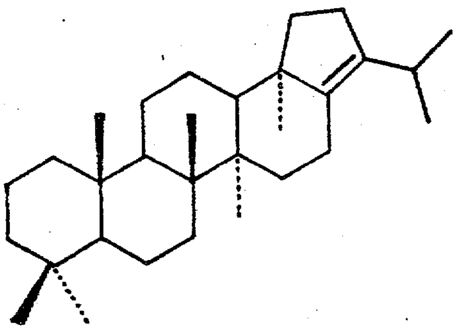
R=H, C_2H_5-C_7H_{15}

II. Hopanes

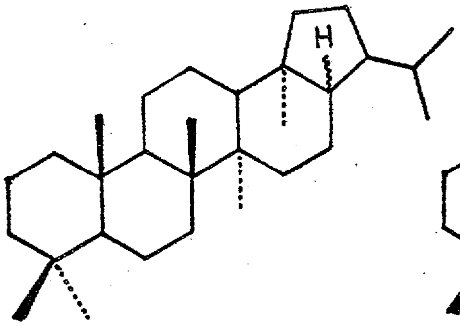


R=H, C_2H_5-C_3H_7

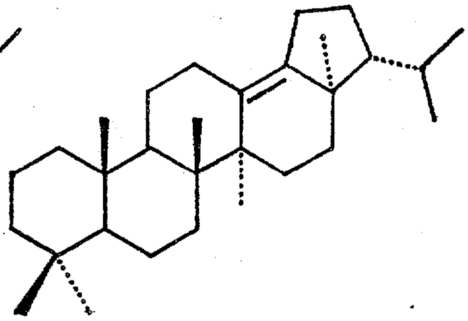
III. iso-Hopanes



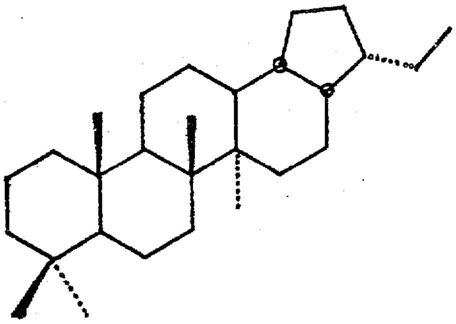
Iv. Hop-17(21)-ene



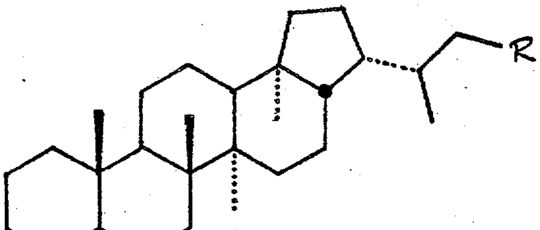
v. Moretanes



VI. iso-Hop-13(18)-ene

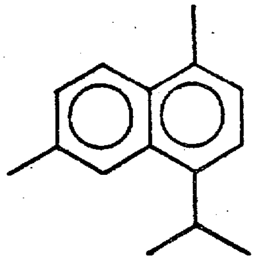


VII. 17α,18α,21β(H)-28,30-Bisnorhopane

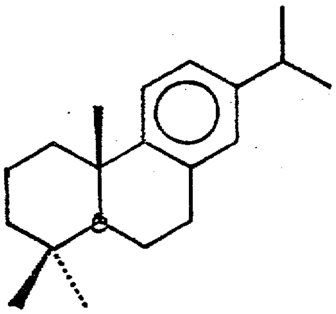


R=CO_2H, CH_2CO_2H, $CH_2CH_2CO_2H$

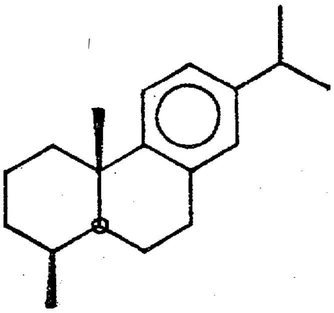
VIII. Extended 17β (H)-hopanoic acids



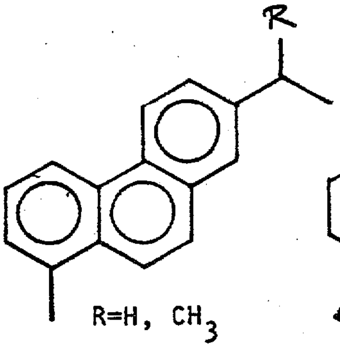
lx. Cadalene



x* Dehydroabietane

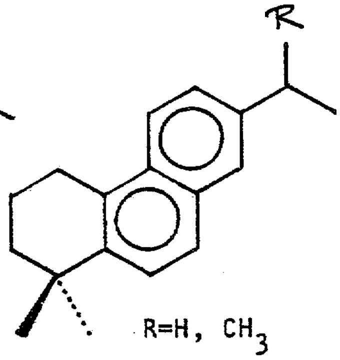


xl. Dehydroabietin



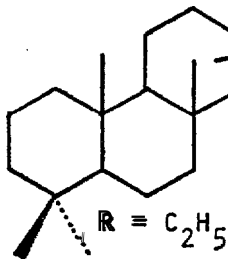
R=H, CH_3

X11. Retenes



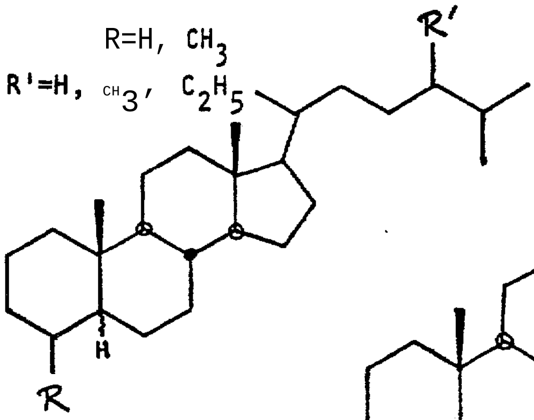
R=H, CH_3

XIII. Simonellites



$R = C_2H_5-C_8H_{17}$

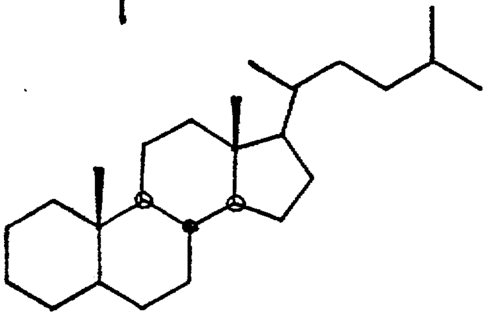
Xiv. Extended diterpanes



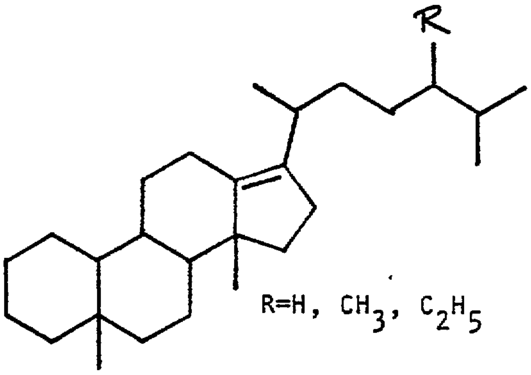
$R=H, CH_3$

$R'=H, CH_3, C_2H_5$

XV. Steranes

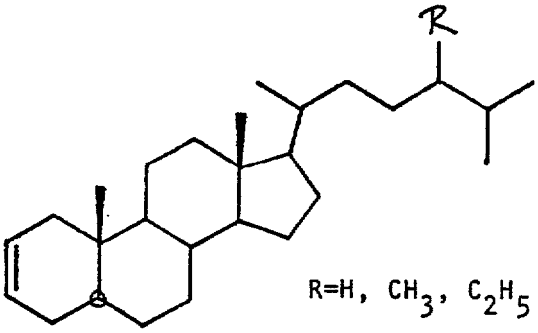


Xvi. Norcholestane



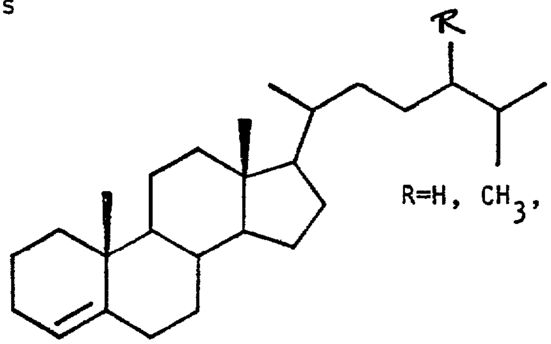
$R=H, CH_3, C_2H_5$

XVII. Diasterenes



$R=H, CH_3, C_2H_5$

XVIII. Ster-2-enes



$R=H, CH_3, C_2H_5$

X1X. Ster-4-enes

submitted to Environmental Science and Technology

EXTRACTABLE ORGANIC MATTER IN MUNICIPAL WASTEWATERS :
1. PETROLEUM HYDROCARBONS-TEMPORAL VARIATIONS AND MASS EMISSION RATES TO THE OCEAN[1]

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and
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ABSTRACT

Thirty-eight samples of final effluent were collected from the major municipal wastewater dischargers in southern California during 1979. The $CHCl_3$-soluble organic substances isolated from unfiltered and filtered samples were separated chromatographically and analyzed for gravimetric yields of total, aliphatic and aromatic hydrocarbons. Mean total hydrocarbon contents of those effluents having received mainly primary treatment ranged from 6.1 to 16.3 mg/l, whereas sludge concentrations were approximately 340 mg/l. The vast majority of these hydrocarbons are associated with particulate matter; however, their composition (∿ 54% aliphatic) was virtually identical for all effluents whether unfiltered or filtered. The temporal variations of wastewater total hydrocarbon concentrations were from 13 to 37% and appear to be independent of sampling frequency.

From these data, southern California's treatment plants are estimated to discharge more than 17.4 x 10^3 metric tons hydrocarbons/year *or* 4.6g-cap^{-1} day-1 to coastal waters. This is approximately double the input rate of petroleum hydrocarbons due to surface runoff in this region. Moreover, it represents nearly 6% of the currently-accepted estimate for the world-wide. input of wastewater-borne petroleum to the ocean. Problems associated with global input assessments of this type are discussed, and a correlative means of estimating wastewater hydrocarbon concentrations is presented.

INTRODUCTION

Information on the composition and variability of organic substances in municipal wastes and their input rates to the ocean is extremely limited. Although there have been isolated studies of sewage constituents of environmental concern (1-6), and certain compound classes (7-10), no comprehensive work has appeared in the literature. Nevertheless, substantial descriptive and statistical data bases are urgently needed for the following reasons: 1) to determine the potential chemical threats, if any, posed by the systematic, chronic discharge of wastes to the environment, and 2) to assess the role municipal wastes play in the overall carbon budget of the coastal zone. In this and succeeding papers (11,12), we provide new data for use in addressing these problem areas.

This report presents background information on the study site, southern California, along with results of hydrocarbon analyses of effluents from the major wastewater dischargers in this area. A 1975 NAS study of petroleum hydrocarbon (PHC) inputs to the marine environment (13) stated that municipal wastes contribute roughly 3.0 x 10^5 metric tons PHC to the sea per annum. This corresponds to approximately 5% of the total yearly global input from all sources. Although highly rated by the NAS panel, the confidence of this estimate is in some doubt due to the paucity of reliable data. Therefore, major objectives of this work were to generate new data on the PHC content of municipal wastewaters and to examine possible predictive tools for use in global inventories. This research is part of a large study aimed at characterizing the terrestrial sources of organic matter to the southern California Bight and constructing a reasonable budget for this coastal system.

Study area

The southern California Bight is a body of water contiguous with the North American continent extending from Pt. Conception, California, in the north to Cabo Colnett, Baja California, in the south (Figure 1). It is roughly bounded on the west by the edge of the continental slope at a water depth of approximately 3000 m (14). As such, the Bight encompasses an area of roughly 100,000 km^2. Owing to the intense human activity in the adjoining urban complex stretching from Los Angeles to San Diego, the possibility of adverse environmental effects has repeatedly been noted (14-17). Localized accumulations of numerous toxic substances have been found in the vicinity of sewage discharge sites (14, 18-20), and it is generally thought that domestic/industrial wastes are among the most serious threats to the ecology of the Bight.

The majority of southern California's municipal wastewaters (∿ 86%) receive only primary treatment and are introduced directly to the ocean via submarine outfall systems at a water depth of 'approximately. 60 meters. The rationale for *this* disposal plan, details of which can be found elsewhere (21), rests upon the effective dispersion of a buoyant wastewater plume by currents at sub-thermocline depths. In 1979, the year of this study, four of southern California's five major treatment plants contributed more than 98% of the total regional waste flow, 3.84 x 10^9 liters/day (22).' The locations of these four plants. are shown in Fig. 1, and a list of their treatment procedures, influent properties and some general effluent characteristics is given in Table I.

Because of its relatively high industrial component and large flow rates, the Joint Water Pollution Control Plant (JWPCP-Los Angeles County Sanitation Districts) has historically discharged the greatest quantities of oil and grease (Table II). Therefore, this facility was targeted for a detailed study of total extractable organic and hydrocarbon contents of its effluent. The other plants studied (cf., Table I) are as follows: 1) Hyperion treatment plant (City of Los Angeles) which discharges two effluents: HYP-7 (sludge + secondary effluent) through the seven-mile outfall into the head of the Santa Monica Canyon, and HYP-5 (primary + secondary centrate) through the 5-mile outfall into Santa Monica Bay, 2) Orange County Plants (OCSD -Orange County Sanitation Districts), and 3) Point Loma Plant (CSD -City of San Diego). Details of the outfall systems and effluent monitoring data tabulations can be found elsewhere (14, 22-27).

Sampling

During 1979, a series of flow-proportioned 24-hour composite samples were collected by personnel at each of four treatment plants (Table I). In the case of JWPCP, HYP-5, OCSD and CSD effluents, duplicate (3-liter) samples were obtained by either automatic sampling devices or manual methods. These samples were mechanically homogenized and placed in calibrated, organic-free glass bottles sealed with teflon-lined lids. One of the two samples was adjusted immediately to pH 1 with $CHCl_3$-extracted 6N HCl and preserved with 200 ml hexane. This procedure was intended to terminate biological activity, minimize evaporative losses and initiate extraction. Both bottles were then refrigerated on location. Sample pickup never exceeded three hours from the time of collection/ preservation. Sampling of the HYP-7 (sludge) effluent, was performed in a similar fashion; however, only 600-900 ml volumes were necessary due to the high suspended solids and "oil and grease" contents (cf., Table I).

HYP-5, HYP-7, OCSD and CSD effluents were each collected at approximately the same time on a quarterly basis. The JWPCP effluent was sampled more frequently. In this study, 24-hour composites were taken at daily (8 consecutive days), weekly (6 consecutive weeks) and monthly (12 consecutive months) intervals.

Methodology

Upon return to the laboratory, two liters of the untreated sample were fittered using pre-combusted Whatman GF/A glass fiber filters and a specially-designed all-glass filtration system. The filtrates were then preserved with 200 ml hexane and 6N HCl as before. Only 500 ml samples of HYP-7 [sludge) filtrate were generated in this way. If not extracted immediately, unfiltered and filtered samples were stored at 10°C until a later time. Particulate from the remaining undisturbed sample were stored frozen for subsequent elemental/ isotopic analyses.

Liquid/liquid extractions were performed in separator funnels using the 200 ml hexane preservative solution followed by $CHCl_3$ (100 ml/liter sample--three times). $CHCl_3$-extracted NaCl was added to the mixtures to help break emulsions. Furthermore, all extractions were preceded by rinsing the sample bottle to recover lipid materials possibly adhering to the glass walls. For the HYP-7 (sludge] effluent, the hexane was followed by six $CHCl_3$ extractions (150 ml $CHCl_3$/500-750 ml sample). In most cases, an emulsion layer remained after the last extraction. This was broken by centrifugation (2,000 rpm), and the $CHCl_3$ layer was combined with the extracts. Subsequent steps included concentration by rotary evaporation, water and sulfur removal, esterification, and thin-layer chromatographic separation of the esterified extractable into five organic fractions, one of which contained the total hydrocarbons (THC). In some cases, the THC fraction was further chromatographed to isolate aliphatic (Al) and aromatic (Ar) hydrocarbon subfractions. Technical details are given elsewhere (28).

Data presented here include gravimetric results for the total extractable organics (TEO), THC, Al and Ar fractions'. These measurements are based upon triplicate weighings of solution residues using a Mettler ME 22 electromicrobalance. Replicate determinations showed the precision to be (coefficient of variation) ± 5% or less. Molecular analysis of the hydrocarbon (11) and non-hydrocarbon (12) components will be discussed separately.

As a check on the extraction efficiency, exhaustive extractions were pet--formed on two samples: JWPCP (3/14/79-unfiltered) and HYP-7 (10/15/79-unfiltered) (cf., Table III); gravimetric measurements were made on each sequential extract. The results indicate that 95% of the TEO and 97-99% of the THC were recovered by the methods used in this study. Gravimetric yields of blanks treated by the same procedure were below detection limits.

RESULTS AND DISCUSSION

General Findings

Concentrations of total extractable organics (TEO), total hydrocarbons (THC) and aliphatic (Al) and aromatic (Ar) hydrocarbons measured in the five effluents are listed in Table III. Also given are values for "oil and grease" determined by treatment plant personnel on grab samples taken the same day (29}. In nearly all bases, the values of TEO exceed those for oil and grease. This is probably the result of differences in the extraction solvents (Freon ^{R}is used for oil and grease determinations) and variations in technique.

Unfiltered samples of HYP-7 (sludge) effluent have 10-20 times theTEO and THC contents of other effluents, the hierarchy thereafter being JWPCP > CSD > OCSD > HYP-5. These differences most likely reflect variations in the nature of influent composition and degree of treatment. Filtered samples of HYP-7 effluent contain roughly 2-3 times the TEO and 4-5 times theTHC content of the other effluents. Because the filters used here do not completely retain colloidal particulate matter (mean particle retention size ≃ 0.9 µm; ref. 30), elevated levels of extractable substances in HYP-7 filtrates probably reflect an enrichment in the mass off'ine colloids. The other effluent filtrates have fairly similar TEO and THC concentrations despite varying total concentrations in unfiltered samples. This suggests that the aqueous phase of these effluents may have attained a common practical limit for the "accommodation" of organics. The" surprisingly high percentage ofTEO found in filtrates of the JWPCP, HYP-5, OCSD and CSD effluents (21 .5-52.1%) is due to the presence of water-soluble polar materials such as fatty acids, alcohols, sterols and phenols (12). With the exception of the HYP-5 wastewater, hydrocarbons were associated to a large extent (75.1 - 97.6%) with filterable particulate matter, a characteristic noted previously by others (31). The high percentage of hydrocarbons in the HYP-5 filtrate is probably related to the low overall THC content of this effluent.

Aliphatic hydrocarbons represented slightly greater than half the total hydrocarbons in both unfiltered (54.2 ± 2.2%) and filtered (53.0 ± 2.2%) samples of all effluents. The fact that Al and Ar sub-fractions did not exhibit fractionation between the unfiltered and filtered sample's may mean that equilibrium has not been established in these aqueous mixtures. Typically, Ar/Al ratios are greater in filtrates owing to the higher aqueous solubilities of aromatic hydrocarbons (28). A possible explanation is that fine colloids capable of passing through the filter and having the same composition as the bulk sewage. may dominate the dissolved constituents of the filtrates. Thus, any fractionation associated with the solution process would be masked. Another remarkable finding was the similarity in the hydrocarbon compositions of different effluents. This" suggests that wastewater treatment plants of southern California are probably receiving hydrocarbon mixtures from similar sources, each plant differing only in the amounts they treat and ultimately discharge.

The total hydrocarbon concentrations found here (6.1 to 16.3 mg/l; 341 mg/l-sludge) are similar to those previously reported (6, 31, 32). Because so few data are available, it is difficult to establish whether the variations are due to regional differences in hydrocarbon usage, disposal and treatment removal efficiencies or simply non-representative sampling. The possibility of temporal variation in the composition of sewage requires that the optimal sampling methodology and frequency be established. In recognition of this fact, we attempted to examine the temporal variation of TEO and THC concentrations by sampling the JWPCP effluent over different time intervals. As Fig. 2 illustrates, oil and grease levels measured daily at the JWPCP can change dramatically. This is partly due to the fact that the analyses were performed on grab, not composite, samples and are therefore subject to considerable fluctuation. Our measurements for TEO and THC contents on daily, weekly and monthly intervals (Table IV) show virtually the same levels of variation regardless of sampling frequency. The differences between the daily means and those of the weekly and monthly samples, however, indicates that consecutive daily sampling, although more exact if done year around, may be non-representative when performed over short intervals of time. Compositing of samples on a weekly or monthly basis might better satisfy both the statistical requirements and the practical (i.e., economic, time) limitations of monitoring. However, the preservation of samples for other than hydrocarbon analyses over these periods is questionable in viewof the lability of certain non-hydrocarbon lipid constituents.

Mass Emission Rates

One of the main goals of this project was to compute mass emission rates (MER) of wastewater-borne hydrocarbons to the coastal waters of southern California. Although these estimates are based upon relatively few measurements, they represent the most reliable data against which other inputs can be evaluated at this time. Values for the MER's of total suspended solids, oil and grease, TEO and THC given in Table V were calculated according to the formula:

Mass Emission Rate (metric tons/yr, rota) = $10^{9} \cdot \sum_{i=1}^{n} \bar{F}_i \cdot {}' i \quad \cdot \bar{c}_i$

where:

F'_i = mean flow for time interval i (liter/day),

t_i = number of days in time interval i,

$\bar{c}_i$ = mean analytical concentration of parameter during time interval i (mg/l),

n = maximum number of time intervals per year (JWPCP-12; HYP-5, HYP-7, OCSD, CSD-4).

For the JWPCP estimate, mean values of 74.4 mg/l (TEO) and 16.3 mg/l (THC) were used to approximate the lost November sample. Gross estimates of aliphatic and aromatic hydrocarbon MER's were calculated using the MER values for THC and applying data obtained from the few individual chromatographic separations that were performed (Table III).

From the present results (Table V),. it appears that the JWPCP contributes nearly one-half (45.477) of the petroleum hydrocarbons discharged by all wastewater treatment plants in southern California. This is very close to its relative input rate of oil and grease (Table II). The remaining hydrocarbon input is more or less evenly divided among the other outfall systems. The dominance of the JWPCP must be due to the relatively higher hydrocarbon burden of the effluent because flow and total suspended solids (MER's) represent only 35% and 39%, respectively, of the total . In contrast, the HYP-7 sludge effluent, which represents a mere 0.5% of the total yearly flow, contributes 21%, 6.2%, and 13.1% of the combined suspended solids, oil and grease and THC input, respectively, a reflection of its high (lipid-rich) solids content.

On the basis of a limited number of hydrocarbon. analyses of wastewater effluents from treatment plants in Rhode Island, Barrington and Quinn (32) estimated the total coastal U.S. input of PHC to the ocean at between 28,000 and 140,000 metric tons/year (rota). Subsequently, Storrs (33) calculated an annual U.S. mass emission rate of approximately 200,000 metric tons. This estimate was based upon an assumed unit input of 8 g-cap^{-1} day-l and a coastal population of 68 million. When computed on a daily per capita basis (cf., Tables I, V) southern California effluents discharge 3.3 to 6.0 g-cap^{-1} day^{-1} with a mean value of 4.6 g-cap^{-1} day^{-1}. Assuming this mean value to be representative of similar discharges nationwide, and a coastal population of 68 million persons, the total U.S. input should total roughly 113,400 mta. This estimated MER falls within the range proposed by Barrington and Quinn (32) and represents a remarkable 41% of the NAS-computed global input from municipal wastewaters (13). The combined MER of sewage-borne PHC to southern California waters (17.4 x 10^3 rota) comprises 5.8% of the global wastewater input (13). These results seem to indicate that either southern California treatment plants discharge especially large quantities of petroleum hydrocarbons in their wastes or that the NAS global estimate is 1 Ow.

The other major route by which surface waters are delivered to the ocean is runoff. In southern California, *rivers* and streams discharge only one-third the volume of water to the Bight as do wastewater treatment plants (3), and recent calculations for all of southern California (28) place the surface runoff mass emission" rates of TEO and THC at approximately 17.9 x 10^3 mta and 9.69 x 10^3 rota, respectively. Thus, municipal wastes contribute 5.1 and 1.8 times as much TEO and THC to the ocean as runoff. The discrepancy between these ratios arises from differences in the lipid compositions of waste and runoff waters. The extractable organic matter of sewage contains roughly 22% THC, whereas data for urban storm runoff indictes that hydrocarbons comprise about 51% of the extractable material. It should be noted that relative to wastewaters, surface runoff is subject to greater temporal and spatial variations in the composition and total concentration of extractable organics.

In considering potential environmental impacts to the marine ecosystem, it is also vital to recognize the contrast in their modes of delivery. Municipal wastes are effectively discharged. from four point sources in southern California on a more or less continuous basis at sub-thermocline depths. Surface runoff, on the other hand, is generated by intermittant, and oftentimes dramatic, storm events which are superimposed on chronic dry weather flows. These highly seasonal discharges emanate from more than 150 rivers , streams and drainage channels terminating in surface waters of the ocean. Differences such as these undoubtedly affect the transport and ultimate fate of terrigenous organic matter from these sources.

Estimating the hydrocarbon content of wastewaters

From the viewpoint of input assessment, periodic measurements of total hydrocarbon concentrations in municipal wastewaters would seem desirable. However, the legal requirements for such monitoring do not presently exist, nor are they likely to in the near future. Hence, the impetus to develop a simple, indirect and universally-applicable method for estimating PHC burdens in wastewaters is obvious. Past assessments have relied on largely unsupported assumptions of the THC content of oil and grease. With refinement, this approach . might be attractive because oil and grease levels. are commonly monitored in treatment facilities world-wide. Therefore, we investigated the possibility of correlating our TEO and THC measurements with oil and grease data obtained by treatment plant personnel.

Casual inspection of contemporaneous data for the JWPCP effluent in Fig. 2 suggests that correlations among THC, TEO and oil and grease concentrations exist. To be valid, however, a correlation used for estimation on a regional scale, must be applicable for a number of effluents. Thus, we analyzed the data for all effluents together. Fig. 3 illustrates the analytical curves obtained by linear regression under two different conditions, that is, with and without the HYP-7 sludge data.

The correlation between TEO and THC data for all five effluents (Fig. 3a, curve 1) is exceptionally good, indicating that with respect to hydrocarbon content,the composition of the extractable organics is very consistent among these wastewaters. We also explored the possibility of excluding the sludge data from the regression analysis. Practically speaking, there is some justification for doing so because undiluted sludge is usually disposed by pyrolysis, landfilling or offshore dumping, not be continuous discharge through relatively shallow water outfalls. Thus, most effluents discharged directly to the ocean will have received a combination of primary and/or secondary treatment and should have similar characteristics to those of the JWPCP, HYP-5, OCSD and CSD wastewaters. When the regression analyses are performed on all but the sludge data, the correlation of TEO with THC remains very good (r = 0.91), and the slope and intercept are similar (cf., Fig. 3a, curve 2) to those obtained for the analysis using the complete data set. Thus, exclusion of the sludge data does not present a serious statistical problem for the correlation of TEO and THC measurements.

When considering the correlation of THC with oil and grease, however, a different situation arises. Because oil and grease measurements were performed by plant personnel on entirely different (grab) samples than those used for the THC determinations, there is considerable sampling-related error associated with plot of THC versus oil and grease (Fig. 3b, curve 1). In addition, the analytic curve does not appear to fit the non-sludge effluents very well. This may be due to the fact that the HYP-7 sludge, a highly-concentrated effluent, is analyzed for oil and grease by a modification of the standard method which may not have the same extraction efficiency as that used for the other effluents (34).

If the linear equation for the THC vs oil and grease correlation for all the data (curve 1) is used in conjunction with annual mean values of oil and grease concentration and flow (Table 1) to calculate a combined hydrocarbon MER for the dischargers, a value of 11,290 mta is obtained. This is in very poor agreement with that shown in Table V (17,610 mta). MER values for individual dischargers are even more deviant. " In fact, because they-intercept of the line (curve 1), 22.3 mg/l, exceeds the mean annual concentration of oil and grease in HYP-5 effluent, a negative MER is calculated when this equation is used.

Performing the regression analysis in the absence of the sludge data produces somewhat less satisfying statistical results (i.e., the "r" value is lower), however, the ability to accurately estimate THC mass emission rates is greatly improved. The final expression obtained by linear regression of the THC and oil and grease data (without HYP-7 data; curve 2) was:

$$y = 2.01\,x + 10.4 \quad (r = 0.72)$$

where:

Y = concentration of oil" and grease (mg/l),

x = concentration of total hydrocarbons (mg/l).

Using the average values of oil and grease concentrations and flow given in Table I, MERs were calculated using this formula:

JWPCP	8443
HYP-5	2014
HYP-7	1600
OCSC	2465
CSD	2475
Total	16,997

By comparison with the data given in Table V, the predicted individual MERs show adequate agreement, whereas the grand total agrees quite well. This crude test simply demonstrates the self-consistency of the method. More data for other effluents may provide a means of evaluating whether or not the correlation found here is generally applicable and/or subject to changes with time. Such a tool will obviously be of value in estimating the wastewater input of petroleum hydrocarbons because of its simplicity, and applicability to existing monitoring data.

Conclusions

The results of our analyses of municipal wastewaters in southern California have shown that large quantities of petroleum hydrocarbons (17,400 rota) are currently being discharged to the ocean in this area of the world. Indeed, it appears that calculated global PHC inputs due to sewage may have been underestimated in the past. The environmental significance of these findings is clouded, at best. This is because: 1) the nature and quantities of specific organic compounds in wastewaters are largely unknown and 2) the fate of complex mixtures of natural and anthropogenic organic substances in the ocean are only . poorly understood. We intend to address the detailed molecular composition of sewage in subsequent writings (11,12); however, the environmental fate of organic wastes will remain an important and difficult subject for future investigations.

Acknowledgements

We thank the following individuals for their help in obtaining samples and monitoring data: JWPCP - Duane Fischer, W. Montgomery; Hyperion - J. Nagano, F. Wada, K. Mikawa; OCSD - G. Pamson, F. Tanner; CSD -A. Langworthy, J. Chaffin. Henry Schafer provided access to monitoring data and made helpful discussions. Financial assistance from the Department of Energy and Bureau of Land Management (Contract No. EY-76-3-03-0034).

REFERENCES

(1) Erickson, M.D.: Pellizari, E.D. Bull. Env. Cont. Toxic. 1979, 22, 688.

(2) Young, D.R. "Priority Pollutants in Municipal Wastewaters", Southern California Coastal Water Research Project., Annual Rept., 1978, 103.

(3) Burlingame, A.L.; Kimble, B.J.; Scott, E.S.; Walls, F.C.; de Leeuw, J.W.; deLappe, B.W.; Risebrough, R.W. In "Identification and Analysis of Organic Pollutants in Mater"; Keith, L.H., Ed.; Ann Arbor Science: Ann Arbor, 1976; p. 557.

(4) Garrison, A.W.: Pope, J.D.; Allen, F.R. "GC/MS Analysis of Organics in Domestic Wastewaters" ibid.; p. 517.

(5) Harrison, R.M.; Perry, R.; Wellings, R.A. Water Res. 1975, 9, 331.

(6) Tanacredi, J.T. J. Water Pollut. Control Fed. 1977, 49, 216.

(7) Manka, J.; Rebhun, M.; Mandelbaum, A.; Bortinger, A. Environ. Sci. Technol. 1974, 8, 1017.

(8) Loehr, R.C.; de Navarra, C.T. J. Water Pollut. Control Fed. 1969, 41, R142.

(9) Hunter, J.V.; Heukelekian, H. ibid. 1965, 37, 1142.

(10) Bunch, R.L..; Barth, E.F.; Ettinger, M.B. ibid. 1961, 33, 122.

(11) Eganhouse, R.P.; Kaplan, I.R. "Extractable Organic Matter in Municipal . Wastewaters. 2: Petroleum Hydrocarbons-Molecular Characterization (Unpublished).

(12) Eganhouse, R.P.; Kaplan, I.R. "Extractable Organic Matter in Municipal Wastewaters. 3: Non-hydrocarbon Constituents (unpublished).

(13) National Academy of Sciences "Petroleum in the Marine Environment"; Washington, D.C., 1975.

(14) "The Ecology of the Southern California Bight: Implications for Water Quality Management", Southern California Coastal Water Research Project, Technical Report 104, March 1973.

(15) Faisst, W.K. Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1976.

(16) Peterson, L.L. ibid., 1974.

(17) Grigg, R.W.; Kiwala, R.S. Calif. Fish and Game Quarterly 1970, 56, 145.

(18) Young, D.R.; McDermott, D.J.; Heesen, T.C.; Jan, T.K. In "Marine Chemistry in the Coastal Environment"; Church, T.M., Ed.; American Chemical Society: Washington, D.C., 1975; p. 424.

(19) MacGregor, J.S. Fishery Bull. 1976, 74, 27.

(20) Galloway, J.N. Geochim. Cosmochim. Acts 1979, 43, 207.

(21) Brooks, N.H. In "Waste Disposal in the Marine Environment"; Pearson, E.A., Ed.; Pergamon Press: New York, 1960; p. 246.

(22) Schafer, H.A. Southern California Coastal Water Research Project, Biennial Report, 1979-1980, p. 235.

(23) McDermott, D.J. Southern California Coastal Water Research Project, Annual Report, 1975, p. 163.

(25) Schafer, H.A. Southern California Coastal Water Research Project, Annual Report, 1976, p. 57.

(26) Schafer, H.A. Southern California Coastal Water Research Project, Annual Report, 1977, p. 19.

(27) Schafer, H.A. Southern California Coastal Water Research Project, Annual Report, 1978, p. 97.

(28) Eganhouse, R. P.; Kaplan, I.R. Environ. Sci. Technol. 1981, 15, 310.

(29) "Standard Methods for the Examination of Water and Wastewater", 14th cd.; American Public Health Association: Washington, D.C., 1975; p. 515.

(30) Sheldon, R.W. Limnol. Oceanogr. 1972, 17, 494.

(31) Van Vleet, E.S.; Quinn, J.G. Environ. Sci. Technol. 1977, 11, 1086.

(32) Barrington, J.W.; Quinn, J.G. J. Water Pollut. Control Fed. 1973, 45, 704.

(33) Storrs, P.N. "Petroleum Inputs to the Marine Environment from Land Sources" Background papers, Workshop on Input, Fates and Effects of Petroleum in the Marine Environment. National Academy of Sciences, Airlie, Virginia, 1973.

(34) Mikawa, K. Personal communication 1981.

Table I. Description of the Major Southern California Wastewater Dischargers and Average Concentrations of Some Important Constituents, 1979[a]

Discharger	Agency/ municipality	Industrial/ Domestic Influent[b]	Population Served (millions)	Nature of Effluent Treatment	Total Effluent Flow (MLD)	Total Suspended Solids (mg/1)	Oil & Grease (mg/1)
Joint Water Pollution Control Plants (JWPCP)	Los Angeles County Sanitation Districts	18/82	3.65	Primary, Digested Sludge Centrate	390	195	39.9
Hyperion Plant:	City of Los Angeles, Bureau of Sanitation	15/85	3.10				
HYP-5:				Primary, Secondary	1336	75	19.0
HYP-7:				Digested Sludge, Secondary	18	7060	400.
Orange County Plants (OCSD)	Orange County Sanitation Districts	25/75	1.70	Primary, Secondary	712	140	26.0
Point Loma Plant (CSD)	City of San Diego	7/93	1.35	Primary	484	143	36.7

[a] Data taken from ref. 22.

[b] Given as percentages of the total plant inflow.

Table II. Mass Emission Rates (metric tons/year) of Oil and Grease for Major Municipal Wastewater Dischargers in Southern California from 1971-1979[a]

Year	JWPCP	HYP-5	HYP-7	OCSD	CSD	TOtal	JWPCP (% total)
1971	30,000	6550	6330	ND	4600	---	-- --
1972	36,500	9210	4040	7450	3440	60,640	6002
1973	29,300	8380	6130	8430	4980	57,220	51.2
1574	26,3oo	8470	5860	8210	5900	54,740	48.0
1975	28,900	9530	5760	8230	4000	56420	51.2
1976	30,600	9950	3860	10,300	4100	58,810	52.0
1977	21,300	8380	3700	10,100	5340	48,820	43.6
1978	21,900	8940	3270	7800	6800	48,710	45.0
1979	20,200	9270	2450	6760	6490	45,170	44*7

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[a] Data obtained from routine effluent monitoring data (14, 22-27).

"TABLE 111. Concentrations (mg/l) of oil and grease, total extractable organics, total hydrocarbons and aliphatic and aromatic hydrocarbons in Southern California wastewater effluents, 1979a.

Sampling Date	Sample Type[b]	Oil and Grease	Total Extractable Organics		Total Hydrocarbons[c]	
			Unfiltered	Filtered	Unfiltered	Filtered
JWPCP						
1/15/79	1,4	36.0	59.8	28.0	10.6	2.18
2/15/79	1	33.0	75.0	20.0	14.2	1.78
3/7/79	2,3	50.9	71.0	26.9	13.4	
3/8/79	3	72.6	83.5	31.8	22.6	
3/9/79	3	58.6	79.6	29.0	22.0	
3/10/79	3	39.3	64.7	26.6	13.0	
3/11/79	3	39.0	66.1	24.7	15.8	
3/12/79	3	49.3	79.0	26.1	16.2	
3/13/79	3	56.3	79.7	25.1	18.5	
3/14/79	2,3	31.3	71.2	27.2	14.3 (8.0/6.3)	2.36 (1.18/1.18)
3/21/79	2	50.0	85.7	22.6	20.2	
3/28/79	2	47.0	62.7	24.8	13.6	
4/4/79	2	45.3	71.5	22.6	16.6	1.53
4/17/79	1,4	48.3	71.9	d	17.3	d
5/15/79	1	29.7	67.5	21.1	13.0	1.29
6/15/79	1	42.0	77.9	25.8	15.6	2.13
7/16/79	1,4	33.7	79.8	23.5	15.9	2.18
8/15/79	1	38.5	83.6	29.0	20.9	3.29
9/13/79	1	33.0	69.0	22.3	18.2	1.61
10/15/79	1,4	31.0	65.6	23.6	16.1	2.19
11/15/79	1'	40.6	d	d	d	d
12/13/79	1	34.0	75.0	d	14.0	d
$\bar{x} \pm s$		42.7±10.8	73.3± 7.4	25.3 ± 3.0	16.3± 3.2	2.05 ± 0.56
HYP-5						
1/15/79	4	13.0	47.3	17.2	5.1 (2.9/2.2)	1.92
4/18/79	4	20.0	48.8	23.4	6.9	3.04 (1.71/1.33)
7/16/79	4	22.0	43.8	22.8	5.7	2.90
10/16/79	4	17.0	46.2	21.4	6.5	3.10
$\bar{x} \pm s$		18.0±3.9	46.5±2.1	21.2±2.8	6.1±0.8	2.74±0.55

TABLE 111. (continued)

Sampling Date	Sample Type[b]	Oil and Grease	Total Extractable Organics		Total Hydrocarbons[c]	
			Unfiltered	Filtered	Unfiltered	Filtered
HYP-7						
1/15/79	4	456	1088	81.00	397 (211/186)	17.6 (9.4/8.2)
4/18/79	4	425	994	64.5	374	13.2
7/16/79	4	355	796	50.3	297	9.4
10/15/79	4	476	717	41.5	297 (165/133)	7.1 (3.8/3.3)
$\bar{x} \pm s$		428±53	899±172	59.3±17.3	341±52	11.8±4.6
OCSD[e]						
1/15/79	4	31.6	40.3	19.3	5.7 (3.0/2.7)	1.23 (0.63/0.60)
4/12/79	4	84.0	63.2	20.2	10.9	1.63
7/16/79	4	22.9	47.3	23.0	7.0	1.73
10/16/79	4	24.9	50.1	32.9	7.8	1.73
$\bar{x} \pm s$		25.8±3.9	52.2±9.6	23.8?6.2	7.8±2.2	1.53*0.26
CSD						
1/16/79	4	67.4	56.3	12.1	11.8	1.22
4/1.4/17/79	4	32.1	58.9	2?.1	8.2 (4.2/4.0)	1.78 (0.94/0.84)
7/17/79	4	27.0	65.3	23.3	10.4	2.21
10/16/79	4	41.2	69.1	22.2	18.7	2.66
$\bar{x} \pm s$		41.9±18.0	62.4±5.8	19.715.1	12.3±4.5	1.97±0.61

a = Data for oil and grease concentrations obtained from monthly and annual reports of the sanitation districts.

b = Sample type: l-monthly, 2-weekly, 3-daily, 4-quarterly.

c = Aliphatic/aromatic concentrations are given in parentheses below the THC values.

d = Sample lost.

e = Data for oil and grease concentrations are quarterly means.

TABLE IV. Variations in the concentration of total extractable organics and total hydrocarbons in JWPCP final effluent as a function of sampling frequency

	Daily	Weekly	Monthly
<u>Total Extractable Organics</u>			
Unfiltered	74.4±7.0	72.4±8.3	72.3±6.8
Filtered	27.2?2.3	24.8?2.2	24.5±3.2
<u>Total Hydrocarbons</u>			
Unfiltered	17.0±3.7	15.6±2.8	15.5?2..8
Filtered	--		2.05±0.56

a = All results given as means ± standard error (mg/l) for 24-hour composite samples.

TABLE V. Mass Emission Rates (metric tons/year) of Wastewater Constituents from Major Dischargers in Southern California, 1979^{a}

	JWPCP	HYP-5	HYP-7	OCSD	OSD	Total
Total Suspended Solids	99,080	39,050	51,800	36,560^{b}	25,540	252,040
Oil and grease	18,890 (14.2)	8,760 (10.2)	2,830	6,720^{b} (10.8)	8,160 (16.6)	45,360
Total Extractable Organics	37,360 (28.0)	22,630 (25.2)	5,950	13,860 (22.2)	10,980 (22.3)	90,680
Total Hydrocarbons	7,990 (6.00)	2,950 (4.60)	2,260	2,040 (3.29)	2,160 (4.38)	17,400
Aliphatics	4,470	1,680	1,230	1,070	1,110	9,560
Aromatics	3,520	1.270	1,030	970	1,050	7,840

a = Total suspended solids and oil and grease calculations based upon data from Table III; per capita mass emission rates ($g\text{-}cap^{-1}\ day^{-1}$) are given in parentheses.

b = Calculations based upon quarterly averages.

LIST OF FIGURES

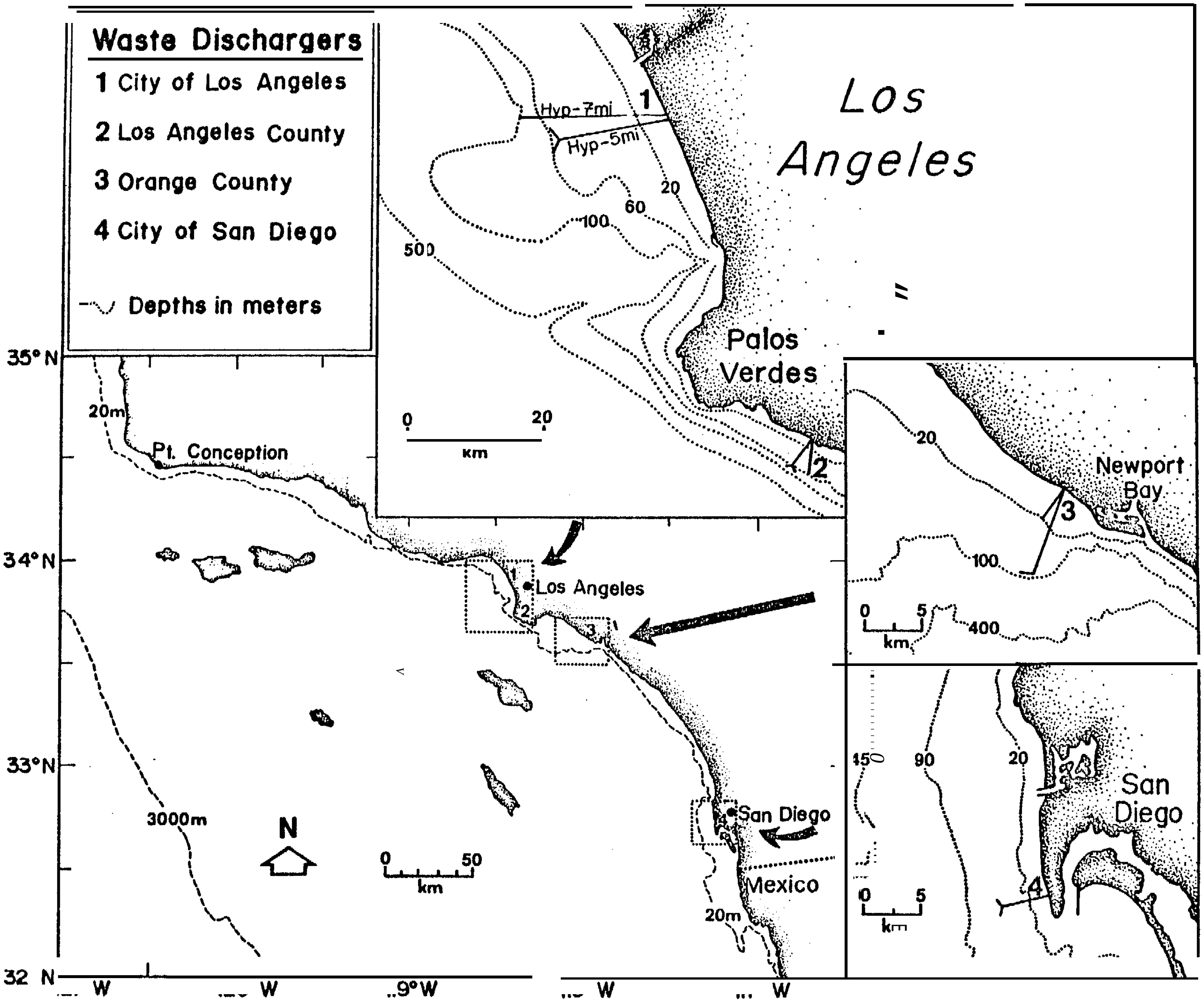
Waste Dischargers
1 City of Los Angeles
2 Los Angeles County
3 Orange County
4 City of San Diego
Depths in meters
Los Angeles
Palos Verdes
Hyp-7mi
Hyp-5mi
1
2
20
60
100
500
0
20
km
Newport Bay
3
20
100
400
0
5
km
San Diego
4
20
90
45
0
5
km
35° N
34° N
33° N
32 N
20m
Pt. Conception
Los Angeles
San Diego
Mexico
20m
3000m
N
0
50
km
W
W
.9°W
W
W

Figure 1

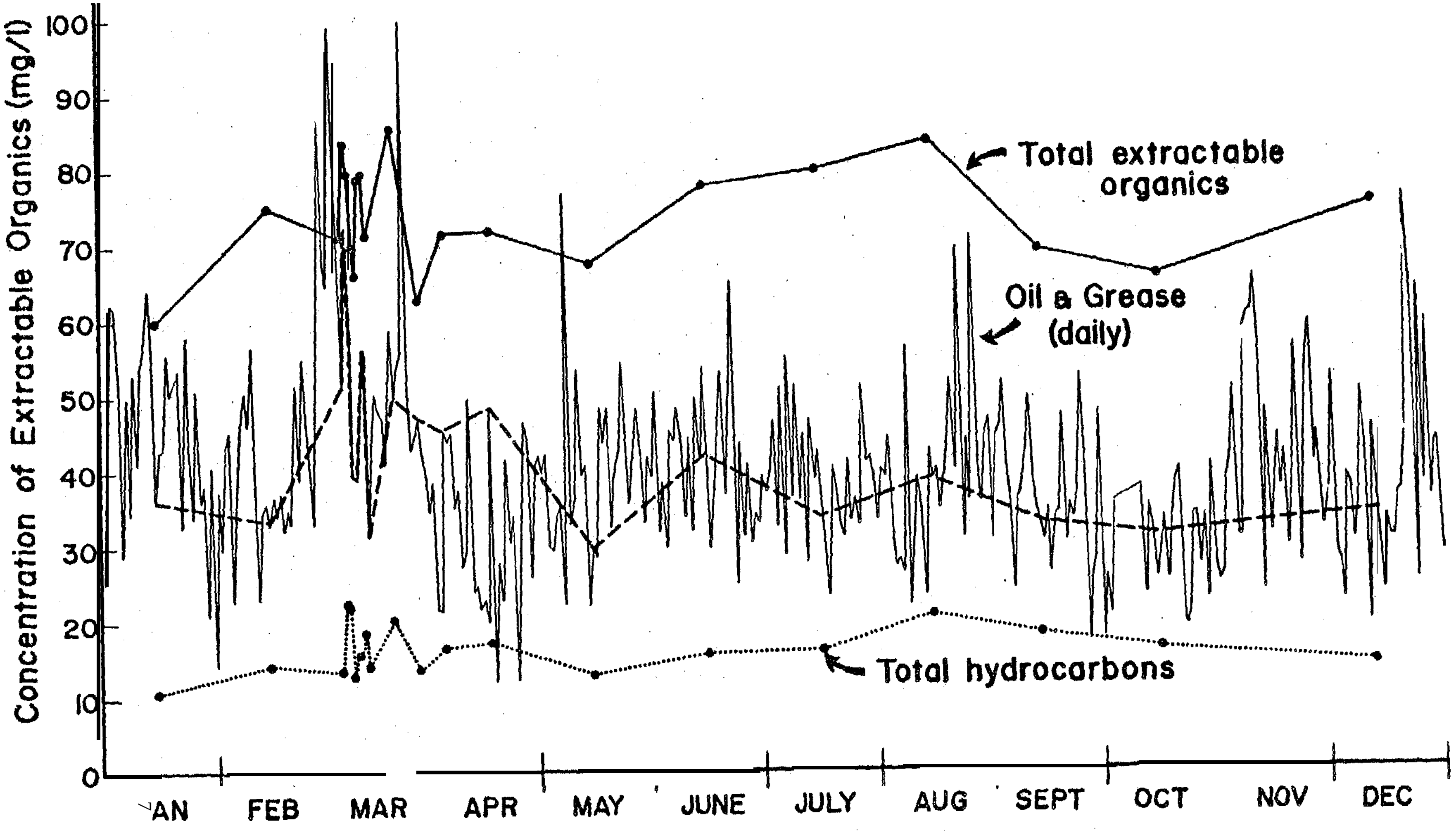
Concentration of Extractable Organics (mg/l)
0
10
20
30
40
50
60
70
80
90
100
JAN
FEB
MAR
APR
MAY
JUNE
JULY
AUG
SEPT
OCT
NOV
DEC
Total extractable organics
Oil & Grease (daily)
Total hydrocarbons

Figure 2

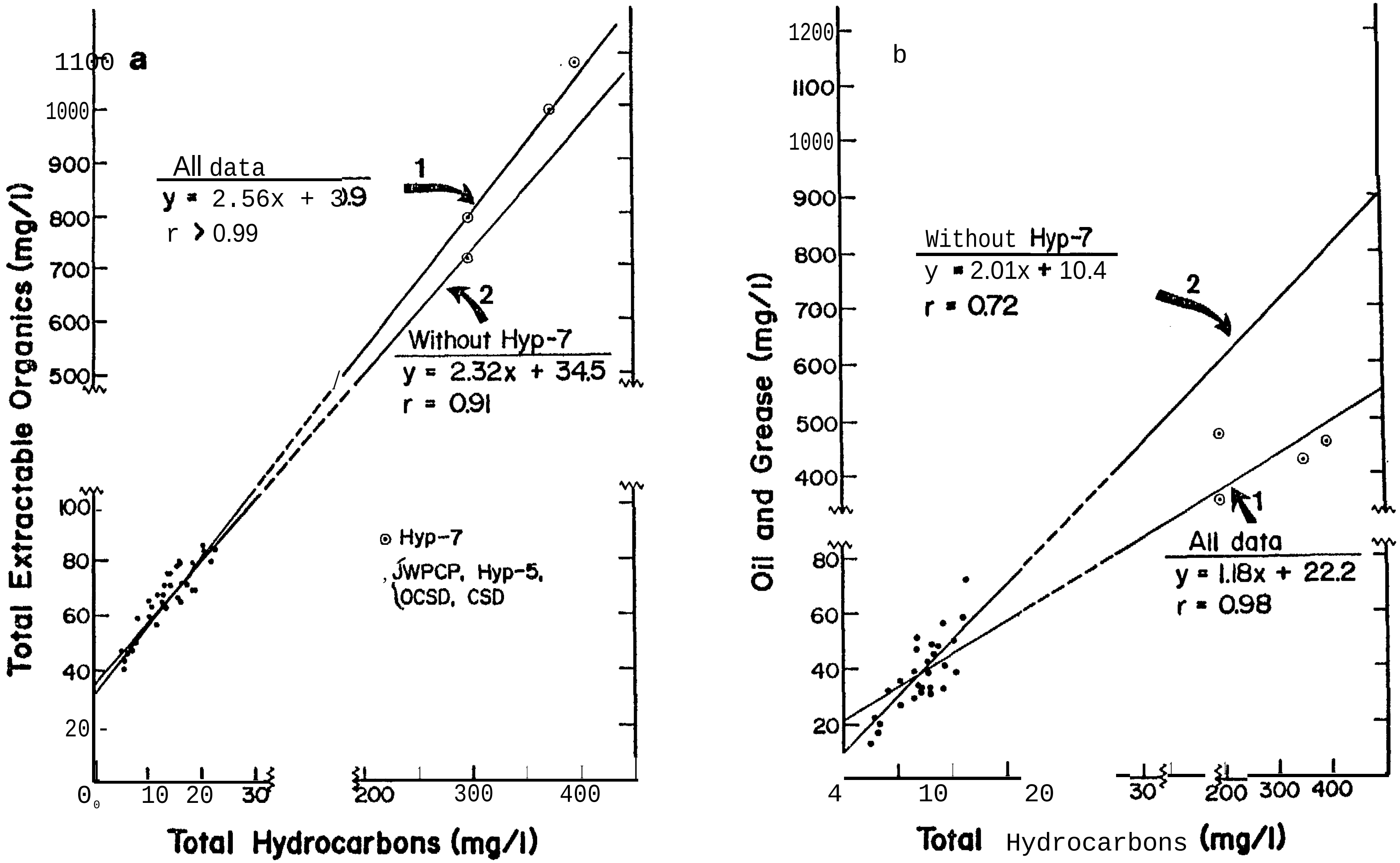
a
1100
1000
900
800
700
600
500
100
80
60
40
20
0
10
20
30
200
300
400
Total Extractable Organics (mg/l)
Total Hydrocarbons (mg/l)
All data
y = 2.56x + 3.9
r > 0.99
1
2
Without Hyp-7
y = 2.32x + 34.5
r = 0.91
⊙ Hyp-7
● WPCP, Hyp-5, OCSD, CSD
b
1200
1100
1000
900
800
700
600
500
400
80
60
40
20
4
10
20
30
200
300
400
Oil and Grease (mg/l)
Total Hydrocarbons (mg/l)
Without Hyp-7
y = 2.01x + 10.4
r = 0.72
2
1
All data
y = 1.18x + 22.2
r = 0.98

Figure 3

MARCHEM 340

HEAVY METALS BEHAVIOR IN COASTAL SEDIMENTS OF SOUTHERN CALIFORNIA: A CRITICAL REVIEW AND SYNTHESIS*

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ABSTRACT

Katz, A. and Kaplan, I. R., 1981. Heavy metals behavior in coastal sediments of southern California: a critical review and synthesis. *Mar. Chem.*, 10: 000–000.

The present paper reviews and discusses the studies on heavy metals behavior in coastal sediments of southern California which have been published since 1970.

The available data allow for the estimation of pollution-free 'base-line' concentrations of some heavy metals in southern California sediments (Ag, 0.4 ppm; Cd, 0.4 ppm; Cr, 25 ppm; Cu, 9 ppm; Ni, 15 ppm; Pb, 10 ppm; and Zn ppm, 44 ppm) which may be used as references for monitoring future metal pollution.

The transport of most, if not all, heavy metals through the near-shore and shelf environments is controlled by their association with particles, a significant fraction of which is sewage-derived and rich in organic carbon. Changes in the relative abundances of the heavy metals are brought about mainly by settling differentiation of their host particles, and much less so by diagenetic solubilization. The bulk of the heavy metals are transported, within fine-grained particles, out from the shelf into deep ocean regions.

Simple linear mixing of polluted outfall materials with clean natural sediments cannot explain the distribution of heavy metals in near-shore and basinal sediments in southern California, unless significant protective effects of organic coatings (near outfalls) and of grain-size distributions are taken into account. Heavy metal pollution from oil seepages are significant for only a very limtied number of metals (Ni, Ba, etc.) and only on a local scale.

The urgent need for standardization of heavy metal leaching techniques is demonstrated and emphasized.

INTRODUCTION

The interest of geochemists in the fate of heavy metals in estuarine and coastal environments has increased in recent years, in the main, for the following reasons.

(1) Because of the recognition that important controls on the cycling of

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suspensions become more concentrated. The reactivity of a particulate-bound metal is obviously very different from that in true solution, depending upon mineralogy, nature of association, and site of occlusion in the particle.

(4) The bulk of the heavy metal mass, whether 'inorganic', 'biogenic', or 'anthropogenic' in origin, passes through coastal waters in the particulate form (Turekian et al., 1973; Benninger et al., 1975; Harris et al., 1975; Troup and Bricker, 1975; Turekian, 1977; Wallace et al., 1977) and some of the complexity in the transport and fluxes of such particulate in the ocean has been discussed by Brun-Cottan (1976), Biscaye and Eittereim (1977), Lal (1977), Lerman et al. (1977), Wallace and Duce (1978a, b), Baker et al. (1979), Aller et al., (1980) and by Hunter (1980). Successful modeling of heavy metals necessitates the distinction between their various sources by differential leaching techniques which depend on the nature of the material analyzed, types of metals investigated and purpose of the investigation (see Rohatgi and Chen, 1975; Rutherford adn Church, 1975; Faisst, 1976; Eganhouse et al., 1978; Bruland and Franks, 1979a; Chow and Earl, 1979a; Galloway, 1979; Kettering, 1979; Word and Meams, 1979; Hunter, 1980). The general concept is that weak acid—low temperature leaching of particulates release H^+-exchangeable and carbonate-bound heavy metals, dilute mineral acids followed by oxidative agents, extract 'biogenic' and/or 'anthropogenic' metal contributions, and complete dissolution of the residue represents the 'inorganic' or 'refractory' silicate fraction. It is unclear whether the basic hypothesis is true, and comparison of data obtained from different studies is frequently meaningless.

(5) The deployment of radionuclides for monitoring fluxes of heavy metals in the coastal environment and lakes (Koide et al., 1972; Chow et al., 1973; Koide et al., 1973; Bruland et al., 1974b; Goldberg and Bruland, 1974; Erlenkeuser et al., 1974; Koide et al., 1975; Benninger, 1976; Patterson et al., 1976; Goldberg et al., 1977; Mc Caffrey, 1977; Bertine et al., 1978; Goldberg et al., 1978; Hedge et al., 1978; Benninger et al., 1979; Bruland et al., 1979a; Ng and Patterson, 1979 ;Turekian and Volchok, 1979; Aller et al., 1980; KrishnaSwami et al., 1980; Shirahata et al., 1980; Spencer, 1980), provides two important advantages: some of them can be determined rather accurately at extremely low levels; and more significantly, they furnish the needed time-scale to estimate rates of metal cycling. Although heavy metals are often measured along with radionuclides, their assumed analogous behavior in the coastal environment should be verified for each element and in each case, due to the viability in environmental conditions, especially oxidation—reduction at the sediment-water interface.

(6) Experimental investigations of the behaviour of trace metals in seawater suffer from reagent, laboratory equipment and laboratory atmosphere contamination, which may contribute more trace metal than is present in the original seawater. A second problem, removal of trace metals onto container walls (e.g., Spencer et al., 1970), appears in certain cases to be a more complex matter than simpl y chemical adsorption. Finally, in simulation systems,

the ratio between the mass of the heavy metal in solution to that of the surface area of the system's boundary is very small in comparison to any natural situations which they are intended to simulate. Thus, it may be advantageous to follow heavy metal behavior in well-defined 'natural laboratories', in which the oceanographic and sedimentological conditions are known, rather than continue heavy metal research along the same lines as in the past.

The southern California coastal zone is inhabited by 11–12 million people and is highly industrialized, resulting in the release of large masses of heavy metals and in the discharge of the bulk of the freshwater, some 3.6 x 10^9 l per day, (Young et al., 1975) which continuously flows into the Southern California Bight, through five sewarage systems (Fig. 1).

The surface runoff volume amounts to an (average) equivalent of approximately 1.5 x 10^9 l clay-l, mostly contributed by a few fall and winter storms. The annual municipal wastewater input into the Southern California Bight in the last decade has probably varied little. Calculations based on wastewater flow data" taken from Schafer (1978) show a mean annual, daily-averaged flow of 3.609 *0.16 (1σ) x 10^9l day^{-1} for the period 1971–1977, with a fairly constant value for total suspended solids concentration, excpet for a significant (~18%) drop in 1977.

Thus, the bulk of the heavy metals is introduced into the coastal waters via a few point sources along the coast. Hence, the behavior of heavy metals may be learned from their dispersion modes in the sediments between their emission points and., the deeper ocean. The necessary oceanographic, geological and sedimentological background for such studies has been provided by several authors. A review of the earlier and historic developments is given by Emery (1960).

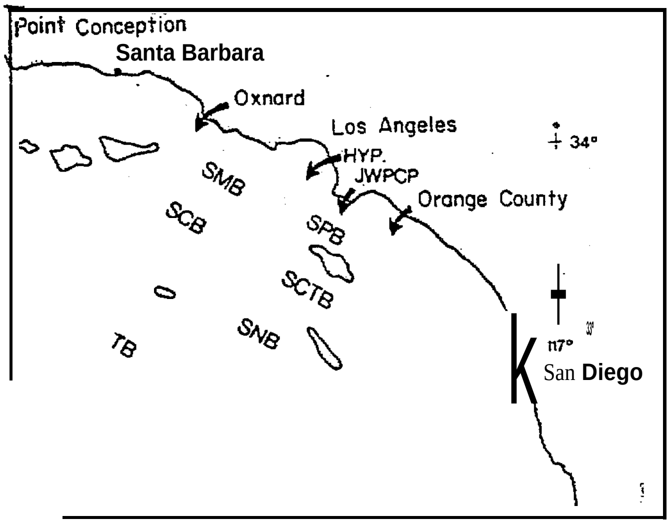


Fig. 1. Location map of investigated area, Southern California.

The present paper presents an attempt to review and evaluate the last decade's voluminous bibliography on heavy metals in the southern California coastal waters. An attempt has also been made to emphasize important accords or discrepanices between available sets of data and to interpret them in terms of heavy metal transport and removal out of the water column.

PREVIOUS STUDIES ON HEAVY METALS IN THE SOUTHERN CALIFORNIA COASTAL ZONE

Table 1 reviews heavy metal research papers and reports on southern California coastal sediments and waters published mostly since 1970. Sedimentation rate and dating studies (Bruland, 1974; Goldberg and Bruland, 1974; Koide et al., 1972, 1973, 1975, 1976), sediment-type characterization and mixing studies (Peters et al., 1978; Sweeney and Kaplan, 1980) or sediment dispersion studies (Hendricks, 1975, 1978) important for heavy metal interpretation have also been included, as well as a few studies relevant to atmospheric fluxes (Shirahata et al., 1980) or to metal concentrations in the Pacific (Bruland et al., 1979 b). The first column in the table lists the various papers in alphabetic order; the second and third columns detail the chemical elements dealt with, and the sites which were sampled. The next nine columns define materials and subjects studied in each case. The materials include dissolved elements ('dissolved') or metals attached to suspended particulates ('particulate'). Heavy metal data on sediment surface and core samples, plants and animals, various atmospheric materials (aerosols, dust, brushfire smoke, etc.) and wastewater are indicated by crosses under the headings 'sediments, 'organisms', 'atmospheric' and 'sewage', respectively.

The 'sewage' column includes all man-made materials discharged into the southern California coastal waters. Laboratory experiments of heavy metal fractionation, adsorption-resorption, sedimentation, etc., are indicated in the 'experimental' column, whereas modeling of heavy metal behavior is listed under 'theoretical'. Papers containing calculations of heavy metal flux are marked under 'flux'. Data other than heavy metal information (organics, nutrients, isotopes, major ions, etc.) are listed under 'other' and sediment dating studies are indicated under 'dating'.

Some 55% of all the studies cited are based on sediment analysis, about 40% relate to particulate composition and about 37$% to sludge- and sewage-chemistry. Few studies (24%) have been directed at the dissolved heavy metals, and over 60% of these are dedicated to experimental investigations, mostly of sewage and sludge behavior. The same is true for studies of atmospheric heavy metal sources. This trend of research reflects, in part, the ease of sediment analysis relative to seawater, and the fact that much of the research was conducted by the Southern California Coastal Water Research Project (SCCWRP), where the emphasis was placed on anthropogenic materials and their effects on sediments and marine life rather than on the behavior of trace metals in seawater itself. The relative scientific interest can be rated as follows (numbers in parentheses designate percent of papers, out of

TABLE I

Literature review of heavy metal studies performed in southern California between 1970—1980 in marine coastal environments

Source	Elements	Sites	Dissolved	Particulate	Sediments	Organisms	Atmospheric	Sewage	Experimental	Theoretical	Flux	Other	Dating
Anderhalt and Reed (1979)	Sedimentological study	PC, SB, SM, SP, OS, SD		x	X							Carbonate, Organic carbon, Mineralogy	
Bertine and Goldberg, (1977)	Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	SCLB; SCTB			X						x		^{210}Pb
Bertine et al. (1978)	Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	BR		X	x		X				x		^{137}Cs ^{210}Pb $^{238,239',240}$Pu
Brooks et al. (1968)	Ca, Cd, Co, Cu, Fe, K, Mg, Na, Ni, P, Sr, Zn	SBB, SCB, SCTB, TB	X							X			
Bruland (1974)	Radionuclides only	SMB, SPB, SBB, SCLB, SOB, etc.			x					x			^{210}Pb, ^{226}Ra ^{228}Th/^{232}Th
Bruland et al. (1974a)	Ag, Al, C, Ca, Cd,	SBB, SOB, SMB, SPB		x	x		x	x			x		^{210}Pb
Bruland and Franks (1979a)	Cd, Cr, Cu, Fe, Ni, Pb, Zn	Inner and Outer Southern California Continental shelf		x	x				x		x	U, Th series radioelides	
Bruland and Franks (1979b)	Cd, Cr, Cu, Fe, Ni, Pb, Zn	Non-specific	X	X	x				X			Techniques	
Bruland and Franks (1979c)	Cd, Cr, Cu, Fe, Ni, Pb, Zn	Non-specific	x	x	x				x			Techniques	
Bruland et al. (1979a)	None	SBB, SPB, SMB, SNB			X					x			^{228}Th/^{232}Th, ^{210}Pb
Bruland et al. (1979b)	Cd, Cu, Ni, Zn	37°05'N, 123°22'W	X						x				
Bruland et al (1978a)	Cd	Ne Pacific and Gulf of California	x	x							,x	PO_4^{3-} NO_3^-	
Bruland et al, (1974b)	None	Gulf of California	X	X							x	^{210}Pb, ^{226}Ra	
Chen and Hendricks	Cd, Cr, Cu, Fe, Hg,	HYP		x				x	x				
Chen et al. (1974)	Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	HYP		x				x	x				

TABLE [illegible] continued)

Chow et al. (973)	Pb	SMB, SBB, SPB, SOB			x		x				x	Pb and Th Isotopes	
Chow and Earl (1979a)	Cd, Cr, Cu, Fe, Ni, Pb, Zn	SMB, SPB, SBB, SCTB, SD trough, SMG, SRO, SCB		x	x						x		
Chow and Earl (1979b)	Cd, Cr, Cu, Fe, Ni, Pb, Zn	as above		x	x				x				
Crisp et al. (1979)	H, C, N (+organics)	SNB, SPB		x	x							C, N, S, Isotopes; Organics	
Eganhouse (1976)	Hg	PVP		x	x			x			x		
Eganhouse and Young (1976)	Hg	PVP Coast				x							
Eganhouse and Young (1976a)	Hg Hg	SB to SD Coast and islands				x							
Eganhouse and Young (1978a)	Hg	PVP Coast and SCT island				x							
Eganhouse and Young (1978b)	Hg	PT, SAL and PVP				x							
Eganhouse et al. (1978	Hg, C	PVP		x	x			%	x	x			
Faisst (1976)	Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	HYP and PVP outfalls	x	x				x	x	x			
Flegal and Martin (1977)	Ag, Cd, Cu, Fe, Mn, Sr, Ti, Zn	California and Mexico coastlines				x							
Friedlander (1973)	Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn	Pasadena					x		x	x		Al, Ba, Br, C, Ca, Cl, K, Mg, Na, S, Si	
Galloway (1972)	Ag, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Zn	HYP, PVP, OC outfalls			x			x		x	x		
Galloway (1979)	Ag, Cd, Co, Cr,	HYP, PVP, OC outfalls			x			x		x	x		
Goldberg and Bruland (1974)		Various SC basins			x					x		Review	Sediment dating
Grigg (1978)	Ag, Cd, Cr, Cu, Ni, Pb, Zn	PVP, LJ			x			x				DDT, PCB	
Hansen et al. (1979)	Al, Ba, Cr, Fe, V	SC inner and outer basins and coast		x	x				x				

TABLE I *(continued)*

Source	Elements	Sites	Dissolved	Particulate	Sediments	Organisms	Atmospheric	Sewage	Experimental	Theoretical	Flux	Other	Dating
Hendricks (1974)	(Model)	PVP		x	x			x		x		Aerobic/unaerobic mobilization model	
Hendricks (1975)	(Model)	PVP		x	x			x		x		Particulate dispersion model	
Hendricks (1978)	(Model)	P V P		x	x			x		x		Sediment dispersion model	
Hendricks and Young	Cd, Cr, Cu, Pb, Zn	PVP		x	x			x	x	x		Modelling	
Herring and Abati (1978)	Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	HYP, PVP, OC and SD outfalls		x	x			x	x	x		Dispersion model	
Hershelman et al, (1977)	Ag, Cd, Cr,Cu, Hg, Ni, Pb, Zn	PVP			x			x					
Hirao and Patterson (1974)	Pb, Ba, Sr, Ca	TC, LA, SF				x	x					Pb Isotopes	
Hedge et al. (1978)	Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	LJ, BC	x	x			x				x	Pb and Pu Isotopes	
Huntzicker et al. (1975)	Pb	La basin and coastal waters		x			x				x	CO	
Jan et al. (1977)	Ag, Cd, Cr, Cu, Hg, Ni, Pb, Zn	PVP, OC outfalls, SCT, SMBY				x							
Jan and Young (1976)	Cr	HYP, PVP, OC, SD, OX, outfalls and sea-water	x	x				x	x	x		Cr oxid. states	
Jan and Young (1978)	Ag, Cd, Cr, CU, Fe, Ni, Pb, Zn	Non-specific	x									Analytical procedure	
Johnson (1974)	Hg	PVP		x	x			x					
Kalil (1976)	u	Near and offshore SC basins			x						x	C, S, P, N, Ca, Mg, alk.	^{14}C
Kalil (1978)	Cr, Cu, Mn, Ni, U	SCTB, TB			x							Organics, C-Isotopes	

TABLE I *(continued)*

Kettering (1979)	Cd, Cr, Cu, Ni, Pb,	PVP			x			x				H_2O, C	
Kline and Goldberg (1970)	Hg	LJ, PVP, HYP			x	x							
Knezevic and Chen (1977)	Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pi, V, Zn	La harbor, PVP			x			x	x			Humic and fulvic acids	
Koide et al. (1973)	Radionuclides only	SBB, BC, LTA, LTI, TL, LM			x					x			^{228}Th/^{232}Th, ^{210}Pb
Koide et al. (1976)	Radionuclides only	SCLB, BC, SBB, SPB, SMB, TL, LM			x	x				x			^{226}Ra, $^{238+239}$Pu ^{210}Pb
Koide et al. (1975)	Radionuclides only	SBB, SOB			x								$^{239+240}$Pu
Koide et al. (1972)	Radionuclides only	SBB			x								^{210}Pb
Krishnaswami et al. (1976)	Radionuclides only	Pacific Ocean		x			x					^{14}C, Pu-, Th-^{210}Pb and ^{226}Ra Radionuclides	
Lazrus et al. (1970)	Cu, Fe, Mn, Ni, Pb, Zn	AVN(+ Nationwide)	x				x				x		
Liljestrand and Morgan (1978)	Mn, Pb	Pasadena					x					Major ions, PH	
Lu and Chen (1977)	Ag, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb,		x		x				x	x		Organics, PO_4^{3-} N, $S^=$	
Martin and Knauer (1979)	Cd, Cr, Cu, Fe, Ni, Pb, Zn	NTB, COP, SMG, PC				x							
McDermott (1974)	Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn	PVP, HYP, OC, SD and OX outfalls		x				x				Organics, nutrients volatiles, suspensoids	
McDermott and Alexander (1976)	Ag, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Si, V, Zn	SB channel, SM bay			x	x						Hydrocarbons	
McDermott and Young (1974)	Ag, Cd, Cr, Cu, Nil	PVP and SB channel				x							
Mearns (1974)	Cr					x			x				
Mitchell (1974a)	Ag, As, Cd, Cr, Cu, Ni, Pb, Zn	HYP						x				Cyanide, Phenols	
Mitchell (1974b)	Zn, Cr	PVP			x				x		x		

TABLE I *(continued)*

Source	Elements	Sites	Dissolved	Particulate	Sediments	Organisms		Sewage	Experimental	Theoretical	Flux	Other	Dating
Mitchell and McDermott (1975)	Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn	PVP, HYP, OC, OX outfalls						x			x	Organics, volatiles, nutrients, suspensoids	
Morel et al, (1975)	Ag, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	PVP outfall	x	x	x			x		x	x		
Murray and Ku (1977)	Pb	TB, SNB, PVP shelf			x						x		^{210}Pb
Myers (1974)	c	PVP outfall		x	x			x	x	x	x	Carbon system (including Isotopic)	
Ng and Patterson (1979)	Ba, Pb	SBB, SMB, SPB, SNB			x					x	x	Pb Isotopes	
Nozaki and Tsunogai (1973)	None	North Pacific	x				x				x	^{210}Pb	
Oshida (1976)	Cr		x			x			x				
Oshida (1977)	Cr		x			x			x				
Oshida and Wright (19%)	Cr		x			x			x				
Patterson et al. (1976)	Pb	LJ, PVP outfall, SCT	x	x			x	x	x		x	Pb Isotopes	
Peters et al. (1978)	C, N	SCTB, SBB, TB, SP shelf			x							C, N Isotopes	
Rohatgi and Chen (1975)	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	HYP, La river	x	x				x	x				
Schafer (1976)	Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn	PVP, HYP, OC, SD, OX outfalls		x				x			x	Organics, N, Suspensoids	
Schafer (1977)	Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn	PCP, HYP, OC, SD, OX outfalls		x				x			x	Organics, N, Suspensoids	
Schafer (1978)	as above	as above		x				x			x	as above	
Schafer and Bascom (1976)	Ag, Cd, Cr, Cu, Hg, Ni, Pb	HYP			x			x				Volatiles	

TABLE I *(continued)*

Sherwood (1976)	Cd, Cr, Cu, Ni, Pb, Zn	PVP			x	x			x			DDT, PCB	
Sherwood and Wright (1976)	Cr	PVP				x			x				
Sherwood and McCain (1976)	Ag, Cd, Cr, Cu, Pb, Zn	PVP				x			x			Ca, K, Mg, Na	
Shokes and Mankiewitz (1979)	Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	SBB, SMB, SPB, SNB		x	x					x	x	Organics, sedim. parameters	
Shirahata et al. (1980	Pb, Ba, Sr, Ca	Thompson canyon, California			x		x			x	x	Pb, Po, Pu and Cs radionuclides	^{210}Pb
Shokes et al. (1979)	Al, Bs., Cd, Cr, Cu, Fe, Ma, Ni, Pb, V, Zn	Non-specific			x				x			Methodology	
Sholkovitz (1973)	None	SBB	x							x		Majors	
Sholkovitz and Gieskes (1971)	None	SBB	x							x		Majors (flushing model)	
Sholkovitz and Soutar (1975)	None	SBB (bottom)	x									Majors	
Soutar et al. (1977)	No new data	SBB, SPB, SOB		x	x					x	x		
Sweeney (1978) --	No metals analysed	PVP outfall		x	x			x				C, N (elemental and Isotopic)	
Sweeney et al. (1980)	u	PVP outfall			x			x		x		N, C, S Isotopes	
Sweeney and Kaplan (1980)	No metals analysed	PVP outfall			x			x		x		as above	
Sweeney et al. (1978)	as above	PVP, SBB			x			x		x	x	N Isotopes	
Wakeman (1974)	Cr, Cu, Hg, Ni, Pb, Zn	SF Bay	x	x	x								
Word and Mearns (1979)	Ag, Cd, Cr, Cu, Ni, Pb, Zn	71 stations between PC and SD			x							Biological, organic and biochemical data	
Young (1974)	As, Sb, Se	PVP outfall			x			x					
Young (1978)	Ag, As, Be, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Tl, Zn	HYP, SD, OC, PVP treatment plants	(x)	x				x				Nutrients, trace organics, suspensoids	
Young and Afexander (1977)	Ag, Cd, Cr, Cu, Ni, Pb, Sn, Zn	SP, SD, NP harbors and control stations				x						PCB	

TABLE I *(continued)*

Source	Elements	Sites		Particulate	Sediments	Organisms	Atmospheric	Sewage	Experimental	Theoretical	Flux	Other	Dating
Young et al. (1979)	Ag, Cd, Cr, Cu, Ni, Pb, Sn, Zn	SD and NP harbors		....		x						PCB	
Young and Jan (1975a)	Cr	HYP	x					x	x			Oxidation states of CR	
Young and Jan (1975b)	Cd, Cr, Cu, Ni	PVP outfall	x	x				x					
Young and Jan (1976)	Ag, Cd, Cr, Cu, Ni, Pb, Zn	PVP, SCT, SB island				x							
Young and Jan (1977)	Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	8 stations between CP and SD, and 3 on SCT		(x)			x				x	Brushfire input	
Young et al. (1977)	Cd, Cr, Cu, Ni, Pb, Zn	6 power stations between VEN and OC	x	x	"		x	·			x	Cooling water discharges	
Young et al. (1973)	Hg	SBB			x						x		Varve count
Young and McDermott (1975)	Cr, Cu, Ni, Zn	SD Harbour				x						PCB	
Young et al. (1975)	Ag, As, Cd, Cu, Sb, Se, Zn	SC (general)	x	x	x		x	x			x	DDT, PCB	
Young and Mearns (1978)	Ag, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	PVP, NP, SS				x						Cs, K, DDT, PCB	

Locations; AVN – Avalon, California; BC — Baja, California; BR –"Barrett Reservoir (California); COP - Coal Oil Point; CP — Carpenteria; HYP — Hyperion Outfall (SMB); LA – Los Angeles; LJ – Ja Jolla; LM – Lake Mendota, (Wisconsin); LTA – Lake Tahoe; LTI – Lake Titicaca (Peru/Bolivia); NTB – North Tanner Bank; NP – Newport; OC - Orange County; OS — Oceanside; OX – Oxnard; PC – Point Conception; PVP - Pales Verdes Peninsula; SB Santa Barbara; SBB – Santa Barbara Basin; SC — Southern California; SCB – Santa Cruz Basin; SCLB - San Clemente Basin; SCT – Santa Catalina Island; SCTB – Santa Catalina Basin; SD – San Diego; SF – San Francisco; SMB – Santa Monica Basin; SMBY – Santa Monica Bay; SMG — San Miguel Island; SNB – San Nicolas Basin; $OB – Soledad Basin; SP – San Pedro; SPB – San Pedro Basin; SRO – Santa Rosa Island; SS — Salton Sea; TB — Tanner Basin; TC - Thompson Canyon (California); TL – Trout Lake (Wisconsin); VEN – Ventura, a total of 11^{9}0, cited): Cr (53); Cu (51); Pb (50); Zn (48); Ni (45); Cd (45); Ag, Fe (30); CO, V (9), As (7); Se (5), Ba (5); Sb, U (3); Mo, Sn, Ti (2); Tl (1). This reflects the 'classical' recognition of Ag, Cu, Cr, Ni and Zn as important industrial pollution tracers, and the high toxicity of heavy metals such as Hg, Pb and Cd. Low ratings for some highly toxic metals (e.g., As, Sb, Tl) very probably result from technical problems.

Most of the studies center on the major outfalls of southern California, mainly the Joint Water Pollution Control Plant (JWPCP) off Whites Point, the Hyperion plant in the Santa Monica Bay and the Orange County outfalls off the Santa Ana River mouth.

BACKGROUND LEVELS OF HEAVY METALS IN THE SEDIMENTS

Natural ('background') concentrations of heavy metals in southern California coastal sediments may be estimated in two ways:

(1) by analysis of surface sediments in non-polluted areas, wherever they exist;

(2) by analysis of core samples antedating modern pollution.

The surface sediment data are presented in the studies of Young et al., (1975), Bruland and Franks (1979 a,b,c), Chow and Earl (1979a, b), Hansen et al. (1979), Shokes and Mankiewicz (1979), and Word and Mearns (1979). Core data can be found in Galloway (1972), Chow et al. (1973), Bruland et al. (1974a), Bertine and Goldberg (1977), Kalil Jr. (1978), Galloway (1979), Kettering (1979), Ng and Patterson (1979) and Shokes and Mankiewicz (1979).

Lateral heavy metal distributions

Word and Mearns (1979) analyzed Ag, Cd, Cr, Cu, Ni, Pb and Zn in surface sediments sampled along the southern California 60 m water-depth countour, thereby minimizing depthdependent concentration variations (reported by Chow and Earl, 1979a; Table II). Their data show heavy metal spikes superimposed over the natural background near the major outfalls (JWPCP and Hyperion). Table II presents calculated average background concentrations for the north-western section (stations 4,5 and 11–17) and the south-eastern region (stations 50-64) and calculated concentration ratios between the most polluted sample and the 'background'. Five out of the seven metals studied (Ag, Cd, Cr, Cu and Zn) display statistically indistinguishable background concentrations in the north and in the south.

The selection here of 'background' stations from Word and Mearns (1979) leans heavily on their definitions of 'man-affected' (i.e., polluted) areas. Even very low heavy metal concentrations are not necessarily 'natural', but may have been achieved by dilution of pollutants with low heavy metal content 'natural' material. Thus, little can be gleaned from absolute heavy metal concentrations in such environments. Instead, identification of the source (anthropogenic or 'natural') of heavy metals in 'clean' environments can be

TABLE H

Average and maximum concentrations of heavy metals in non-polluted and polluted southern California surface sediments (calculated from Word Mearns', data 1979). All values are in dry weight ppm units (1s)

Metal	Background north-west	Background south-east	Background average	Pollution peak	Peak/ background
Ag	0.51 ± 0.56	0.31 ±0.32	0.41	18.1	44.2
Cd	0.55 ± 0.35	0.3 ±0.19	0.43	60.8	143.0
Cr	29.7 ± 10.1	21.3 *4.3	25.5	1317.0	51.6
Cu	6.94 ±3.2	11.1 ±6.3	9.02	782.0	86.7
Ni	23.228.1'	7.63 ±3.1	15.4	107.0	6.9
Pb	6.02 ±3.0	15.0 ±2.0	10.5	537.0	51.1
Zn	44.6 ±9.1	44.3 ±14.4*	44.4	2096.0	47.2

* The Zn value at station 63 (172 ppm) was excluded from the calculation.

attempted by comparing the concentration ratio between two metals in a distinctly polluted area to the ratio between the same metals in a supposedly 'clean' area. Similar ratios would support a dilution origin for the respective metals in the 'clean' samples.

The slope of a dilution line can be calculated by linear regression computation on the concentrations of the selected heavy metal pairs measured in surface sediments from the vicinity of a sewer outfall. In doing so, the following assumptions should hold tree:

(1) no significant metal fractionation takes place across the area sampled;
(2) metal deposition is synchronous in all stations sampled;
(3) the metal ratios are reasonably constant, at least on the (pollutant) emission-removal time-scale.

Assumption (1) can be confirmed by a high statistical correlation coefficient on the heavy metal pair regression line. The second and the third assumptions are reasonable in light of dispersion models (Hendricks 1975; 1978) and experiments (Hernng and Abati, 1978), and in view of available emission-rate data (Schafer, 1976, 1977, 1978). Additional support for assumption (3) is provided by the similarity, in heavy metal data, between surface sediment and water column intercepted particles reported by Bruland and Franks {1979a).

Table III details the linear regression parameters (b = line intercept on y at $X = 0$, a = line slope and r = correlation coefficient) for metal/Zn concentration ratios in surface sediments in the vicinity of the Whites Point outfall (Word and Mearns, 1979, stations 30-35). Zinc was selected as the 'normalizer' because of its relatively high concentration in the samples and its low analytical error. The average background metal/Zn ratios, as calculated from Table H, are given in the next column and the JWPCP mass emission rate ratios for 1977 (calculated from data given by Schafer, 1978) are presented for comparison. Graphical representations of the same data are given in Fig. 2.

TABLE III

The ratio between the concentrations of Ag, Cd, Cr, Cu, Ni and Pb and the concentrations of Zn in highly polluted and 'clean' sediments (calculated from Word and Mearns, data 1979)

Metal	*r*	*b*	*a*	Background ratio	JWPCP 1977 emission ratio[c]	Total emission ratios, SC[c]
Ag[a]	0.9628	3.5	0.0072	0.0092	0.0095	0.019
Cd	0.9925	−0.7	0.029	0.0097	0.030	0.038
Cr[b]	(0.9233)	(300)	(0.55)	0.57	0.45	0.48
Cu	0.9901	69	0.35	0.20	0.30	0.40
Ni	0.9755	19	0.041	0.35	0.29	0.23
Pb	0.9938	19	0.25	0.24	0.23	0,16
Zn	1	0	1	1	1	1

[a] Excluding station 32, for which the Ag value is probably erroneously low.

[b] The relation between Cr and Zn is obviously non-linear. (see Fig. 2c).

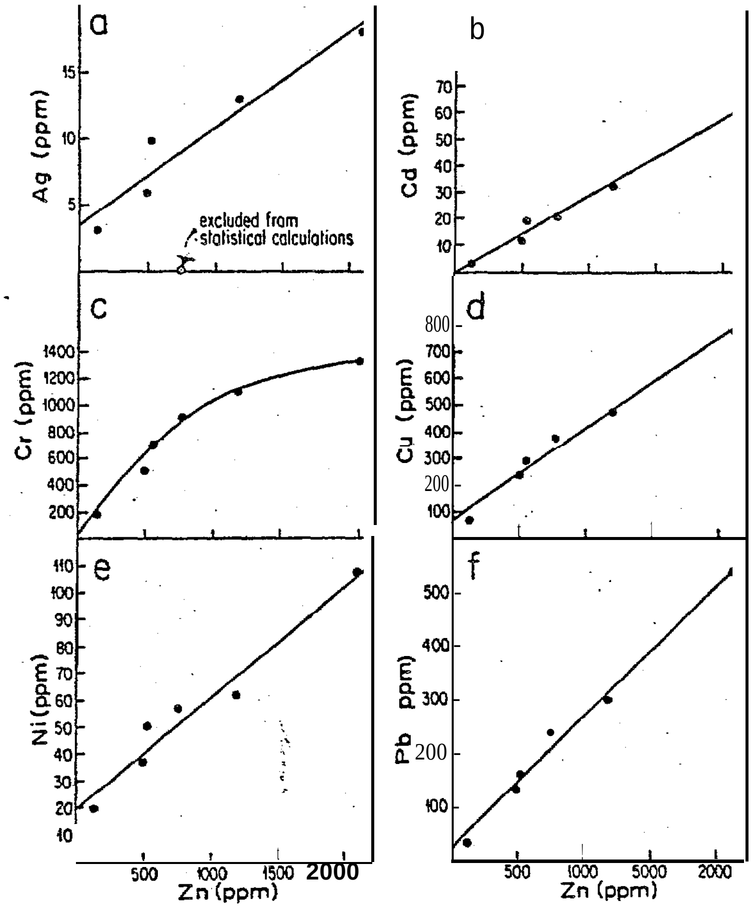
[c] Calculated from Schafer's (1978) data.

All the metals, with the exception of chromium, display very good linear relationships with zinc. The chromium curve is bent towards the Zn-axis, indicating a fractionation between the two metals. The authors' calculation, however, cannot distinguish between sedimentologically-induced (settling fractionation between particles with different Cr/Zn ratios) and chemically-induced (preferential solubilization of chromium or zinc from the particles) differentiation between Cr and Zn.

Ag, Cu and Ni show positive, statistically significant intercepts of the regression lines. Hence, the concentrations of these elements (and of Zn) in the background stations cannot be explained by simple dilution of municipal waste with natural material with similar heavy metal ratios.

The Cd/Zn and the Pb/Zn ratios can be linearly extrapolated, within data scatter, through the origin (Figs. 2b and 2f), and may represent, therefore, a simple dilution relationship between natural and anthropogenic components with similar Cd/Zn and Pb/Zn ratios. The difference, by a factor of 3, between the slope of the Cd/Zn regression line and the average background Cd/Zn ratio is not disturbing regarding the very large relative scatter (± 63%) on the background Cd values (Table II). The line slope and average background Pb/Zn ratio are practically identical.

The metal/Zn line slopes (*a* values in Table III) are mostly in good accord with mass emission rate ratios calculated from Schafer's (1978) data for JWPCP for 1977, the year in which Word and Mearns (1979) collected their samples. The emission Ni/Zn ratio is higher, by a factor of about 7, than the corresponding line slope. On the other hand, the background ratio is higher than the 1977 emission ratio. A preferential dispersion (or solubilization) of Ni (relative to Zn) from the outfall may explain both observations.



Pig. 2.Relationship between the concentrations of **Ag,** Cd, Cr, **Cu, Ni, Pb** and the concerttration of **Zn** in **highly** polluted surface sediments of **Palos** Verdes (drawn and calculated from Word and Mearns data, 1979).

The Cd/Zn emission ratio for JWPCP and the calculated a value are practically identical, supporting our previous interpretation of the background value. Finally, a comparison **of** the total southern California emission rate ratios for 1977 (last column in Table III) with the JWPCP and with the a values demonstrates the strong local signature imprinted by the JWPCP outfall on its vicinity. Mass emission {1977) metal/Zn ratios for all the five southern California outfall systems, calculated from Schafer's (1978) data, are presented in Table IV.

The previously-discussed data of Word and Mearns (1979) can be compared with a few of Chow and Earl (1979a, b) data which were obtained from sufficiently shallow coastal stations (Table V). Background concentrations of leachable and total heavy metals from Table V and from Table H are presented for comparison in Table VI.

TABLE IV

Metal/Zn 1977 emission rate ratios for the five largest southern California outfalls (calculated from Schafer's (1978) data).

Heavy metal	JWPCP	Hyperion 5-mile	Hyperion 7-mile	Orange County	Point Loma	Oxnard	$\bar{x}$ ± 1S.D.
Ag	0.0095	0.094	0.067	0.024	0.10	0.082	0.063 ±0.038
Cd	0.030	0.063	0.046	0.11	0.10	0.082	0.072 ±0.031
Cr	0.45	0.41	0.46	0.41	0.32	0.23	0.38 ±0.088
Cu	0.30	0.62	0.55	0.81	0.74	1.1	0.7020.28
Ni	0.29	0.56	0.15	0.32	0.47	1.9	0.62 ±0.65
Pb	0.22	0.094	0.077	0.23	0.47	0.45	0.26 ±0.17

Table VI shows that Word and Meams leachable metal data are higher, by a factor 'of between 2 and 7, than the corresponding leachable determined by Chow and Earl and are, in fact, closer to Chow and Earl's total concentrations. No systematic differences are discernible between the three sets of data. Consequently, the higher background values obtained by Word and Mearns are probably related to the sample dissolution techniques rather than to contamination. Chow and Earl's extraction of leachable metals involved sample shaking in 1 N $HN0_3$ at room temperature whereas Word and Mearns twice leached their samples in 5.5 N HNO_3 followed by near evaporation and then boiled the residual HNO_3 -treated sample with concentrated HCL This procedure, which is very oxidative (free chlodine must evolve during the second state), is clearly more effective in metal leaching than is that of Chow nd Earl, and satisfactorily accounts for the differences in the results obtained.

Historical (buried) heavy metal background levels

Table VII summarizes the concentrations of heavy metals in the oldest (lowermost) samples recovered from shallow and basinal cores along the southern California cost. The data for San Pedro, Santa Monica, Santa Barbara and Soledad Basins are from Chow et al. (1973), Pb only, Bruland et al. (1974a) and/or from Shokes and Mankiewicz (19'79). Bruland et al's data were estimated from their Fig. 3. The San Clemente data has been calculated from Bertine and Goldberg (1977, Table I). The data on the outfall cores is from Galloway (1979) and/or from Kettering (1979). Despite the different dissolution techniques applied, and the very different environments sampled, the data scatter in Table VII is mostly within 30—50?% of the corresponding average values, which is similar to surface sediment data (Tables II and V).

Except for the JWPCP Pb analyses, which show a very wide range (6.2—300 ppm) and have, therefore, been excluded from the average calculation, the deepest core samples near outfalls are not significantly higher in heavy

TABLE V

Background concentrations of leachable (L) and total (T) heavy metals (in ppm) in shallow-water southern California sediments, selected from Chow and Earl (1979a)

General area*	Station	Depth (m)	Cd		Cr		Cu		Fe		Ni		Pb		Zn	
			L	T	L	T	L	T	L	T	L	T	L	T	L	T
PC (winter)	831	102	0.34	0.38	6.1	42.3	1.1	8.4	3358	14368	5.6	13.0	3.5	13.0	12.0	29.1
SB (winter)	800.	25	0.40		1.7		1.6		1172		1.4		2.9		5.6	
SB (summer)	800	26	0,35	0.40	2.7	26,8	2.2	5.6	1878	8442	4.0	14.0	3.3	17.3	7.0	25.1
SB (winter)	801	70	0.19	“	5.0		1.9		3769		2.6		5.8		16.5	
SB (summer)	801	68	0.29	0.98	5.5	47.2	1.7	9.1	3515	18928	1.7	19.3	5.5	17.8	15.3	44.3
SB Bay (winter)	873	78	0.27	0,40	9.0	66.7	5.4	19.8	8000	35776	6.6	29.3	9.5	20.3	32.6	91.9
PVP (winter)	820	89	0.10	0.18	6,7	51.4	4.8	15.3	2090	30322	2.0	16.7	6,7	18.0	12.3	72.8
PVP (winter)	819	34	0.12		7.1		3.5		1423		1.1		6.7		11.5	
PVP (summer)	819	33	0.21	0.36	8.0	52.5	4.1	10.8	1692	26168	0.8	14.7	7.5	20.4	13.7	62,6
PVP (winter	824	31	0.13		5.8		5.4		1197		0.9		9.0		10.1	
PVP (summer)	824	32	0.16	0.36	5.9	37.0	5.6	12.4	1306	19231	0.9	10.8	7.4	23.1	10.6	46.4
oceanside (winter)	851	139	0.13	0.48	2.9	70.6	4.0	27.0	2803	40740	2.4	23.7	6.5	16.6	9.1	104.5
SD (winter)	861	33	0,009	0,062	0.7	11.5	0.2	2.6	846	10901	0.2	2.0	1.4	8.7	1.6	14.0
SD (winter)	862	58	0.037	0.37	1.8	28.9	2.2	14.1	1124	19308	0.8	8.0	3.4	13.9	6.7	46.5
Average			0.20	0.40	4.9	43.5	3.1	12.5	2441	22418	2.2	15.2	5.6	16.9	11.8	53.7
± ‘J..			0.12	0.24	2.6	18.2	1.8	7.1	1872	10622	1.9	7.8	2.4	4.2	7.2	29.2

* For key to locations, see footnote to Table 1.

TABLE VI

Average background leachable and total metal concentrations from Chow and Earl (1979a) and leachable data from Word and Mearns (1979), in ppm*

Metal	CE (L)		WM (L)		CE (T)	
	$\bar{x}$	Metal/Zn	$\bar{x}$	Metal/Zn	$\bar{x}$	Metal/Zn
Cd	0.2	0.0169	0.43	0.0097	0.40	0.0074
Cr	4.9	0.415	25.5	0.574	43.5	0.810
Cu	3.1	0.263	9.02	0.203	12.5	0.233
Ni	2.2	0.186	15.4	0.347	15.2	0.283
Pb	5.6	0.475	10.5	0.236	16.9	0.315
Zn	11.8	1	44.4	1	53.7	1

* CE (L) = Chow and Earl (1979a), leachables; WM (L)= Word and Mearna (1979), leachables; CE (T) = Chow and Earl (1979a), total.

metals than those from basins, and even seem to be depleted in Cu, Fe, Ni and Zn. However, all the heavy metals (except Pb) have higher average background concentrations in the basin cores (Table VII) than in the near-shore sediments (Tables II and V). The Pb core data for basin sediments are similar to those from Word and Mearns (1979), and lower, but still similar, to the 'total' surface data of Chow and Earl (1979a).

From all these observations, it can be concluded that the core and surface sediment background values are 'real', and that they have not been influenced by recent coastal pollution. This rules out bioturbation and/or diffusion as effective vertical or lateral heavy metals transport mechanisms -within southern California sediments, on a time scale of 50 years at least, and places constraints on diagenetic solubilization of these metals. The higher Cu, Fe, Ni and Zn concentrations in the basins reflect the higher (metal rich) clay content of the sediments in these environments, relative to coastal zone near shore sediments.

Kettenring's (1979) data from the Pales Verdes sediments present the only one exception, however. He analyzed cores from 8 stations sampled at increasing distances from the outfall. The data from the farthest station from the outfall is in good accord with data from elsewhere in southern California (Table VII). Yet, an increase in heavy metal content shows up in core bottom samples from stations near the outfall. In the longest core extracted (station 7C, December, 1977), which is also the closest to the outfalls, heavy metal content is still above background even at a depth of 50 cm below the water interface. The rather great thickness of polluted sediment penetrated by the corner may represent a short period of high sedimentation rate rather than diffusion of bioturbation.

TABLE VII

Historical (= core base) heavy metal background levels (in ppm)

Metal	Basins*						Outfalls			Average background (subsurface)
	SPB	SMB	SBB	SNB	SCLB	SOB	JWPCP	HYP	Orange County	
$\bar{x}$	1.8	1.3	1.3			2	0.6	0.7	1.5	1.31 ±0.5
Ag Range										
n	(1)	(1)	(1)			(1)	(1)	(1)	(1)	
$\bar{x}$	1.0	1.0	1.75				0.7	0.22	0.53	0.87 ±0.5
Cd Range			1.5–2.0				0.42–1.0			
n	(1)	(1)	(2)				(2)	(1)	(1)	
$\bar{x}$	13	11	8.0		14	4	9.3	5		9.19 ±3.8
Co Range										
n	(1)	(1)	(1)		(1)	(1)	(1)	(1)		
$\bar{x}$	94.5	92.5	107	66	97	120	46.0	62	34	79.9 ±29
Cr Range	89–100	90–95	94–120				39–53			
n	(2)	(2)	(2)	1)	(1)	(1)	(2)	(1)	(1)	
$\bar{x}$	44	43	31.5	48	61	32	22	13	14	34.3 ±16
Cu Range	43–45	42–44	30–33				21–23			
n	(2)	(2)	(2)	(1)	1	(1)	(2)	(1)	(1)	
$\bar{x}$	4.58	4.68	3.58	2.58	3 [illegible]	2.0	2.7	2.00		3.22 ±1.7
Fe(%) range	4.16–5.0	4.36–5.0	3.5–3.66							
n	(2)	(2)	(2)	1)	(1)	(1)	(1)	(1)		
$\bar{x}$	462	385	295	5[illegible]	377	150	390	230	450	363 ±120
Mn Range	425–500	370–400	290–366							
n	(2)	(2)	(2)	(1)	(1)	(1)	(1)	(1)	(1)	
$\bar{x}$	55	60.5	45.5	65	84	55	14.5	15	50	49.4 ±22
Ni Range	50–60	55–66	40–5[illegible]				12–17			
n	(2)	(2)	(2)	(1)	(1	1	(2)	(1)	(1)	

TABLE VII *(continued)*

$\bar{x}$	9.3	11	17	10	6.1	6	(113)	6.9	10	
Pb Range	8-11	11–11	16–18			6-6	(6.2–300)			9.54 ± 3.6
n	(3)	(3)	(3)	(1)	(1)	(2)	((3))	(1)	(1)	
$\bar{x}$	118	123	114	127	178	80	63	57	110	
Zn Range	115–121	120–126	110–119				51–75			108 ± 37
n	(2)	(2)	(2)	(1)	(1)	(1)	(2)	(1)	(1)	

* For key to locations, see footnote to Table I.

Remarks on the pollutant mixing mode!

Shokes and Mankiewicz (1979) suggested that anthropogenic metals may be associated with sediment particle surfaces and, if so, can completely be leached with weak acid, in contrast with the refractory, lattice-bound metal fraction, which can be released from a sample only by total dissolution. They proposed that linear regression analysis of total vs. leachable metals [$T = f(L)$] may be used to distinguish the mass of metals derived from pollution (as reflected in high correlation coefficients) from the average background (refractory) concentration represented by the zero-leachable intercept. Shokes and Mankiewicz applied their model to all the heavy metals they studied, and found almost perfect correlations for Pb, Cd and Cr. and good correlations for a few others.

However, almost all the heavy metals investigated by Shokes and Mankiewicz (1979, Table 11-24.0-3) have slopes [$T = f(L)$] significantly greater than unity, including Pb, Cd and Cr with slopes of 1.4, 1.3 and 1.6, respectively. Increases in these trace metal concentrations above background were ascribed by the authors to be derived from pollution only. The following argument is intended to show that such a mixing model is an oversimplification of the real situation.

Let P and N be the concentrations of a heavy metal in a polluted, and in a natural fraction comprising a sediment mixture, respectively. The total concentration of the metal (T) in the mixture, and the leachable (polluted) contribution (L) of this metal to the sediment are given by

$$T = XP + (1 - X)N \qquad (1)$$

$$L = XP \qquad (2)$$

where X designates the fraction of pollutant in the sediment mixture. Substituting eq. 2 in eq. 1 and rearranging, T is obtained as a linear function of L

$$T = N + L(P - N)/P \qquad (3)$$

In eq. 3, the slope of the $T = f(L)$ regression line is given by $(P - N)/P$. Since the concentration of the metal in the natural sediment, $N \geqslant 0$, the slope of the line can only have a value of $\leqslant 1$. Steeper slopes indicate that processes other than, or superimposed on, pollutant mixing have taken place. The significance of Shokes and Mankiewicz's greater-than-unity slopes is that the leachable heavy metal fraction of the sediment gradually increases from the outfalls toward the cleaner environments at greater distance and/or depth from the pollution sources. Such an increase may be explained by either one or both of the following mechanisms:

(1) The gradual sedimentation of larger particles near the outfalls leaves finer grains, with a larger specific surface area, to deposit in the less-polluted environments. Upon leaching of these sediments with weak acid, the finer particles will yield higher L/T heavy metal ratios, shifting the $T = f(L)$ slope toward values greater than unity;

(2) Organic coatings on particles, which suppress heavy “metal leaching in the laboratory, are probably abundant in the reducing environment of the outfalls. Smaller particles which are transported through oxic waters towards the ‘cleaner’ reaches of the ocean lose their organic shield (along with the small fraction of metals in it). Later, during acid leaching, their heavy metal load is released more easily than that of the coated, coarser outfall materials, and change the slope in the observed manner.

Figure 3 shows total vs. leachable metal concentration lines for three hypothetical mixing systems differing in the N/P ratios. The upper limit slope of unity is obtained for the system in which $N/P = O$. The Cr line of Shokes and Mankiewicz (1979) with a slope of 1.75, for the San Pedro, Santa Barbara, Santa Monica and San Nicolas basins, is included for comparison. Clearly, no simple pollutant dilution model can account for this steep slope.

HEAVY METAL TRANSFER MECHANISMS

The following arguments indicate that active migration of particulate and/or dissolved heavy metals takes place after their introduction into the ocean at the outfall sites:

(1) Only 1% fo the particulate organic carbon discharged from the JWPCP

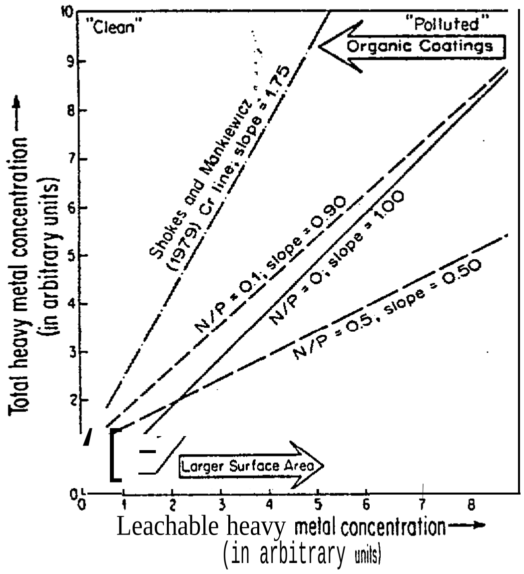


Fig. 3. Theoretical mixing lines for leachable vs. total heavy metals in sediments composed of polluted and natural materials. N = concentration of metal in natural endmember; P = concentration of metal in polluted endmember. Highest slope possible = 1.00 (for N/P = 0). Larger surface area of sediments in deeper environments, and coatings by organic materials near outfalls are considered responsible for the >1:00 slopes found by Shokes and Mankiewicz (1979).

outfalls at Whites Point between 1934 and 1971 has been retained as sediment on the Palos Verdes Shelf (Myers, 1974, p. 137; recalculation of the data presented by Myers' results yields an actual value of about 0.5%). Because the heavy metals are associated with organic carbon-rich particulates in the effluent, the massive loss of particulate carbon from the coastal zone cannot remain without an effect on the accompanying heavy metals. That this is so can be demonstrated by several observations, e.g. excellent linear correlation coefficients between organic carbon and heavy metals can be calculated from Kettenring's (1979) data, Cr, Cu, Fe, Ni, Pb and Zn were found (Faisst, 1976) to approximate, in their behavior, organic-rich particulate in sludge-seawater mixtures and Sweeney et al. (1980) have shown that several heavy metals follow effluent organic carbon near the discharge points (see also Galloway, 1979 and Hendricks and Young, 1974).

(2) Figure 2 shows that already in the vicinity of the outfalls some fractionation between Cr and Zn has taken place;

(3) Metal concentration ratios, calculated from Kettenring's (1979) data, show gradual changes in surface sediments sampled at increased distances from the outfalls (Fig. 4);

(4) Galloway (1979) used metal concentrations and sedimentation rates to demonstrate that less than 10% of the metals injected into the ocean via the outfall system are retained in the sediments in its vicinity.

(5) Based on Hendricks and Young's (1974) demonstration that the sediment deposition near, the JWPCP outfall is almost completely sewage-derived,

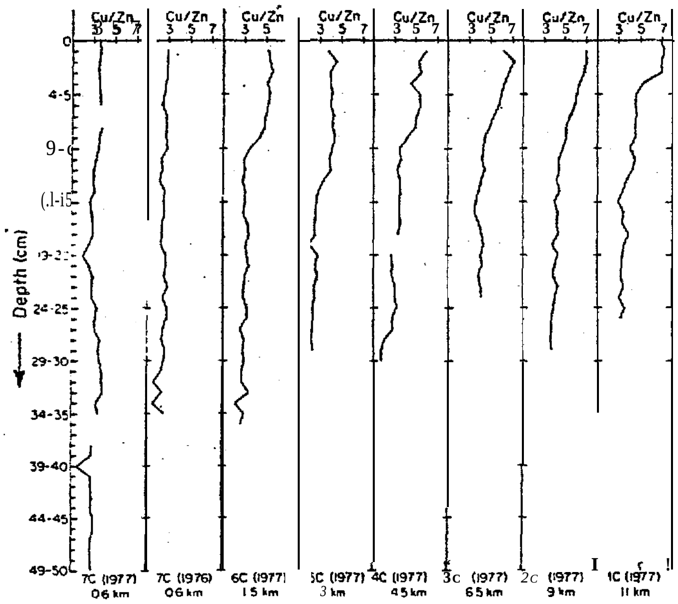


Fig. 4. Cu/Zn concentration ratios in sediment cores recovered from seven stations near the JWPCP outfall off Whites Point (drawn from Kettering, 1979 data).

Sweeney et al. (1980) showed that less than one-half of the particulate effluent organic carbon persists below the site of emission, and must have been decomposed and mobilized prior to burial, along with the heavy metals bound to it;

(6) Bruland and Franks (1979a) found a strong imprint of the Los Angeles outfalls on the concentrations of heavy metals (mainly Pb and Zn) in suspended particulate collected approximately mid-way between Whites Point and Santa Cataline Island;

(7) Sedimentary records for approximately the last 50 years show significantly heavy metal spikes in the San Pendro (Cr, Cu, Cd, Mn, Pb and Zn), Santa Monica (Cr, Cd, Pb and Zn), and Santa Barbara (Pb, atmoshperic?) Basins (Shokes and Mankiewicz, 1979);

(8) Particle dispersion from an outfall system (Point Loma, near San Diego) was studied by Herring and Abati (1978) who released fluorescent-labelled particulate into the wastewater system and traced their dispersal pattern. They found that the onshore-offshore particle dispersion is significantly larger than that predicted by theoretical consideration, despite the prevailing upcoast current in this region;

(9) Combination of Herring and Abati's (1978) PLOP (pollutant loading on particulate) experimental data with 1976 metal emission rates compiled by Schafer (1977) show that only a small fraction of the heavy metals introduced into the ocean remains near the outfalls. For example, the dispersion area of nearly 20 km? adjacent to the Whites Point outfall will receive, via rapid-settling particles (> 0.01 cms- ^{1}), the following percentages of heavy metals (relative to the total mass of metals emitted through the outfall): Ag, 5.5; Cd, 6.3; Cr, 4.0; Cu, 3.0; Ni, 2.3; Pb, 4.6; Zn, 3.5. The contribution of metals associated with finer, slower-settling particles in the vicinity of Whites Point outfall will be even smaller, because these particles will largely be carried away.

The transport of heavy metals from the outfalls can be accomplished by either one, or a combination of, the three following mechanisms: (a) removal by association with suspended particulates; (b) rapid solubilization of the heavy metals in the water column before burial; and (c), diagenetic solubilization and diffusion of the metals from the sediments into the overflying waters.

There are practically no data available *on* soluble heavy meals in interstitial waters or in the ocean near the outfalls. Thus, a direct confirmation of heavy metal transport by step (c), based on in-situ observations, is not possible at this time.

Solubilization of heavy metals upon mixing of effluent particulate with seawater in southern California has been studied in short-term laboratory simulation experiments by several authors (e.g. Chen and Hendricks, 1974; Mitchell, 1974b; Morel et al., 1975; Rohatgi and Chen, 1975; Young and Jan, 1975b; Faisst, 1976; Patterson et al., 1976; Eganhouse et al., 1978). The fractions of heavy metals released, upon dilution of sewage with seawater, vary within very large ranges. The degree of solubilization in the laboratory seems to depend mainly on dilution ratio, source and treatment of the sewage material tested, pE, pH, duration of experiment, temperature and particle size. Except for Ni (and perhaps also Mn and Co), for which a relatively high mobilization in solution seem to be agreed upon, the available data does not provide an adequate basis for even a qualitative (relative) mobilization model. For example, Cd and Pb, which have been reported to be non-mobile, or even enriched in the PVP sediments (Morel et. al., 1975) behaved differently (up to 60% release for Cd and up to 19% release for Pb) in Chen and Hendricks (1974) dilution experiments.

Myers (1974) reported that over 99% of the organic carbon in the vicinity of the Whites Point outfalls on the Pales Verdes shelf is lost to deeper ocean regions. Even if all the sediment deposited near the outfalls is sewage-derived (as suggested by Hendricks and Young, 1974), and about 50% of the remaining organic carbon decomposes in the water column" (in order to explain a drop in organic carbon concentration from 34% in the sewage to 13% in the sediment), this is still a small fraction of the carbon that escapes with the fine particulate by current transport from the outfall vicinity. It is very' likely that the heavy metal load associated with these particles follows the path of its host without significant fractionation, unless individual heavy metals are inhomogeneously distributed between different size fractions of particulate. The latter possibility haa been indicated by Faisst's (1976, p. 96) heavy metal filtration-fractionation experiments, where Cr, Cu and Zn preferentially associate with smaller particles and Pb favors larger ones.

The prevailing transport mechanism (particulate; water column solubilization, diagenetic mobilization) may have characteristic imprints on the core data near the JWPCP outfalls. Table VIH, which summarizes the important criteria for these modes of transport, is in part based on: (a) metals being homogeneously distributed among particles at all sites; and (b) the fact that current regime, settling-depth and effluent plume configuration are such that particles which remain suspended in the water for a few days will be carried far away. (The significance of this condition is that heavy metal removal by water column solubilization becomes indistinguishable from particulate transport within a few days or less.)

Kettenring's (1979) study of the Pales Verdes sediments provides the necessary data basis for the examination of these criteria (Table VIII). The Cu/Zn ratio was selected as an example for this purpose (because of the relatively high abundances and low analytical error in determination of these metals) and the data is graphically presented in Fig. 4.

Figure 4 is in good accord with the particle transport critera listed in Table VIII. The SCCWRP reports show that the mean annual emission rate, Cu/Zn ratio, at Pales Verdes was 0.308 (± 0.019) for the period 1974–1977 (inclusive). This value is nearly identical with the surface 'sediment ratios at station 7C "which is the closest sampling site to the outfalls,' but does not directly underlie them (see fig. 1 in Kettennng, 1979, and fig. 4, this report). All

TABLE VIII

Heavy metal ratio discrimination criteria for different transport mechanisms

Criterion	Particle transport (A)	Water column solubilization (B)	Diagenetic solubilization (c)
1 Metal ratio in surface sediment	Emission ratio intermediate between outfall and more remote surface stations	Same for all stations	Dictated by local environment (Eh, pH, etc.)
2 Metal ratio-depth relationship in individual cores	Parallel to emission ratio vs. time trend	No simple relationship to emission history	No simple relationship to emission history
3 Magnitude of metal fractionation (relative to	Increasing away from outfall then levelling off	Same for all stations	Dictated by local environment (Eh, PH, etc.)
4 Background sediment dilution effects on heayv metal ratios	Strongly discernible	Weakly or non-discernible	Masked by local processes

other stations exhibit surface Cu/Zn ratios larger than the' emission ratio. If we allow for extrapolation of the Cu/Zn ratio from the stations to the area immediate y below the outfalls, criterion 1A (Table VIII) will be satisfied.

Whereas the Cu/Zn ratios increase towards shallower core depths in stations 1—6, this is not the case near the outfalls (station 7). At the same time, however, no systematic increase in the Cu/Zn emission ratios has been reported for the. JWPCP outfalls for the period 1974–1977. We also do not know, however, where and by what sediment thickness this period is represented in the core data. Yet, Schafer's (19'78) total emission data for the combined Southern California sewer systems indicate an almost continuous increase in the Cu/Zn ratio from a value of 0.297 (in 1971) to 0.486 (in 1977). The rather constant Cu/Zn ratio in the JWPCP effluent and the gradual elevation of this ratio in the total southern California effluent towards more recent years is consistent with criterion 2A (Table VIII) and Fig. 4. The area close to the outfalls is supplied mainly by the rapid settling JWPCP effluent particulates with a relatively constant Cu/Zn ratio. Areas farther away from the outfalls receive smaller particles, with a longer mixing history in the ocean, and may thus be more influenced by the total gradually increasing, Cu/Zn ratio of the combined effluent. The Cu/Zn ratio can also be increased by admixture of clean, natural sediment in which the Cu/Zn ratio is much higher (Fig. 2d). Figure 4 also shows that whereas large differences in the Cu/Zn ratios are evident between stations 5-6-7, the Cu/Zn in the more distant stations 1, 2, 3 and 4 are similar. The detailed picture is by no means a perfect one. The different stations plot on non-parallel lines; station 5 data fall, at least in part, between those of station 4 and of station 7. These and other discrepanices are probably caused by particle size distribution, dilution by natural sediment, and mixing with pollutants discharged from other sewers.

However, Kettenring's (1979) data lend significant support for the view that heavy metals in the coastal zone of southern California are mostly not mobilized by dissolution, but remain attached to particulate material, with which they are finally carried away into the open ocean.

Heavy metals from oil seeps and offshore drilling

Only few data on heavy metal contributions to the southern California coastal waters from natural oil seeps and offshore drilling operations are available. The problem has been addressed by Delaney (1.972), Chapin (1972), Nikolaj et al. (1972), Reed and Kaplan (1977), Hansen et al. (1979), Shokes and Mankiewicz (1979) and Shokes et al. (1979). The metals of concern are mainly Ni and V, which are enriched in crude oils due to their complexation by porphyrins (Hunt, 1979, p. 485), and Ba which may constitute up to 90% (as barite) of drilling mud (Hansen et al., 1979). The contributions of V and Ni from oil seeps into the Southern California Bight are very small in comparison with the mass of these metals residing in the sediments and/or emitted into the ocean through sewers. The average concentrations of V in clayey, benthic, southern California sediments is 103 ± 32 ppm (-Hansen et al., 1979) on the order of one half of the concentrations of vanadium reported by Reed and Kaplan (1977) for oil seep samples from Coal Oil Point (110 ppm), La Goleta (158 ppm) and Isla Vista (245 ppm). Contribution from such a source can, therefore, be considered insignificant *even* on a local scale.

The Ni concentrations in the same soil seep samples are 44,65 and 115 ppm, compared with the average 'background' Ni concentration of 15.4 ppm (Table 11). A significant local contribution of Ni, from an oil seep to its immediate sedimentary environment, especially in isolated basins is, therefore, possible but it becomes very small relative to the input of Ni through the southern California sewers, and is negligible in comparison to the total flux of Ni into the coastal *zone.* The total flux of crude oil from Southern California seeps amounts to less than 6 x 10^4 t y^{-1} (calculated after Wilson, 1973), which is equivalent to ~7 t Ni y^{-1} if the highest (115 ppm) concentration in oil is used, whereas the total flux of Ni from sewers is between 230 and 340 t y^{-1}, or 30—50 times more (Schafer, 1976; 1977; 1978). The lowest total Ni accumulation rate reported from particle interceptor measurements takes place in the Santa Monica basin (17 mg particles cm^{2}y-l, with 50 ppm Ni, after Chow and Earl, 1979), which corresponds to a flux of 0.85 µg Ni cm-z Y^{-1} . This is equivalent to a total flux of ~2 x 10^6 t Ni y-* to the entire Southern California Bight, or some five orders of magnitude higher than the mass of Ni contributed by oil seeps.

A similar calculation can be done for barium. The average fluxes of Ba to the Santa Monica, San Pedro and Santa Barbara basins have been reported to be 16, 27 and 52 µg cm^{-2} y^{-1}, respectively (Ng and Patterson, 1979). Recalculating these data for the total area (~2600 km^2) of the Southern California Bight, one obtains a total Ba flux in the range of 4.16 x 10^7 – 1.35 x 10^8 t y^{-1}. This is obviously larger, by orders of magnitude, than the amounts of Ba which may be introduced into the same area via drilling operation. In addition, a significant fraction of drilling muds are recycled in the drilling operation, decreasing pollution effects.

The foregoing discussion does not rule out minor local pollution effects, near petroleum seeps or drilling sites, which should be monitored periodically.

SUMMARY

Heavy metal studies on the coastal and shelf sediments of Southern California have provided the following information: .

(1) 'Baseline' or 'background' concentration levels have been established for several heavy metals in various near-shore and basinal environments. They can be used as references for monitoring possible future metal pollution.

(2) The history and magnitude of heavy metal pollution has been evaluated in detail in a few deep basins and in selected shallow water areas (mainly

near sewer outfalls). Radioactive dating has provided, in a few-cases at least, an excellent absolute time-reference for assessment of the rate of change in trace metal pollution.

(3) The majority of heavy metals enter the coastal waters of Southern California associated with particulate material via waste outfalls. The coarse-grained particles, along with their metal loads, are deposited as such near the outfall and are removed altogether from the system. The bulk of the finer particulate do not remain on the shelf, but are carried out in suspension from the coastal and shelf environments by ocean currents, without a significant solubilization of heavy metals in the coastal water column or in the sediments. However, the evaluation of heavy metal transport mechanisms (such as size fractionation of metals on particulates, geographical dispersion modes of the particulate, effect of specific sewage and industrial effluent treatment methods on particulate transport efficiency, etc.) needs much additional, stud y, before a better understanding of the process can be achieved.

(4) The data obtained from experimental simulation of heavy metal behavior vary within wide ranges and are confusing, reflecting the multiplicity of factors which affect the settling rates and metal release processes from particulates in wastewater—seawater mixing systems.

(5) Heavy metal contributions to the coastal environment from oil seepages can become significant only on a very ‘local’ scale, and only a very few metals (Ni, Ba, etc. (are of some concern. These contributions are very small compared with anthropogenic fluxes and become negligible with regard to their total fluxes into southern California ocean waters.

(6) The understanding of heavy metal behavior in the southern California coastal environment will greatly benefit from the study of the following subjects: (a) the relationships between the concentrations of heavy metals in interstitial solutions and the distance of the core sites from outfalls; (b) the relationships between the heavy metal and organic carbon compositions in water column particulate, and in the sediments around outfalls. Such an evaluation may detect heavy metal size fractionation at increasing distances from the emission sites; (c) direct sedimentation rate measurements (by sediment traps) around outfalls. Such are very important for accurate assessment of particle fluxes and yields. (d) standardization of heavy metal leaching techniques.

A very detailed experimental study of various leaching agents and conditions, which should be applied to various sediment types, and particulate (primary, treated, and final effluent particulates, etc.), in order to evaluate a ‘standard’ method which will selectively remove metals bonded differently to particles between the principal metal—solid bonds.

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REFERENCES

Aller, R. C., 1977. The influence of marcobenthos on chemical diagenesis of marine sediments. Ph.D. Dissertation, Yale Univ., New Haven, CT.

Aller, R. C., Benninger, L.K. and Cochran, J. K., 1980. Tracking particle associated proceases in nearshore environments by use of ^{234}Th/^{238}U disequilibrium. Earth Planet Sci. Lett. (in press).

Aderhalt, R. and W.E. Reed (1979). Sediment texture and organic carbon characterization in the Southern California OCS. In: Southern California Baseline Study Benthic Year 2, Vol. 2. Report 15.0, SAI-77-917-LJ.

Baker, E. T., Feely, R.A. and Takahashi, K., 1979. Chemical composition, site distribution and particle morphology of suspended particulate matter at DOMES sites A, B and C: relationships with local sediment composition. In: L.L. Bischoff and D.Z. Piper (Editors), Marine Geology and Ocenaography of the Pacific Manganese Nodule Province Marine Science, Vol. 9. Plenum: New York, NY, 163-201.

Benninger, L. K., 1976. The uranium-series radionuclides as tracers of geochemical processes in Long Island Sound. Ph.D. Thesis, Yale Univ., New Haven, CT, 151 pp.

Benninger, L. K., Lewis, D.M. and Turekian, K. K., 1975. The use of natural Pb -210 as a heavy metal tracer in the river-estuarine system. In: T.M. Church, (Editor), Marine Chemistry in the Coastal Environment, ACS Symp. Ser. 18: 202–210.

Benninger, L. K., Aller, R.C., Cochran, J.K. and Turekian, K. K., 1979. Effects of biological sediment mixing on the ^{210}Pb chronology and trace metal distribution in a Long Island Sound sediment core. Earth Planet Sci. Lett., 43: 241–259.

Bertine, K.K. and Goldberg, E. D., 1977. History of metal pollution in Southern California coastal zone-reprise. Environ. Sci. Technol., 11: 297—299.

Bertine, K. K., Walawender, J.J. and Koide, M. 1978. Chronological strategies and metal fluxes in semiarid lake sediments. Geochim. Cosmochim. Acts, 42:1559-1571.

Biscaye, P.E. and Eittereim, S. L., 1977. Suspended particulate loads and transport in the nepheloid layer of the abyssal Atlantic Ocean. Mar. Geol., 23: 155–172.

Brewer, P.G. and Spencer, D. W., 1970. Trace element intercalibration study. Woods Hole Inst. Tech. Rep: pp. 70–62.

Brewer, P.G. and Spencer, D. W., 1975. Minor element models in coastal waters. In: T.M. Church (Editor), Marine Chemistry in the Coastal Environment, ACS Symp. 18, pp. 80-96.

Brooks, R. R., Presley, B.J. and Kaplan, I. R., 1968. Trace elemetns in the interstitial waters of marine sediments. Geochim. Cosmochim. Acts, 32: 397—414.

Bruland, K. W., 1974. Pb-210 geochronology in the coastal marine environment. Ph.D. Dissertation, Univ. California, San Diego, CA, 106 pp.

Bruland, K.W. and Franks, R. P., 1979a. Trace metal characterization of water column particulates. Southern California Baseline Study, Benthic, Year 2, Vol. 2, Rep. No. 7.0, SAI-77-917-LJ.

Bruland, K.W. and Franks, R.P., 1979b. Trace metal characterization of water column particulate. Southern California Baseline Study, Benthic, Year 2, VOI. 3, Final Report, Rep. No. 7.0, SAI-77-917-LJ.

Bruland, K.W. and Franks, R. P., 1979c. Trace metal characterization of water column particulate. Southern California Baseline Study, Benthic, Year 2, Vol. 4, Rep. No. 7.0, SAI-77-917-LJ.

Bruland, K. W., Bertine, K., Koide, M., and Goldberg, E. D., 1974a. History of metal pollution in Southern California coastal zone. Environ. Sci. Technol., 5: 425–432.

Bruland, K. W., Koide, M. and Goldberg, E. D., 1974b. The comparative marine geochemistries of Lead 210 and Radium 226. J. Geophys. Res., 79: 3083—3086.

Bruland, K. W., Knauer, G.A. and Martin. J.M., 1978. Cadmium in northeast Pacific waters. Limnol. Oceanogr., 23:618-625.

Bruland, K. W., Franks, R.P., Bellows, J., and Soutar, A., 1979a. Age dating of box cores. Southern California Baseline Study, Benthic, Year 2, Vol. 2, Final Report, Rep. No. 12.0, SAI-77-917-LJ.

Bruland, K. W., Franks, R.P., Knauer, G.A. and Martin, J. H., 1979b. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the namogram per liter level in seawater. Anal. Chim. Acts, 105:233-245.

Brun-Cottan, J. C., 1976. Stokes settfing and dissolution rate model for marine particulates as a function of size distribution. J. Geophys. Res., 81: 1601–1606.

Carmody, D. J., Pearce, J.B. and Yasso, W. E., 1973. Trace metals in sediments of the New York Bight. Mar. Pollut. Bull., 4:132-135.

Chap in, D-W., 1972. Source identification of tar deposits from the Santa Barbara Channel coastline by trace metal analysis- Unpublished M.Sc. Thesis, Univ. California, Santa Barbara, CA.

Chen, K.Y. and Hendricks, T., 1974. Trace metals on suspended particulate. SCCWRP Annu. Rep., 1974, El Segundo, CA. pp. 147–152.

Chen, K. Y., Young, C.S., Jan, T.K. and Rohatgi, N., 1974. Trace metals in wastewater” effluents. J. Water Pollut. Control Fed., 49.

chow, T. J., 1979. Trace metal distribution in Southern California Offshore Continental Shelf benthic sediments. Southern California Baseline Study, Vol. 2, Rep. No. 8, Final Report.

Chow, T.J. and Earl, J., 1979a. Trace metal distribution in Southern California OCS benthic sediments. Southern California Baseline Study, Benthic, Year 2, Final Report, Vol. 2, Report No. 8; SAI-77-917-LJ.

Chow, T.J. and Earl, J., 1979b. Trace metal distribution in Southern California OCS benthic sediments. Southern California Baseline Study, Vol. 4, Rep. No. 8, SAI-77-917-LJ.

Chow, T.J., Bruland, K.W., Bertine, K.K., Soutar, A., Koide, M. and Goldberg, E. D., 1973. Lead pollution: records in southern California coastal sediments. Science, 181:551-552.

Corliss, J. B., Dymond, J., Gordon, L.I., Edmond, J. M., Von Herzen, R.P., Ballard, R. D., Green, K., Williams, D., Bainbridge, A., Crane, K and Van Andel, T. H., 1979. Submarine thermal springs on the Galapagos Rift. Science, 203: 1073—1083.

Craig, H. and Weiss, R. F., 1970. The GEOSECS 1969 intercalibration station: introduction, hydrographic features and total $C0_2 - 0_2$ relationships. J. Geophys. Res., 75: 7641-7647.

Crisp, P.T., Brenner, S., Venkatesan, M. I., Ruth, E. and Kaplan, I.R., 1979. Organic chemical characterization of sediment-trap particulate from San Nicolas, Santa Barbara, Santa Monica and San Pedro basins, California. Geochim. Cosmochim. Acts, 43: 1791—1801.

Delaney, R. C., 1972. Trace metal weathering effect and characterization of oily pollutants from the Santa Barbara Channel. Unpublished M. SC. Thesis, Univ. California, Santa Barbara, “CA.

Drake, D. E., 1974. Distribution and transport of suspended particulate matter in submarine canyons off Southern California. In: R.J. Gibbs (Editor), Marine Science, VOl-4. Plenum Press, New York, NY, pp. 133–154.

Drever, J.I. (Editor), 1977. Sea Water, Cycles of the Major Elements, Benchmark Papers in Geology No. 45. Dowden, Hutchinson and Ross, 344 pp.

Dyrssen, D. and Wedborg, M., 1974. Equilibrium calculations on the speciation of elements in seawater. The Sea, Vol. 5. Wiley, New York, NY, Chapter 5, pp. 181—195.

Edmond, J. M., Measures, C., **McDuff,** R. E., **Chan,** L.H., Collier, R., **Grant,** B., Gordon, L.1. and **Corliss,** J. B., 1979. Ridge-crest hydrothermal activity and the balances of the major and minor elements in the ocean: the **Galapagos data. Earth** Planet, **Sci. Lett.,** 46: 1-18.

Eganhouse, R. P., 1976. Mercury *in* sediments. **SCCWRP Annu.** Rep., 1976, El Segundo, CA, pp. 83–89.

Eganhouse, R.P. and Young, D. R., 1976a. Mercury in **benthic** animals. **SCCWRP Annu.** Rep., 1976, **El** Segundo, CA, pp. 111–115.

Eganhouse, R.P. and Young, D. R., **1976b.** Mercury in mussels. SCCWRP **Annu.** Rep., --- 1976, El Segundo, CA, PP. 105–109.

Eganhouse, R.P. and Young, D. R., 1978a. Total and organic mercury in **benthic** organisms *near* a major submarine wastewater out fail system. Bull. Environ. Contain. **Toxicol.,** 19:958-766.

Eganhouse, R.P. and Young, D. R., **1978b.** In-situ uptake of mercury by the intertidal mussel, My *tilus californianus.* Mar. **Pollut.** Bull., 9: 214—227.

Eganhouse, R. P., Young, **D.R.** and Johnson, J. N., 1978. Geochemistry of mercury in Pales Verdea sediments. Environ. **Sci. Technol.,** 12: 1151–11 57.

Emery, K. O., **1960.** The Sea Off Southern California: A Modern Habitat of Petroleum. John Wiley, New York, NY, 366 pp.

Erlenkeuser, H., Suesa, E. and **Willkomm,** H., 1974. Industrialization affects heavy metal and carbon isotope concentrations in recent Baltic Sea sediments. Geochim. **Cosmochim.** Acts, **38:** 823—842.

Evans, D. W., **Cutshall,** N. H., Cross, **F.A.** and Wolfe, D. A., 1977. Manganese cycling in the Newport River estuary, North Carolina. Estuarine Coastal Mar. **Sci.,** 5:7 1—80.

Faisst, W. K., 1976. Digested sludge: delineation and modeling for ocean disposal. Ph.D. Thesis, **Calif.** Inst. **Technol.,** Pasadena, CA, 193 pp.

Flegal, R.A. and Martin, J. H., 1977. Contamination **of** biological samples by ingested sediment. Mar. **Pollut. Bull.,** 8:90-91.

Friedlander, S. K., 1973. Chemical element balances and identification of air pollution sources. Environ. **Sci. Technol.,** 7: 235—240.

Galloway, J., 1972. Man's alteration of the **natural geochemical cycle** of **selected** trace metals. Ph.D. Dissertation, Univ. California, San Diego, CA.

Galloway, J. N., 1979. Alteration of trace **metal geochemical** cycles due to marine discharge of wastewater. **Geochim. Cosmochim.** Acts 43: 207—2 18.

Goldberg, E. D., 1972. Man's role in the major sedimentary **cycle.** In: D. Dyrssen and D. Jagner (Editors), The Changing Chemistry of the *Oceans.* **Proc.** 20th Nobel **Symp., Göteborg,** pp. 267—288.

Goldberg, E. D., 1975. Marine **pollution.** In: **J.P.** Riiey and G. **Skirrow** (Editors), **Chemical** Oceanography, Voi. 3. Academic Press, Chap. 17, pp. 39–89.

Goldberg, E.D. and **Bruland,** K. W., 1974. Radioactive **geochronologies.** In: E. I). Goldberg (Editor), The Sea, Voi. 5, Wiley, New York, NY, pp. 451–489.

Goldberg, E. D., **Gamble,** E., Griffin, **J.J.** and Koide, M., **1977. Pollution** history of Narragansett Bay as recorded in its sediments. Estuarine **Coastal** Mar. **Sci.,** 5:549-561.

Goldberg, E. D., Hodge, V., **Koide,** M., Griffin, J., **Gamble,** E., **Bricker,** P. O., **Matisoff,** G., **Holdren, G.R.** and **Braun,** R., 1978. A pollution history of Chesapeake Bay. Geochim. **Cosmochim.** Acts. 42:1413-1425.

Grigg, R. W., 1978. Long-term changes in rocky bottom communities off Pales Verdes. Southern California Coastal Water Research Project, **Annu.** Rep., **El** Segundo, CA, pp. 157-184.

Hansen, N., Sims, R., **Abusamra,** A., **Shokes,** R., Reed, J. and Orphan, V. 1979. Vanadium, barium and other trace **metals** in sediment and biological samples using NAA. Southern California **Baseline** Study, **Benthic,** Year 2 **Vol.** 2, Rep. No. 9; **SAI-77-917-**LJ.

Harris, R. L., Helz, G.R. and Cory, R. L., 1975. Processes affecting the vertical distribution of trace components in the Chesapeake Bay. In: T.M. Church (Editor), Marine Chemistry in the Coastal Environment. ACS Symp. Ser. 18, pp. 176-185.

Hendricks, T. J., 1974. The fates of trace metals and particulate. SCCWRP Annu. Rep., 1974, El Segundo, CA, pp. 141-145.

Hendricks, T.J., 1975. A model of the dispersion of wastewater constituents. SCCWRP Annu. Rep., 1975, El Segundo, CA, pp 173-177.

Hendricks, T.J., 1978. Forecasting changes in sediments near wastewater outfalls. Southern California Coastal Water Research Project. Annu. Rep., El Segundo, CA, 127—143.

Hendricks, T.J. and Young, D. R., 1974. Modeling the fates of metals in ocean-discharged wastewaters. Southern California Coastal Water Research Project, Tech- Memo. No. 208, El Segundo, CA.

Herring, J.R. and Abati, A. L., 1978. Effluent particle dispersion. Southern California Coastal Water Research Project, Annu. Rep. 1978, El Segundo, CA, pp. 113–125.

Hershelman, G.P., Jan, T.K. and Schafer, H.A., 1977. Pollutants in sediments off Palos Verdes. SCCWRP Annu. Rep., 1977, El Segundo, CA, pp. 63-68.

Hirao, Y. and Patterson, C. C-, 1974. Lead aerosol pollution in the high Sierra overrides natural mechanisms which exclude lead from a food chain. Science, 184:989-892.

Hedge, V"., Johnson, S.R. and Goldberg, E. D., 1978. Influence of atmoshperically transported aerosols on surface ocean water composition. Geochem. J., 12: 7–20.

Hunt, J. M., 1979. Petroleum Geochemistry and Geology. W.H. Freeman, San Francisco, CA, 617 Pp.

Hunter, K.A., 1980. Processes affecting particulate trace metals in the sea surface microlayer. Mar. Chem., 9:49-70.

Huntzicker, J. J., Friedlander, S.K. and Davidson, C. L., 1975. Material balance for automobile-emitted lead in Los Angeles Basin. Environ. Sci. Technol., 9: 448—456.

Jan, T.K. and Young,., D. R.; 1976. Chromium speciation in municipal wastewater and seawater. SCCWRP Annu. Rep., 1976, El Segundo, CA, pp. 15—22.

Jan, T.K. and Young, D.R., 1978. Determination of microgram amounts of some transition metals in seawater by methyl iso-butyl ketone-nitric acid successive extraction and flameless atomic absorption Spectrophotometry. AnaL Chem., 50: 1250–1253.

Jan, T.K., Moore, M.D. and Young, D. R., 1977. Metals in seafoods near outfalls. SCCWRP Annu. Rep., 1977, El Segundo, CA, pp. 153–157.

Johnson, J. N., 1974. Mercury in bottom sediments off Pales Verdes. SCCWRP Annu. Rep., 1974, El Segundo, CA, pp. 129-132.

Kalil, E.K., Jr., 1976. The distribution and geochemistry of uranium in Recent and Pleistocene marine sediments. Ph.D. Thesis, Univ. California, Los Angeles, CA, 283 Pp.

Kalil, E. K., Jr., 1978. The path of uranium, copper, manganese, nickel and chromium in sediment from Tanner Basin and Catalina Basin. Annu. Rep. DOE/BLM, Contract No. EY-76-S-03-0034.

Kettering, K.N., 1979. The stratigraphy and sedimentation of anthrogenous materials on San Pedro Shelf, California. In: Distribution and fate of biogenic and petroleum-derived substances in marine sediments. Annu. Rep. DOE, Contract No. EY-76-S-03-0034.

Klein, D.H. and Goldberg, E. D., 1970. Mercury in the marine environment. Environ. Sci. Technol., 4: 765–768.

Knezevic, M.Z. and Chen, K. Y., 1977. Organometallic interactions in recent marine sediments. In: T.F. Yen (Editor), Chemistry of Marine Sediments. Ann Arbor, Ann Arbor, MI, pp. 223–241.

Koide, M., Bruland, K.W. and Goldberg, E. D., 1973. Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. Geochim. Cosmochim. Acts, 37: 1171—1187.

Koide, M., Soutar, A. and Goldberg, E. D., 1972. Marine geochronology with Pb-210. Earth Planet. Sci. Lett., 14:442-446.

Koide, M., Griffin, J.J. and Goldberg, E. D., 1975. Records of plutonium fallout in marine and terrestrial samples. J. Geophys. Res., 80: 4153—41 62.

Koide, M., Bruland, K.W. and Goldberg, E. D., 1976. ^{226}Ra chronology of a coastal marine sediment. Earth Planet. Sci. Lett., 31: 31—36.

Krishnaswami, S., Lal, D. and Somayajulu, B. L. K., 1976. Investigations of gram quantities of Atlantic and Pacific surface particulate. Earth Planet. Sci. Lett., 32: 403—419.

Krishnaswami, S., Benninger, L. K., Aller, R.C. and Von Damm, K. L., 1980. Atmospherically-derived radionuclides as tracers of sediment mixing and accumulation in near-shore marine and lake sediments: evidence from ^{7}Be, ^{210}Pb and ^{239}'2W Pu. Earth Planet. Sci. Lett. (in press).

Lal, D., 1977. The oceanic microcosm of particles. Science, 198: 997–1009.

Lazrus, A. L., Lorange, E. and Lodge, J. P., 1970. Lead and other metal ions in U.S. precipitation. Environ. Sci. Technol., 4: 55—58.

Lerman, A., 1979. Geochemical processes. John Wiley, New York, NY, 481 pp.

Lerman, A., Carder, K.L. and Betzer, P. R., 1977. Elimination of fine suspensoids in the oceanic water column. Earth Planet. Sci. Lett., 37: 61–70.

Liljestrand, H.M. and Morgan, J. J., 1978. Chemical composition of acid precipitation in Pasadena, California. Environ. Sci. Technol., 12: 1271–1273.

Lu, J.C.S. and Chen, K.Y., 1977. Migration of chemical constituents in sediment-seawater interfaces. In: T.F. Yen (Editor), Chemistry of Marine Sediments. Ann Arbor Science, Ann Arbor, MI, pp. 181–222.

Mackenzie, F.T. and Wollast, R., 1977. Sedimentary cycling models of global processes. *In:* E.D. Goldberg, I. IV. McCave, J.J. O'Brien and J.H. Steele (Editors). The Sea, Vol. 6. Wiley, New York, NY, pp. 739-783.

Martin, J. and Knauer, G. 1979. Trace metals in selected benthic marine organisms. Southern California Baseline Study, Benthic, Year 2, Vol. 2, Final Rep. 10, SAI-77-917-LJ.

McCaffrey, R.J., 1977. A record of the accumulation of sediment and trace metals in a Connecticut, USA, salt marsh. Ph.D. Dissertation, Yale Univ., New Haven, CT, 156 pp.

McDermott, D. J., 1974. Characteristics of municipal wastewaters, 1971-1973. SCCWRP Annu. Rep. 1974, El Segundo, CA, pp. 89-96.

McDermott-Ehrlich, D. and Alexander, G. A., 1976. Chemical studies of offshore oil platforms. SCCWRP Annu. Rep., 1976, El Segundo, CA, pp. 129-135.

McDermott, D. J.. and Young, D. R., 1974. Trace metals in flatfish around outfalls. SCCWRP Annu. Rep., 1974, El Segundo, CA, pp. 117–121.

Mearns, A.J., 1974. Toxicity studies of chromium. SCCWRP Annu. Rep. 1974, El Segundo, CA, pp. 15–17.

Millero, F.J. (1977). Thermodynamic models for the state of metal ions in seawater. In: J.J. O'Brien and J.H. Steele (Editors), The Sea, Vol. 6. E.D. Goldberg, I.N. McCave, Wiley, New York, NY, pp. 653-693.

Mitchell, F. K., 1974a. Comparison of primary and secondary treatment. SCCWRP Annu. Rep., 1974, El Segundo, CA, pp. 163-165.

Mitchell, F. K., 1974b. Properties of ocean sludge. SCCWRP Annu. Rep. 1974, El Segundo, CA, pp. 159–1 62.

Mitchell, F.K. and McDermott, D. J., 1975. Characteristics of municipal wastewater discharges, 1974. SCCWRP Annu. Rep., 1975, El Segundo, CA, pp. 163—165.

Morel, F.M.M. and Morgan, J. J., 1972. A numerical method for computing equilibria in aqueous chemical systems. Environ. Sci. Technol., 6: 58—67.

Morel, F. M. M., Westall, J.C., O'Melia, C. R., and Morgan, J.J., 1975. Fate of trace metals in Los Angeles County wastewater discharge. Environ. Sci. Technol., 9: 756—7 61.

Morgan, J.J. and Sibley, T. H., 1975. Chemcial models for metals in coastal environments. ASCE Coastal Engin. Conf., Dover, DE.

Murray, S.M. and Ku, T. L., 1977. Recent deposition of lead off the coast of Southern California. In: T.F. Yen (Editor), Chemistry of Marine Sediments, Ann Arbor Science, Ann Arbor, MI, pp. 151-156.

Murray, J.W. and Brewer, P. G., 1977. Mechanisms of removal of manganese, iron and other trace metals from sea water. In: G.P. Glasby (Editor), Marine Manganese Deposits, Oceanographic Series 15. Elsevier, Amsterdam, pp. 291–326.

Myera, E.P., 1974. The concentration and isotopic composition of carbon "in marine sediments affected by a sewage discharge. Ph.D. Thesis, Cal. Inst. Technol., Pasadena, CA.

Ng, A. and Patterson, C. C., 1979. Chronological variation in barium concentration, lead concentration and lead isotopic composition in sediments of four southern California offshore basins. Southern California Baseline Study, Benthic, Year 2, Vol. 2, Rep. No. 14.

Nikolaj, P. J., Schlueter, R.S. and Allen, A. A., 1972. Investigation of the nature, extent and fate of natural oil seepage off southern California. 4th Annu. Offshore Technol. Conf., Houston, TX, Pap. OTC 1549.

Nozaki, Y. and Tsunogai, S., 1973. Lead-210 in the North Pacific and the transport of terrestrial material through the atmosphere. Earth Planet. Sci. Lett., 20: 88–92.

Oshida, P.S., 1976. Effects of chromium on reproduction in polychaetes. SCCWRP Annu. Rep., 1976, El Segundo, CA, pp. 161-167.

Oshida, P. S., 1977. A safe level of hexavalent chromium for a marine polychaete. SCCWRP Annu. Rep., 1977, El Segundo, CA, pp. 169-180.

Oshida, P.S. and Wright, J. L., 1976. Acute responses of marine invertebrates to chromium. SCCWRP Annu. Rep., 1976, El Segundo, CA, pp. 155-159.

Patterson, C. C., Settle, D. and Glover, B., 1976. Analysis of lead in polluted coastal seawater. Mr. Chem., 4:305-319.

Peters, K.E., Sweeney, R.E. and Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter." Limnol. Oceanogr., 23: 598—604.

Pinta, M., 1978. Modern Methods for Trace Element Analysis. Ann Arbor Science, Ann Arbor, MI, 492 pp. (translated from French).

Reed, W.E. and Kaplan, I.R., 1977. The chemistry of marine petroleum seeps. J. Geothem. Explor., 7: 255—293.

Rohatgi, N. and Chen, K.Y., 1975. Transport of trace metals by suspended particulates on mixing with seawater. J. Water Pollut. Control. Fed., 47:2298.

Rutherford, F. and Church, T. M., 1975. Use of silver and zinc to trace sewage sludge dispersal in coastal waters. In: T.M. Church (Editor), Marine Chemistry in the Coastal Environment. ACS Symp. Ser. 18, pp. 440–452.

Schafer, H. A., 1976. Characteristics of municipal wastewater discharges, 1975. SCCWRP Annu. Rep., 1976, El Segundo, CA, pp. 57-60.

Schafer, H.A., 1977. Characteristics of municipal wastewater discharges, 1976. SCCWRP Annu. Rep., 1977, El Segundo, CA, pp. 19–23.

Schafer, H. A., 1978. Characteristics of municipal wastewater discharges, 1977. SCCWRP Annu. Rep., 1978. El Segundo, CA, 97–101.

Schafer, H.A. and Bascom, W.., 1976. Sludge in Santa Monica Bay. SCCWRP Annu.Rep., 1976, El Segundo, CA, pp. 77–82.

Schindler, P. W., 1975. The regulation of trace metal concentrations in natural water systems: a chemical approach. Int. Assoc. Great Lakes Symp., Geneva Park, Ont. October, 1975.

Settle, D.M. and Patterson, C. C., 1980. Lead in Alabcore: guide to lead pollution in Americans. Science, 207:1167-1176.

Sherwood, M.J., 1976. Fin erosion disease induced in the laboratory. SCCWRP Annu. Rep., 1976, El Segundo, CA, 149—153.

Sherwood, M.J. and Wright, J. L., 1976. Uptake and effects of chromium on marine fish. SCCWRP Annu. Rep., 1976, El Segundo, CA, 123—128.

Sherwood, M.J. and McCain, B. B., 1976. Comparison of fin erosion disease. Los Angeles anti Seattle. SCCWRP Annu. Rep. 1976, El Segundo, CA, pp. 143—147.

Shirahata, H., Elias, R. W., Patterson, C.C. and Koide, M., 1980. Chronological variations in concentrations and isotopic compositions of anthropogenic lead in sediments of a remote subalpine pond. Geochim. Cosmochim. Acts, 44: 149—162.

Shokes, R.F. and Mankiewicz, P. J., 1979. Natural and anthropogenic fluxes of chemicals in the Southern California Bight as related to the potential impacts of offshore drilling. Southern California Baseline Study, Benthic, Year 2, Vol. 2, Rep. No. 24; SAI-77-917-LJ.

Shokes, R., Sims, R., Guttman, M., Laughon, S., Hansen, N., Abusamra, A. and Reed, J., 1979. Natural and anthropogenic fluxes of chemicals into the Southern California Bight as related to the potential impacts of offshore drillings. Southern California Baseline Study, Benthic, Year 2, Vol. 3, Rep. No. 24; SAI-77-917-LJ.

Sholkovitz, E. R., 1973. Interstitial water chemistry of the Santa Barbare basin sediments. Geochim. Cosmochim. Acts, 37: 2043–2973.

Sholkovitz, E. R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and sea water. Geochim. Cosmochim. Acts, 40: 831—845.

Sholkovitz, E.R. and Gieskes, J. M., 1971. A physical chemical study of the flushing of the Santa Barbara Basin. Limnol. Oceanogr., 16:479489.

Sholkovitz, E.R. and Price, N. B., 1980. The major element chemistry of suspended matter in the Amazon estuary. Geochim. Cosmochim. Acts, 44: 163—171.

Sholkovitz, E.R. and Soutar, A., 1975. Changes in the composition of the bottom water of the Santa Barbara Basin: effect of turbidity currents. Deep-Sea Res., 22: 13-21.

Sibley, T.H. and Morgan, J.J., 1975. Equilibrium speciation of trace metals in freshwater: seawater mixtures. Int. Conf. on Heavy Metals in the Environment, Toronto.

Sillén, L.G. and Marten, A. E., 1964. Stability constants of metal-ion complexes. Chem. Sot. Spec. Publ. No. 17, London.

Soutar, A., S.A. Kling, P.A. Crill, E. Duffrin and K.W. Bruland (1977). Monitoring the marine environment through sedimentation. Nature (London), 266: 136—1 39.

Spencer, D.W. (Convener), 1980. Abstracts from a workshop on processes determining the input, behavior and fate of radionuclides and trace elements in continental shelf environments, Gaithersburg, March, 1979. U.S. Dept. of Energy, CONF-790382, Washington, DC.

Spencer, D. W., Robertson, D. E., Turekian, K.K. and Folsom, T. R., 1970. Trace element calibrations and profiles at the GEOSECS test station in the northeast Pacific Ocean. J. Geophys. Res., 75: 7688–7696.

Stumm, W. and Brauner, P. A., 1975. Chemical speciation. In: J.P. Riley and G. Skirrow (Editors), Chemical Oceanography, Vol. 1, Academic Press, London, 2nd edn., pp. 173–239.

Sweeney, R. E., 1978. Use of nitrogen isotopic ratios for tracing industrial and domestic sewage transport above the thermocline on San Pedro shelf. Annu. Rep. DOE/BLM, Contract No. RY-76-S-03-O034.

Sweeney, R.E. and Kaplan, I. R., 1980. Tracing flocculent industrial and domestic sewage transport on San Pedro Shelf, Southern California, by nitrogen and sulfur isotope ratios, Mar. Environ. Res. (in press).

Sweeney, R. E., Liu, K.K. and Kaplan, I. R., 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: B.W. Robinson (Editor), Stable Isotopes in the Earth Sciences. DSIR Bull. 200, New Zealand Dept. Sci. Indust. Res., Wellington, pp. 9–26.

Sweeney, R. E., Kalil, Jr. E. K., and Kaplan, I. R., 1980. Characterization of domestic and industrial sewage in Southern California coastal marine sediments using nitrogen, carbon, sulfur and uranium tracers. Mar. Environ. Res. (in press).

Troup, B.N. and Bricker, O. P., 1975. Processes affecting the transport of materials from continents to oceans. In: T.M. Church (Editor), Marine Chemistry in the Coastal Environment. Am. Chem. Sot. Symp. Ser. 18, pp. 133–151.

Turekian, K. K., 1977. The fate of metafs *in* the oceans. Geochim. Cosmochim. Acts, 41, 1139—1144.

Turekian, K. K., 1979. New Haven Harbor ecological studies. In: Trace Metals. Summary Rep., Yale University, New Haven, CT, Chap. 10.

Turekian, K. K., Kharkar, D.P. and Thomson, J., 1973. Uranium and thorium decay series nuclide abundances in marine plankton. Final Report to Advanced Research Projects Agency, ARPA Order No. 1793, Contract NO0014-67-A-0097 -O022.

Turekian, K.K. and Volchok, H. L-, (Conveners), 1979. The natural radioactive isotopes of beryllium in the environment. Abstracts and a report of a meeting sponsored by Yale University and the US Dept. of Energy, Yale University, New Haven, CT.

Wakeman, T. H., 1977. Release of trace constituents from sediments resuspended during dredging operations. In: T.F. Yen (Editor), Chemistry of Marine Sediments, Aim Arbor Science, Ann Arbor, MI, pp. 173–180.

Wallace, G.T. and Duce, R. A., 1978a. Open ocean transport of particulate trace metals by bubbles. Deep-Sea Res., 25: 827–735.

Wallace, G.T. and Duce, R. A., 1978b. Transport of particulate organic matter by bubbles in marine waters. Limnol. Oceanogr., 23: 1155—1167.

Wallace, G.T., Hoffman, G.L. and Duce, R. A., 1977. The influence of organic matter and atmospheric deposition on the particulate trace metal concentration of North-west Atlantic seawater. Mar. Chem. 5: 143–170.

Watson, M. W., Wood, R.H. and Millero, F.J., 1975. The activity of trace metals in artificial seawater at 25 °C. In: T.M. Church (Editor), Marine Chemistry in the Coastal Environment. ACS Symp. Ser. 18, pp. 112-118.

Wilson, R. D., 1973. Estimate of annual input of petroleum to the marine environment from natural marine seepage. In: Background Papers, for a Workshop on Inputs, Fates and Effects of Petroleum in the Marine Environment. NTIS, Vol. 1, pp. 59—96.

Wood, J.M. and Goldberg, E. D., 1977. Impact of metals on the biosphere. In: W. Stumm (Editor), Global Chemical Cycles and Their Alteration by Man. Dahlem Konferenzen, Berlin, 1977, pp. 137–153.

Word, J.Q. and Meerns, A.J., 1979. " 60-Meter control survey off Southern California. SCCWRP Tech. Memo. No. 229.

Yao, K. M., Habibian, M.T. and O'Melia, C. R., 1971. Water and waste filtration concepts and application. Environ. Sci. Technol., 5: 1105—1112.

Young, D. R., 1974. Arsenic, antimony and selenium in outfall sediments. SCCWRP Annu. Rep., 1974, El Segundo, CA, pp. 133–137.

Young, D. R., 1978. Priority pollutants in municipal wastewater. Southern California Coastal Water Research Project, Annu. Rep., 1978, El Segundo, CA, pp. 103-112.

Young, D.R. and Alexander, G. V., 1977. Metals in mussels from harbors and outfall areas. SCCWRP Annu. Rep. 1977, El Segundo, CA, pp. 159–165.

Young, D.R. and Jan, T-K., 1975a. Chromium in municipal waatewater and seawater. SCCWRP Annu. Rep., 1975, El Segundo, CA, pp. 147–149.

Young, D.R. and Jan, T-K., 1975b. Trace metals in nearshore seawater. SCCWRP Annu. Rep., 1975, El Segundo, CA, pp. 143–146.

Young, D.R. and Jan, T-K., 1976. Metals in scallops. SCCWRP Annu. Rep, 1976, El Segundo, CA, pp. 117–121.

Young, D.R. and Jan, T-K., 1977. Fire fallout of metals off California. Mar. Pollut. Bull. 8: 109-112.

Young, D.R. and McDermott, D.J., 1975. Trace metals in harbor mussels. SCCWRP Annu. Rep., 1975, El Segundo, CA, pp. 139–142.

Young, D.R. and Mearns, A. J., 1978. Pollutant flow through food webs. SCCWRP Annu. Rep., 1978, pp. 185–202.

Young, D. R., Johnson, J. N., Soutar, A. and Isaacs, J. D., 1973. Mercury concentrations in dated varved marine sediments collected off Southern California. Nature (London), 244: 273–275.

Young, D. R., McDermott, D. J., Heesen, T.C. and Jan, T-K., 1975. Pollutant inputs and distributions off Southern California. In: T.M. Church (Editor), Marine Chemistry in the Coastal Environment, ACS Symp. Ser. 18; 424—439.

Young, D. R., Jan, T-K. and Moore, M. D., 1977. Metals in power plant cooling water discharges. SCCWRP Annu. Rep. 1977, El Segundo, CA, 25—31.

Young, D. R., Alexander, G.V. and McDermott-Erlich, D., 1979. Vessel related contamination of Southern California harbors by copper and other metals. Mar. Pollut. Bull., 10:50-56.

Zirino, A. and Yamamoto, S., 1972. A pH dependent model for the chemical speciation of copper, zinc, cadmium and lead in seawater. Limnol. Oceanogr., 17: 661—671.

submitted to Geochim. Cosmochim. Acts

Thermal Alteration of Cretaceus Black Shale by Diabase Intrusions in the Eastern Atlantic:

II. Effects on Bitumen and Kerogen [1,2]

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ABSTRACT

The thermal effects of three (one major and two minor) Miocene diabase intrusions on Cretaceus black shales from DSDP site 41-368 have been analyzed. A concentration gradient was observed, especially for the hydrocarbons, decreasing towards the major intrusion and between the three sills. The thermally-altered samples in the proximity of and between the sills contained elemental sulfur and an excess of thermally-derived pristane over phytane, whereas, the unaltered sediments contained no elemental sulfur, and more phytane than pristane. A maximum yield of the extractable hydrocarbons was observed at a depth of 7 m below the major sill. Two classes of molecular markers were present in this bitumen suite. The first was sesqui-, di- and triterpenoids and steranes, which could be correlated with both terrigenous and autochthonous sources. They were geologically mature and showed no significant changes due to the thermal stress. The second class was found in the altered samples, which contained only polynuclear aromatic hydrocarbons with low alkyl substitution and sulfur and oxygen heterocyclic aromatic compounds. These compounds were derived from pyrolytic reactions during the thermal event.

Kerogen was isolated from all of these samples, but only traces of humic substances were present. The H/C, N/C, $\delta^{13}C$, $\delta^{34}S$ and δD all exhibit the expetted effects of thermal stress. The kerogen becomes more aromatized and richer in ^{13}C, ^{34}S and D in the proximity of and between the sills. Maturation trends were also measured by the vitrinite reflectance and electron spin resonance, where the thermal stress could be correlated with an elevated country rock temperature and an increased degree of aromaticity. The effects of _in situ_ thermal stress on the organic-rich shales resulted in the generation and expulsion of petroliferous material from the vicinity of the sills.

INTRODUCTION

Organic-rich, black shales of Cretaceus age have been recovered from various Deep Sea Drilling Project sites in the Atlantic Ocean (Simoneit, 1980a; Thiede and van Andel, 1977; Schlanger and Jenkyns, 1976) and their paleoenvironmental conditions of sedimentation and petroleum source rock potential have been examined (Demaison and. Moore, 1980; Tissot et al., 1979; Didyk et al., 1978; Comer and Littlejohn, 1976; Kendrick et al., 1977 ;1978). At site 41-368, a Cretaceus black shale was intruded by diabase sills and small quantities of light, extractable hydrocarbons were observed in cores onboard the drilling ship (Lancelot et al., 1975). The"presence of light hydrocarbons was subsequently confirmed (Dow, 1977; Baker et al., 1977a; Simoneit et al., 1978). Geochemical analyses of sediments across these sill intrusions presented an excellent in situ thermal experiment to monitor the thermal effects resulting in expulsion of volatile organic components and the alteration of the residual organic matter (Simoneit et al., 1978). A similar study" for Kimmeridgian shales of Greenland which were intruded by a dyke has been reported (Perregaard and Schiener, 1979).

Site 41-368 is located (Fig. 1) in the Cape Verde Rise (17°30.4'N, 21°21 .2'W; water depth 3,367 m)(Lancelot et al., 1975). Turonian-Albian black shales were horizontally penetrated by two thin (∿20 cm) and one thick (15 m) diabase sills (Natland, 1977). The age of the major intrusive unit was determined by the K/Ar method to be approximately 19 million years (earlyM iocene)(Duncan and Jackson; 1977). The genera? lithology of the Cretaceus section from site 41-368 is shown in Fig. 2.

EXPERIMENTAL

The samples were obtained from the working cores of the DSDP repository. All samples were freeze-dried, powdered and treated in the same manner for extraction, thin-layer chromatographic (TLC) separation, analysis by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), and for kerogen isolation and analysis (Fig. 3).

Lipid Extraction and Separation

The lipid material was extracted by shaking the dry sediments (after carbonate dissolution) with portions of 1:1 chloroform and methanol mixture (Simoneit, et al., 1979). Each extract was checked for the presence of elemental sulfur (Cu wire). Only if the tests were positive, was the extract volume reduced to 20 ml and the bulk of the crystalline sulfur removed. This sulfur was washed with methanol and retained for stable isotope analysis.

The extracts were then derivatized with BF_3 in methanol prior to TLC. Precoated Adsorbosil-5 (20 cm x 20 cm, 250 μm, Applied Science] TLC plates were cleaned by elution with ethyl acetate and then activated at 130°C for 30 min. After application, the samples were eluted in 100% CH_2Cl_2. Each plate was examined under UV light and was then developed in an iodine chamber. The major bands corresponding to the hydrocarbon, fatty acid ester and ketone fractions were scraped off and eluted with CH_2Cl_2 (Simoneit et al., 1979).

Four samples (2,3,15,18) containing substantial amounts of asphaltenes were treated with pentane prior to the TLC separation. Asphaltenes were isolated by precipitation with pentane, shaking, centrifugation, and removal of the supernatant by aspiration. This procedure was repeated several times until the supernatant became colorless. The asphaltenes were air-dried and retained for $\delta^{13}C$ analysis.

In a few cases where the GC traces indicated the presence of complex mixtures of either hydrocarbons or fatty acid esters, separations using urea adduction were performed by the method described (Simoneit, 1975; Gaskell, 1974).

All GC analyses were carried out using a Hewlett Packard Mode? 5830A gas chromatography equipped with a flame ionization detector and glass WCOT columns (30m x 0.25 mm) coated with either OV-10'? or SE-30 (SGE Scientific, Inc.). The operating conditions utilized a temperature program from 100-275*C at 2°C/minute and isothermal at 275°C for one hour, with the injector temperature at 280°C and the detector at 300°C. The concentrations of the resolved compounds were calculated using response factors derived from standards.

The GC/MS analyses were carried out on a Finnigan Model 4000 quadruple mass spectrometer interfaced directly with a Finnigan Model 9610 gas chromatograph equipped with a 30m x 0.25mm glass capillary column (J&W, Inc.), which was wall-coated with OV-101. The GC for the GC/MS analyses was programmed from 40-260°C at 6°C/min., then held isothermal for 80 minutes. The mass spectrometric data was acquired and processed using a Finnigan-Incos Model 2300 data system.

Kerogen Separation and Analysis

The extracted sediments were air-dried and checked for the presence of humic substances by extraction with 0.2 N NaOH. It was found that the amounts of humates were negligible and that this step was not necessary prior to the isolation of kerogen. The samples *were* treated with a 1:1 mixture of 6 N HCl and 60% HF (Baker Analyzed Reagent) for mineral removal until no further reaction occurred. Samples were washed with double-distilled water, and then mixed in a zinc bromide ($ZnBr_2$) solution Of density 2.1 by ultrasonication for 20 minutes. Separation of the kerogen (float) by centrifugation at 2500 rpm for 20 minutes was followed by a Millipore wash using double-distilled water and double-distilled methanol through pre-washed glass fiber filters (55 mm Whatman GF/A). Finally, the kerogen was freeze-dried and weighed.

e

Electron spin resonance (ESR) measurements and elemental analyses (C, H, N and ash) were made using procedures and apparatus described in Peters et al., (1978). Sulfur content was determined by Galbraith Laboratories, Knoxville, Tennessee.

Carbon and hydrogen stable isotope analyses were carried out using the procedures described by Stuermer et al. (1978), where Chicago Pee Dee Belemnite (PDB) and Standard Mean Ocean Water (SMOW), respectively, were the reference standards. . Sulfur stable isotope analyses were carried out by the procedure as described by Kaplan et al. (1970) and Crisp et al. (1979), using troilite from Canyon Diablo Meteorite as reference standard. Nitrogen isotope analyses were carried out by the procedure as described by Cline and Kaplan (1975) and Sweeney et al. (1977), using atmospheric. nitrogen as reference standard. The data are expressed in the δ notation: "

$$\delta^{13}C,\ \delta^{34}S,\ \delta^{15}N,\ \delta D\ (‰) = \left[\frac{R_{sample} - R_{standard}}{R_{standard}}\right] \times 1000$$

where R is the $^{13}C/^{12}C$, $^{34}S/^{32}S$, $^{15}N/^{14}N$ or D/H ratio, respectively.

RESULTS AND DISCUSSION

The sample descriptions, analytical results for the lipids (the solvent soluble organic matter, also called bitumen) and the elemental compositions are given in Table 1. The data for samples 1-23 are given sequentially with increasing depth. Data for additional samples (24-39] are taken from work of various other authors (Erdman and Schorno, 1977; Dow, 1977; Baker *et al.*, 1977; Kendrick *et al.*, 1977; Deroo *et al.*, 1977) for comparison and completeness. Samples 39-41 are composite sediments which were used for thermal simulation experiments carried out in this laboratory (Simoneit *et al.*, in preparation]. The locations of samples 1-23 are indicated in the lithologic column of Fig. 2 by the circled numerals. Some of the preliminary data have been published (Simoneit *et al.*, 1978).

The-sediments in the proximity of the. sills and between the sills (e.g., samples 4-8) appear to be altered by elevated temperatures' (baked]. Samples 10-12 are light gray in color and partially fused, indicating that most of the organic matter had been expelled. Samples 4-12 and the contacts with the intrusions exhibit microfissures, veining and rusty areas, indicating mineralization and alteration due to circulation of hydrothermal fluids..

The organic carbon values vary due to lithologic differences, but they are generally lower near the intrusions (cf., Table 1 Figure 4a). Sample 3, from 20 cm above the upper sill, contains 38% calcium carbonate, indicating that its thermal stress did not exceed about 900°C, the maximum temperature for decomposition of $CaCO_3$. Significant "carbonate values are also observed for other samples (8,1'1 ,14,16,17, 21, 25 and 36). Sample 8 is located about 80 cm above the major sill and appears heavily carbonized. The other carbonate-containing samples are from below the major sill, in the relatively unaltered region.

Total nitrogen contents range from 0.03 to 0.30% and based on the atomic C to N ratios do not appear to show any linear trends due to the thermal stress imposed by the intrusions. Sample 8 is an exception where the C/N = 85.5, and samples 31 and 32 exhibit C/N ∿ 40, which is also high.

Lipids

Based on the lipid data, samples 2, 20-23, 36-39 and 41 resemble typical unaltered black shale as found at other DSDP sites in the Atlantic Ocean (eg., 41-367--Simoneit, 1977a; or others--Simoneit, 1978a, 1980a). The overall yields of total solvent-soluble material for these 10 samples are variable due to the content of asphaltic (in altered samples) or polar material (in unaltered samples) and in some cases, elemental sulfur. The amounts of _n_-alkanes and _n_-fatty acids exhibit a minimum near and between the sills (cf., Table 1}. In unaltered black shales, the phytane (Ph) concentration is much greater than that of pristane (Pr) (e.g., Simoneit, 1980a), reflecting the strongly anoxic paleoenvironmental conditions of sedimentation (Didyk _et_ al., 1978). This relationship is. observed for samples 1,2,21,23,25,38,39 and 41. However, the Pr-to-Ph ratio appears to be strongly affected by the major sill and is > 1.0 above that sill with a maximum of 2.86 in sample 6 (about 3 m above the sill) and then decreases again in the sill proximity. Coming up to the sill from below, a lesser maximum is observed for sample 15 (about 2.5 m below), indicating that more pristane was generated than phytane by thermal release from kerogen, or preferential thermal destruction of phytane. Both the Pr and Ph contents decrease nearer the sill, possibly due to cracking to smaller molecules.

a) homolog distributions

Examples of typical analytical GC traces for fractions from an unaltered sample (number 21) are shown in Fig. 5. The total hydrocarbons exhibit a bimodal hump with phytane as the dominant hydrocarbon (Fig. 5A). The urea adduct fraction (predominantly n-alkanes) is shown in Fig. 5B and the branched and cyclic non-adduct fraction, which has phytane as the major peak, a bimodal unresolved hump, and a series of steroidal and triterpenoidal hydrocarbons, in Fig. 5C. The branched and cyclic fraction was further separated. by TLC into saturated (essentially the same GC as Fig. 5C), alkyl aromatic (naphthenes, low concentration in this sample, GC in Fig. 5D) and polycyclic aromatic hydrocarbons (GC in Fig. 5E). The GC traces of the total fatty acid (as methyl esters) and ketone fractions are shown in Fig. 5F, where n-C_{16} acid is predominant and the homologs range to n-C_{34}.

Examples of typical analytical GC traces for a heavily altered sample (number 6) are shown in Fig. 6. The total hydrocarbons (Fig. 6A) exhibit a broad hump with only minor amounts of n-alkanes, while the urea adducted n-alkanes (Fig. 6B) are minor components, and the branched and cyclic non-adducts (Fig. 6C) are similar to the total. The thermal stress has cracked the n-alkanes to other prodcts, thus reducing their overall concentration. The branched and cyclic fraction was further separated by TLC into saturated (essentially the same GC as Fig. 6C), alkyl aromatic (Fig. 6D) and polycyclic aromatic hydrocarbons (Fig. 6E).

The distributions of the n-alkanes (with Ph and Pr) for the samples investigated here are found in Fig. 7. These distributions and their concentrations vs. those of the isoprenoids for samples 2,20-23, 36-39 and 41 are typical of Cretaceus black shales from the Atlantic (e.g., Simoneit, 1978b, 1980a). The lower weight homologs (<n-C_{25}) exhibit essentially no carbon number predominance, with maxima at n-C_{15}, C_{17} and C_{23}. Such a distribution is attributable to an autochthonous origin from microbiota (Simoneit, 1978b, 1980b).

The higher weight homologs (> n-C_{25}) exhibit a strong odd-to-even carbon number predominance, with maxima at n-C_{29} or n-C_{31}, indicating a plant wax origin

(Simoneit, 1978b, 1980 b). Sample 1 appears to contain a larger autochthonous algal component and it is not a typical black shale (the organic carbon content is only 0.66%). Samples 14-20 and 36 exhibit a progressive dilution of the higher n-alkanes by the more volatile homologs, maximizing at n-C_{17}. Samples 3-12 from the proximity of or between the sills exhibit low levels of n-alkanes with narrow distributions maximizing at n-C_{17}, *or* in some cases n-C_{15}, C_{19}, or C_{22}. Sample 4 shows higher weight homologs (> n-C_{21}) with a strong even-to-odd carbon number predominance, possibly reflecting reduction of oxygenated species. The distribution patterns of the n-alkanes for samples 3-12 do not appear to be derived from primary biogenic production. These alkanes are probably thermal alteration products that formed in situ or were redistributed since the Miocene. The alkane distribution for sample 8 is very narrow, with a higher yield (180 ppm) and CPI (1.21) than its neighbors. This sample is from between the major and middle sills, which are only 1.6 m apart. We suggest that these thermally-altered hydrocarbons have remained more *or less* in situ between the sills since the thermal event.

Examples of some distribution diagrams of the n-fatty acids and the C_{18} isoprenoid ketone (6,10,14-trimethylpentadecan-2-one), are found in Fig. 8 a-g. The fatty acid distributions of samples 2 and 21 are typical of Cretaceous black shales from the Atlantic (e.g., Simoneit, 1980a). The homologs (even carbon number predominance) > n-C_{20} have an allochthonous higher plant origin and the homologs < n-C_{20} appear to be of an autochthonous marine derivation (Simoneit, 1978b, 1980b). The fatty acids of sample 1 are of predominantly a marine origin, with a minor higher plant component. The fatty acids of samples 16-20 (eg., Fig. 8c) indicate various degrees of dilution by lower weight homologs analogous to the alkanes. The significance of these distributions is, however, not clear. Samples 3-12 from the proximities of or from between the intrusions contain low levels of fatty acids with very similar distributions. A strong even-to-odd carbon number predominance is observed, with a maximum at n-C_{16} and essentially *no* homologs > n-C_{22}. These distributions may reflect microbial activity in the cores since collection, and thus less significance can be assigned to these traces of fatty acids. However, unsaturated fatty acids are not detectable, indicating a non-recent origin. The fatty acids may, therefore, have come from thermally stable salts or by redistribution from external sources since the Miocene. The C_{18} isoprenoid ketone, present in low amounts in all samples, may reflect microbial activity or oxidative weathering since recovery and during storage.

The overall yields of total hydrocarbons and the pristane to phytane ratios are plotted versus subbottom depth in Fig. 4b. Maximum yields and ratios are observed about 7 m below and above the major sill. This indicates that the intrusive event distilled the liquid products to approximately those distances, where they have remained superimposed on the endogenous bitumen. Above the sill, it appears that some of the volatilized organic matter may have been lost due to lateral migration through sand or carbonate layers (cf., Fig. 2).

Alkylcyclohexanes, C_nH_{2n}, ranging from n = 12 to 31 are present in the lipids of all samples that were nut pyrolyzed by the sill intrusions. Some examples of distributions are found in Fig. 8 h-k, showing that their ranges extend beyond C_{24}, which may indicate a dual origin. This can be compared with the distribution for a Jurassic siltstone of marine origin in Fig. 8k (DSDP site 330, Simoneit, 1980c), where the range extends *only* to C_{24}, indicating a bacterial origin (Simoneit, 1978b, 1980 b). The homologs > C_{24} may be bacterial metabolizes of terrigenous long-chained compounds.

b) Stable isotope composition

The stable carbon isotope data for the unaltered bitumen ranges from -27.0 to -28.5°/00 , with the exception of sample 24 (Table 1). These values are within the range typical for non-marine lipid matter and the $\delta^{13}C$ of -23.7 ‰ for sample 24 is within the range typical for marine lipids '(Kaplan, 1975; Degens, 1969).

Interstitial gas (predominantly CH_4) from site 368 has been analyzed for $\delta^{13}C$ and composition (Doose et al., 1977). The CH_4 becomes isotonically heavier with depth (-65 to -55 ‰) and is -51 ‰ between the sills. The yield of C_1-C_4 hydrocarbons increases in the sill proximity, which also reflects the effects of the thermal stress imposed by the sill intrusions.

c) Molecular Markers:

Two classes of molecular markers are present in the bitumen of this sample suite. They are the natural biogenic markers which are characteristic of a terrigenous or marine origin, and compounds formed as a consequence of the intrusion. The markers that can be correlated with a biogenic origin consist of sesqui-, di-, and triterpenoids, and steranes.

Sesquiterpenoid residues are found only in samples 1, 2 and. 39 as traces of tetrahydrocadalenes and di- and trimethyltetrahydronaphthalenes. These compounds could be derived from either a marine (algal) or terrestrial (higher plant) origin (Simoneit, 1980d). The diterpenoids are more prevalent in these lipids, while diterpenoid residues and extended diterpanes are found in the unaltered samples from above and below the sills. The diterpenoid residues consist of primarily dehydroabietic acid (I), dehydroabietin (11} and retene (III), with minor amounts of simonellite, norsimonellite, pimanthrene and tetrahydroretene in some of the samples. These compounds are derived from terrestrial resinous plants (Simoneit, 1977b). Extended diterpanes, C_nH_{2n-4}, are found fOr n = 20 to maximum concentrations at n = 21 and 23 and very similar distributions (cf., Fig. 9). Their mass spectra are characterized by a base peak at in/z 191, the molecular ion (M*) and $M^{+}-CH_3$, which fits for the carbon skeleton of Structure IV (Anders and Robinson, 1971). The $C_{26}H_{48}$ homolog is resolved into two diastereomers on GC/MS, indicating. a methyl branching in the side chain. This compound series has been identified in shale and petroleum (Reed, 1977), and in Recent sediments (Simoneit and Kaplan, 1980; Simoneit, unpublished results].

Triterpanes are significant components in all unaltered samples (1,2,12,15, 17<,18,20,21,39 and 41 and traces in 10). Both the extended diterpanes and most triterpanes exhibit a strong fragment ion (base peak) at m/z 191 in their mass. spectra. Thus, the relative distributions of these compounds can be represented by this m/z 191 peak intensity from the GC/MS data. *Some* examples are shown in Fig. 9. The triterpanes in these samples consist predominantly of the 17α(H), 21β(H)-hopane series, with lesser amounts of the 17β(H),21β(H) isomers and the 17β(H),21α(H)-moretanes. "The hopane series comprises 17α(H), and 178(H)- -trisnorhopane (V, R = H), 17α(H),21β(H)-norhopane (V, R = C_2H_5), 17α(H)- and 17 β(H) -hopane (V, R = C_3H_7), and extended 17α(H),21β(H)-hopanes (VI) ranging 'rem C_{31} 'o C_{35} and resolved into the S and R diastereomers at the C-22 position. The moretane series consists of 17β(H),21α(H)-normoretane (VII, R = H), 17β(H),21α(H)-moretane, (VII= CH_3) and 17β(H),21α(H)-homomoretane (VII, R = C_2H_5). No triterpenes were detectable in any sample. Tine homolog distributions are qualitatively similar, and for the samples which contain distillation products superimposed on the endogenous bitumen (12-15, 17, 18, and 20), the pattern is geologically mature. This is based on the predominance of the 17α(H), -21β(H) homologs and a 22S to 22R ratio of about one for the extended 17α(H)-hopanes (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980). Seifert and Moldowan (1980) determined this S/R ratio for mature samples to be in the range of

1.4 to 1.6 by using capillary columns which give baseline resolution of the C-22 epimers. Samples 1, 2, 21, 39 and 41 in the unaffected lithology exhibit an S/R ratio of about 0.5 to 0.7 for the extended 17α(H)-hopanes. The distributions of the extended hopanes are not uniform from C_{31} to C_{35} and the relative concentrations of the moretanes are greater than in the case of samples 12-15, 17, 18 and 20. Laboratory simulation experiments should provide further evidence on whether these distributions and S/R ratio differences are due to dilution by bitumen distillate or are caused by the thermal stress.

Significant quantities of steranes are present in all unaltered samples and consist primarily of the 5α(H) and the 58(H) series (VIII, R = H), with minor amounts of 4-methylsteranes (VIII, R = CH_3), monoaromatic diasteranes (IX) and diasteranes (X). The 5α(H)-steranes (trans) are predominant over the 5β(H)-steranes (cis), i.e., cholestane > coprostane, and range from C_{27} to C_{30}. The C_{30} homolog has a base peak at m/z 217 and a molecular ion at m/z 414 (with M^+-CH_3 at m/z 399) and may be a 24-propylcholestane. This basic skeleton has been identified in some marine organisms (eg., Idler et al., 1971). The ratios of the cis to trans stereomers are 0.3-0.4 for samples 1, 2, 21, 39 and 41 and 0.4-0.6 for samples 12-14, 17, 18 and 20, with 0.7 for sample 15. Ratios for mature source rocks and petroleums have been observed in the range of 0.6-0.8 (eg., Seifert and Moldowan, 1978). Thus, the bitumen distillate appears to be more mature than the endogenous lipids. Some examples of the sterane distributions (based on m/z 217) are found in Fig. 8 1-0. Cholestane (VIII, R = H, R' = H, 5α) is the predominant homolog for all samples. The distributions appear to be of a more terrigenous nature (Goad et al., 1972; Rubinstein, 1972; Gasken, 1974) when compared with samples that are known to contain organic matter from a largely autochthonous marine source, eg., 36-330-10-1 (Jurassic, Simoneit, 1980c).

Aromatic hydrocarbons whose structures can be correlated with an origin from biogenic precursors are found as minor components in the unaltered samples (eg., sample 21, the PAH fraction, cf., Fig. 5e). Various polymethylnaphthalenes and mono-to-trimethylphenanthrenes are present and they are probably derived from sesqui- and diterpenoid residues (Simoneit, 1977b). The major peak (Fig. 5e) is a norsimonellite and lesser amounts of retene, simonellite and dinorsimonellite are present. These are diterpenoid residues from terrigenous sources (Simoneit, 1977b). The dominant peaks abovee 275°C in Fig. 5e were Identified as aromatic triterpenoid derivatives, consisting of 7-methyl-3'-ethyl-1,2-cyclopentenochrysene (XI); (3'-ethylcyclopenteno-7,8)1,1-dimethyl-tetrahydro(1,2,3,4)-chrysene (XII); 8,14,18-trisnormethyl adianta-8,11,13,15,17-pentaene (XIII); 14,18-bisnormethyladianta-13,15,17-triene (XIV) and lesser amounts of possibly 3,4,7-trimethylchrysene; 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene (XV) and 3,3,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene (XVI). These compounds" were identified in shales and petroleum and confirmed by synthesis (Greiner et al., 1976; '1977; Spyckerelle et al., 1977a, b). The pentacyclic analogs (XI-XIV) are derived from olefins (ring E or side chain) of the hopane and/or moretane series by successive dehydrogenation, which proceeded from ring D to A (Greiner et al., 1976; 1977). These compounds can be considered as markers of predominantly marine microbial sources. The tetracyclic analogs eg., (XV, XVI) are probably derived from 3-oxygenated triterpenoids (eg., β-amyrin) by bio- or geo-degradative processes leading to the loss of ring A, followed by successive dehydrogenation which proceeded from ring B to E (Spyckerelle et al., 1977a,b). These compounds are thus potential markers of terrigenous higher plants. Pentacyclic aromatic hydrocarbons (analogs to XI-XIV), where the aromatization would proceed from ring A to D (probably from a ring A olefin), are not detectable in these samples.

The aromatic hydrocarbons of the altered samples exhibit different distributions of compounds (eg., sample 3, Fig. 6c), concentrated more in the lower molecular weight range and consisting of polynuclear aromatic hydrocarbons with low alkyl substitution. The GC/MS data for the total branched and cyclic hydrocarbon fraction (by TLC) from sample 4 is summarized in Fig. 10. The dominant compounds are dibenzothiophene, phenanthrene, methyldibenzothiophenes, methylphenanthrenes and methylfluorenes with lesser quantities of di- and trimethylnaphthalenes, fluorene, methyldibenzofurans, dimethylphenanthrene, pyrene, methylpyrene and chrysene. The presence of dibenzothiophenes, coupled with-the large amount of elemental sulfur, indicates that these compounds are derived from pyrolytic reactions caused by the diabase intrusions.

Asphaltenes and Humic Substances

Asphaltenes are present in some samples (cf., Table 2) and a higher yield is apparent in the thermally-altered samples (Table 2). The H/C ratios are about 1.0, indicating rather aromatic material. The $\delta^{13}C$ data range from -25 to -28 ‰ (Table 2).

Humic substances are present in trace amounts only in unaltered shale (samples 2 and 21) and were not further examined.

Kerogen

The kerogen from unaltered shale at site 368 was found to be geologically immature (Deroo *et al*., 1977; Bogolyubova and Timofeev, 1978). The results of the kerogen analyses are found in Table 2 together with data' for the other samples taken from the work of Deroo *et al.* (1977); Erdman and Schorno (1977); Dow [1977); Baker *et al*. (1977); and Kendrick *et al.* (1977). The ash contents of the isolated kerogens were rather variable, and because of the small sample sizes, further purification was generally impractical. Thus only the f-t/C and

N/C (and not O/C) values could be calculated from the elemental analyses. A plot of H/C vs. depth in the sediment is shown in Fig. 4c. A dramatic decrease of H/C in the sill proximity is evident, indicating aromatization of the kerogen as a result of the thermal stress. The N/C values also exhibit a minimum near the sill; however, they are somewhat more scattered. A correlation plot of N/C vs. H/C is shown in Fig. 11. For comparison, additional data points are plotted for humic acids and kerogens isolated from diverse Recent environments, e.g., lacustrine and marine sediments, peats, algal mats, and soil (Stuermer et al., 1978). The unaltered kerogens from this site cluster in the lower right portion of the plot and the altered kerogens cluster in the lower left (i.e., they are highly aromatic).

a) Vitrinite reflectance

The results of oil immersion vitrinite reflectance (R_o) determinations are given in Table 2 and a plot of R_o vs. distance from the major sill is shown in Fig. 12a. Reflectance values near the intrusion are higher at a given distance above than at the same distance below the sill (Peters et al., 1978). "Cold" reflectance values occur at a distance of less than one sill width (15 m) into the country rock. It appears that the two thin (~ 20cm) sills can be ignored in terms of their effect on the overall maturation of these sediments. The main explanation for the differences in reflectivity above and below the sills is the better transfer of heat upward by volatiles emitted from the magma during solidification and from the pore water of the intruded shale (Peters et al., 1978). Below the sill, these volatiles would be restricted from upward migration by the intrusion. Similar conclusions were reached by Briggs (1935) from studies of coals intruded by sills.' The greater alteration of vitrinite above, rather than below, the sill could not have been due to simple conduction of either heat or pressure. Since the heat would be less able to escape downward, heating by simple conduction must have been more intense and prolonged immediately below the sill.

The country rock temperature history was reconstructed from the vitrinite data (Peters et al., 1978). For a 15-m-thick sill, a 1000°C magma-country rock temperature difference, a 100 cal/g latent heat of crystallization, and a sediment saturated with water at about 600 m depth of" burial, the plot of theoretical temperature versus distance from the intrusion (Fig. 12) was drawn using the method of Jaeger (1959). As shown in the figure, theoretical values of country rock temperature agree fairly well with those based on a calibration using vitrinite reflectance values of Eocene lignitic shale from hydrothermal bomb experiments (Bostick, 1971)..

In addition to an unusual alkane distribution (Fig. 7), sample 8 provides an anomalously low R. value (Fig. 12).. The kerogen contains abundant fragments of "coked" bitumen, characterized by its anisotropic or "mosiac" structure (Crelling and Dutcher, 1978). Smaller quantities of this material were found in samples 6 and 7. Sample 8 is located between the major and overlying minor sills (Fig. 1). The low atomic N/C for this kerogen is in the range of most thermally-polymerized, solidified bitumens (Waples, 1977).

Although the heat provided by the minor sills must have been insignificant compared to the major intrusion; they may have served as impediments to the migration of volatiles and thermally-generated bitumen. The higher thermal conductivity and diffusivity of diabase compared to shale (Lovering, 1936), however, preclude the possibility that the smaller sills acted as traps for heat. The anomalously low reflectance value for the vitrinite in sample 8 may thus be the result of extreme thermal stress on the sapropelic material in the sedimentary matrix and subsequent absorption of trapped, thermally-generated bitumen into the associated vitrinite. This may have retarded the rate of reflectance maturation in the vitrinite.

Vitrinite reflectance values for these samples also correlate with certain geochemical parameters of the kerogen (Table 2), such as the atomic H/C ratio (Fig. 13a), the carbon isotopic ($\delta^{13}C$) composition (Fig. 13b) and the ESR spin density (N) (Fig. 13c). The kerogen appears to become more aromatized or hydrogen deficient in the sill proximity, whereas kerogen from the thermally-unaltered sediment exhibits a more aliphatic character with a relatively high H/C. The $\delta^{13}C$ of the thermally-altered kerogens (cf., Table 2) is heavier than that of the unaltered samples, indicating that the lighter isotope of carbon was preferentially lost 'during the thermal event. An alternative explanation is that a thermally-labile fraction of the kerogen, which was originally of a lighter carbon isotopic composition than the bulk kerogen, was preferentially destroyed (A.N. Feux, personal communication). Similar changes in the carbon isotopic composition of kerogen with maturity have been observed in regionally metamorphosed sediments (Hoefs and Frey, 1976; McKirdy and Powell, 1974), although these metamorphic thermal events lasted much longer than that caused by these diabase intrusions:

b) Electron spin resonance spectroscopy

ESR spectroscopy has been used to find paleotemperatures and the degree of organic maturity for sediments and kerogen (Pusey, 1973; Ishiwatari et al., 1977). Pusey (1973) considered the type of organic matter as a minor factor in his calibration of ESR signals against known paleotemperatures. However, humic-type kerogen has a higher spin density than the sapropelic-type (Ho, 1977; Stuermer et al., 1978). This may account for the variation of ESR data when compared to vitrinite reflectance determinations on the same sample (Burgess,. 1977). The spin density (N) represents the number of unpaired electrons which are stablized by the kerogen structure. This value appears to-be the most reliable ESR criterion for maturity determination (Ho, 1977). Spin density values for kerogens from this site are plotted versus reflectance in Fig. 13c.

A similar curve is obtained when the spin concentration is plotted versus H/C. The latter case closely resembles curves developed from artifical heating of kerogens (Ishiwatari et al., 1977; Peters, 1978). Briefly, as immature kerogen is heated, reflectance values rise and thermally-generated free radicals are stabilized by delocalization over aromatic n-bonds. Eventually, the density of unpaired electrons reaches a maximum, after which further heating results in electron pairing and loss of the free radical absorption.

The kerogens from site 368 are primarily sapropelic, with little variability in original composition throughout the sampled interval (Dow, 1977; Tissot et. al., 1978). Consequently, the correlation of R. with bulk properties of the kerogens (such as elemental composition, carbon isotopic ratio, and spin density) can be attributed primarily to thermal, rather than source effects.

c) Stable isotope compositions

The results of the $\delta^{13}C$, $\delta^{34}S$ and δD determinations on kerogens are found in Table 2. The $\delta^{13}C$, δD and the $\delta^{34}S$ become heavier near the sill., where they range from > -25 ‰ for C, > -100 ‰ for H and > -5 ‰ for S, to about -27 ‰ for C, - 140 ‰ for H and -280/.0 for S (pyrite) in the unaltered kerogens. This indicates a preferential loss of the lighter isotopes (^{12}C, H and ^{32}S) during the thermal activity.

A correlation plot of H/C versus $\delta^{13}C$ is shown in Fig. 13d, which includes some other Recent kerogen data (Stuermer et al., 1978; Simoneit, 1980a). A shift of about 2 ‰ to heavier values is observed for the altered kerogens. Similar shifts were observed in laboratory simulation experiments by Peters et al. (1981).

The sulfur content of the bulk samples (Table 1) consists of pyrite and organic sulfur in the relatively unaltered samples and of large amounts of elemental and organic sulfur in the samples from near the major sill. The $\delta^{34}S$

data for pyrite in kerogen and elemental sulfur are found in Table 2 and they are plotted" versus depth in Fig. 4d. The values of $\delta^{34}S$ in the unaltered shales range from -10 to -28‰ and cover the range for bacterially-produced sulfur ($\delta^{34}S \sim -20$‰ , Kaplan et al., 1963).ncrease in the $\delta^{34}S$ values of the kerogenous and pyritic sulfur adjacent to the major sill to about -1 to -8‰, may be due to the input of magmatic sulfur as-a consequence of leaching processes acting on the diabase after its emplacement. The $\delta^{34}S$ data for the elemental sulfur from the proximity of the-major sill show an average value of about -7.4‰ with no definite trends. This elemental sulfur is probably derived from the disproportionation of pyrite in the presence of organic matter at elevated intrusion temperatures. The isotopic values measured for this elemental sulfur are only about 3‰ enriched in ^{32}S relative to the average values for pyrite associated with the sills.

The $\delta^{15}N$ data are scattered from -0.3 to +4.5‰ and exhibit no apparent isotope effect due to thermal stress.

CONCLUSIONS

The thermal effects of the diabase intrusions on the organic matter of the Cretaceus black shale from site 368 are evident in the following parameters: (1) for the hydrocarbons - total yield, presence of sulfur compounds, and Pr/Ph and (2) for kerogen - H/C, $\delta^{13}C$ and δD (possibly $6^{34}S$), vitrinite reflectance measurements, ESR data and the presence of elemental sulfur (cf. Tables 1 and 2).

The total hydrocarbon yield exhibits a maximum about 7 m below the major sill and a lesser increase at about 6-8 m above that sill. The lower content above the major sill indicates that the expelled volatiles may have migrated out laterally along sand (silt) or carbonate units, whereas below the sill they have remained in relatively high concentrations. The total hydrocarbon yield reaches a minimum in the proximity of the major intrusion; however, a relative increase in hydrocarbon content in sample 8 may be due to entrapment between sills.

The Pr/Ph ratio also approaches a minimum near the major sill. The molecular markers (eg., hopanes) were derived from primarily autochthonous marine sources, with some analogs of a terrigenous origin. The stereochemical distributions of the hopanes indicated almost complete epimeric equilibrium and the intrusions resulted only in the migration of these markers away from the sill without any significant further isomerization. The traces of bitumen in the vicinity of the sills consist primarily of polycyclic aromatic hydrocarbons with some sulfur and oxygen heterocyclic aromatic compounds. These compounds were derived by secondary reactions during the thermal event.

Kerogen was isolated from all samples, but only traces of humic substances were present and asphaltenes were separated from some samples. The kerogens become more aromatic in nature toward the major sill (i.e., hydrogen content decreases--low H/C, Fig. 4c), whereas the kerogens of the relatively unaltered sediments exhibit a more aliphatic character (i.e., higher H/C). The H/C values in the sill proximity fall in therange of 0.1-0.5, which indicates extremely aromatic kerogen. The $\delta^{13}C$, $\delta^{34}S$ and δD data also reflect the effects of the thermal stress due to the intrusion, where the samples nearer the sill are richer in the heavier isotopes ^{13}C, ^{34}S and D. The thermally induced maturation is evident in the vitrinite reflectance and electron spin resonance data,. where the thermal stress could be correlated with an elevated temperature of the country rock and an increased degree of aromaticity.

The major effect of the intrusion on the organic-rich shales was the generation and expulsion of petroliferous bitumen from the vicinity of the sills, leaving behind a hydrogen-depleted carbonaceous residue (kerogen) with a highly aromatic character. Organic matter; in the form of both bitumen and kerogen (also gas) is a sensitive indicator for geothermal events and canbe utilized to assess the genetic sources-of that organic matter.

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REFERENCES

Anders, D. E. and Robinson, W. E. (1971). Cycloalkane constituents of the bitumen from Green River Shale. Geochim. Cosmochim. Acts 35: 661-678.

Baker, E.W., Huang, W.Y., Palmer, S.E., and Rankin, J.G. (1977a). Mass and electron paramagnetic resonance spectrometric analyses of selected organic components of Cretaceous shales of marine origin, in Symposium on Analytical Chemistry of Tar Sands and Oil Shale, Amer. Chem. Soc., New Orleans, March 20-25, 1977: 739-752.

Baker, E.W., Huang, W.Y., Rankin, J.G., Castãno, J.R., Guinn, J.R. and Fuex, A.N. (1977b). Electron paramagnetic resonance study of thermal alteration of kerogen in deep-sea sediments by basaltic sill intrusion. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y.. Lancelot, E. Seibold, et al. (eds. , U.S. Govt. Printing Office, Washington, D.C.: 839-847.

Bogolyubova, L.I. and P.P. Timofeev (1978). Composition of organic matter in "black shales" of the Cape Verde Basin (Eastern Atlantic) and their potential as petroleum source beds. Lithology and Mineral Resources 13; 519-530.

Bostick, N.H. (1971). Thermal alteration of elastic organic particles as an indicator of contact and burial metamorphism in sedimentary rocks . Geoscience and Man 3: 83-93.

Briggs, H. (1935). Alteration of coal-seams in the vicinity of igneous intrusions, and associated problems. Trans. Inst. Mining Eng. 89: 187-219.

Burgess, J.D. (1977). Historical review. and methods of determining thermal alteration of organic materials. Palynology 1: 1-8.

Cline, J.D. and Kaplan, I.R. (1975). Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. Mar. Chem. 3: 27'1-299.

Comer, J.B. and Littlejohn, R. (1976). Content, composition and thermal history of organic matter in Mesozoic sediments, Falkland Plateau. In Initial Reports of the Drilling Drillin Project, Vol. 36, P.F. Barker, I.W. Dalziel et al. (eds Govt. Printing Office, Washington, D.C.: 947-944.

Crelling, J.C. and Dutcher, R.R. (1977). A petrologic study of a thermally-altered coal from the Purgatoire River Valley of Colorado. Geol. Sot. Amer. Bull. 79: 1375-1386.

Crisp, P.T., Brenner, S., Venkatesan, M.I., Ruth, R., and Kaplan, I.R. (1979). Organic chemical characterization of sediments from particle traps in San Nicolas, Santa Barbara, Santa Monica and San Pedro Basins, California. Geochim. Cosmochim. Acts, 43: 1791-1801.

Dastillung, M., and Albrecht, P., (1976). Molecular test for oil pollution in surface sediments. Mar. Poll. Bull. 7: 13-15.

Degens, E.T. (1969). Biogeochemistry of stable carbon isotopes. In Organic Geochemistry, Methods and Results, G. Eglinton and M.T.J. Murphy, eds., Springer-Verlag, Berlin: pp. 304-329.

Demaison, G.J. and Moore, G.T. (1980). Anoxic environments and oil source bed genesis. Organic Geochem. 2: 9-31.

Deroo, G., Herbin, J.P., Roucaché, J., Tissot, B., Albrecht, P. and Schaeffle, J. (1977). Organic geochemistry of some Cretaceus black shales from Sites 367 and 368, Leg 41, Eastern North Atlantic. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., U.S. Govt. Printing Office, Washington, D.C.: pp. 865-873.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C. and Eglinton, G. (1978). Geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature, 272: 216-222.

Doose, P.R., Sandstrom, M.W., Jodele, R.Z. and Kaplan, I.R. (1977). Interstitial gas analysis of sediment samples from Site 368 and Hole 369A. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., U.S. Govt. Printing Office, Washington, D.C.: pp. 861-863.

Dow, W.G. (1977). Contact metamorphism of kerogen in sediments from Leg 41 Cape Verde rise and basin. In Initial Reports of the Deep Sea Drilling Project. Vol. 41, Y. Lancelot, E. Seibold, et al., eds., U.S. Printing Office, Washington, D.C.: pp. 839-847.

Duncan, R.A. and Jackson, E.Il. (1977). Geochronology of Basaltic rocks recovered by DSDP Leg 41, Eastern Atlantic Ocean. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., (eds..), U.S. Govt. Printing Office, Washington, D.C.: pp. 1113-1118.

Erdman, J.G. and Schorno, K.S. (1977). Geochemistry of carbon: Deep Sea Drilling Project, Leg 41. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., U.S. Govt. Printing Office, Washington, D.C.: pp. 849-853.

Gaskell, S.J. (1974). The environmental geochemistry of sterols, Ph.D. Thesis, University of Bristol, England: 321 pp.

Goad, L.J., Rubinstein, I., and Smith, G. (1972). The sterols of echinoderms, Proc. Roy. Soc. Lend. B180: 223-246.

Greiner, A.C., Spyckerelle, C. and Albrecht, P. (1976). Aromatic hydrocarbons from geological sources--I. New naturally occurring phenanthrene and chrysene derivatives, Tetrahedron 32: 257-260.

Greiner, A.C., Spyckerelle, C., Albrecht, P. and Ourisson, G. (1977). Aromatic hydrocarbons from geological sources. Part V. Mono- and di-aromatic hopane derivatives, J. Chem. Res. (S) 1977: p. 334.

Ho, T.T.Y. (1977). Geological and geochemical factors controlling electron spin resonance signals in kerogen: ASCOPE/CCOP Seminar on Generation and Maturation of Hydrocarbons in Sedimentary Basins, Manilla, Sept. 17-19, 1977 (in press).

Hoefs, J., and Frey, M. (1976). The isotopic composition of carbonaceous matter in a metamorphic profile from the Swiss Alps, Geochim. Cosmochim. Acts, 40: 945-951.

Idler, D.R., Safe, L.M. and MacDonald, E.F. (1.971). A new C-30 sterol (z) -24-propyl idenecholest-5-en-3β -ol, (29-methyl isofucosterol), Steroids 18: 545-553.

Ishiwatari, R., Ishiwatari, M., Rohrback, B.G. and Kaplan, I.R. (197'7). Thermal alteration experiments on organic matter from Recent marine sediments in relation to petroleum genesis, Geochim. Cosmochim. Acts, 41: 815-828.

Jaeger, J.C. (1959). Temperatures outside a cooling intrusive sheet, Am. J. Sci., 257: 44-54.

Kaplan, I.R., Emery K.O., and Rittenberg, S.C. (1963). The distribution and isotopic abundance of sulfur in Recent marine sediments off southern California. Geochim. Cosmochim. Acts, 27: 297-331.

Kaplan, I.R., Smith, J.W. and Ruth, E. (1970). Carbon and sulfur concentration and isotopic composition in Apollo 11 lunar samples, Proc. Apollo Lun. Sci. Conf., Geochim. Cosmochim. Acta Suppl. 1, Vol. 2: 1317-1329.

Kendrick, J.W., Hood, A. and Castaño, J.R. (1977). Petroleum-generating potential of sediments from Leg 41, Deep Sea Drilling Project. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al. (eds.), U.S. Govt. Printing Office, Washington, D.C.: pp. 817-819.

Kendrick, J.W., Hood., A., and Castaño, J.R. (1978). Petroleum-generating potential of sediments from Leg 40, Deep Sea Drilling Project. In Initial Reports of the Deep Sea Drilling Project, Vol. 40, Suppl. J.M. Bolli, W.B.F. Ryan, et al., U.S. Govt. Printing Office, Washington, D.C. : pp. 671-676.

Lancelot, Y., et al. (1975). The eastern North Atlantic, Geotimes, 20:18-21.

McKirdy, D.M. and Powell, T.G. (1974). Metamorphic alteration of carbon isotopic composition in ancient sedimentary organic matter: New Evidence from Australia and South Africa. Geology, 2; 591-595.

Natland, J. (1977). Composition of basaltic rocks recovered at sites 367 and 368 Deep Sea Drilling Project, near the Cape Verde Islands. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al., U.S. Govt. Printing Office, Washington, D.C.: pp. 1107-1112.

Perregaard, J. and E.J. Schiener (1979). Thermal alteration of sedimentary organic matter by a basalt intrusive (Kimmeridgian Shales, Milne Land, East Greenland). Chem. Geol. 26; 331-343.

Peters, K.E. (1978). Effects on sapropelic and humic proto-kerogen during laboratory-simulated geothermal maturation experiments, Ph.D. Thesis, Univ. of Calif. at Los Angeles: 172 pp.

Peters, K.E., Simoneit, B.R.T., Brenner, S., and Kaplan, I.R. (?978). Vitrinite reflectance-temperature determinations for intruded Cretaceus black shale in the Eastern Atlantic- In Symposium in Geochemistry: Low Temperature Metamorphism of Kerogen and Clay Minerals, Oltz, D.F. (cd.), SEPM Mtg., Oct. 5, Los Angeles, 1978: 53-58.

Peters, K. E., B.G. Rohrback and I.R. Kaplan (1981). Carbon and hydrogen stable isotope variations in kerogen during laboratory-simulated thermal maturation. AAPG. Bull. (In press).

Pusey, W.C. (1973). Paleotemperatures in the Gulf Coast using the ESR-kerogen method: Transactions--Gulf Coast Assoc. Geol. Sot., 23: 195-202.

Reed, W.E. (1977). Molecular compositions of weathered petroleum and comparison with its possible source. Geochim. Cosmochim. Acts 41: 237-247.

Rubinstein, I. (1973). A study of marine sterols, Ph.D. Thesis, Univ. of Liverpool, England.

Schlanger, S.O. and Jenkyns, H.C. (1976). Cretaceus oceanic anoxic events: Causes and consequences. Geol. en Mijnbouw 55: 179-184,

Seifert, W. K. and Moldowan, J.M. (1978). The effect of biodegradation on steranes and terpanes in crude oils. Conf. on Fossil Fuel Chem. and Energy, Laramie, Wyo., July 1978.

Seifert, W. K. and J.M. Moldowan (1980). The effect of thermal stress on source rock quality as measured by hopane stereochemistry. In Advances in Organic Geochemistry 1979, (A.G. Douglas and J.R. Maxwell, eds.), Pergamon Press, Oxford, in press.

Simoneit, B.R.T. (1975). Sources of" organic matter in oceanic sediments, Ph.D. Thesis, Univ. of Bristol, England: 300 pp.

Simoneit, B.R.T. (1977a). Leg 41 sediments lipids--Search for eolian organic matter in Recent samples and examination of a black shale. In Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot, E. Seibold, et al. (eds.), U.S. Govt. Printing Office, Washington, D.C.: pp. 855-858.

Simoneit, B.R.T. (1977b). Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acts 41: 463-476.

Simoneit, B.R.T. (1978a). Lipid analyses of sediments from site 364 in the Angola Basin, DSDP Leg 40. In Initial Reports of the Deep Sea Drilling Project, Vol. 40, Suppl., H.M. Bolli, W.F.B. Ryan, et al., U.S. Govt. Printing Office, Washington, D.C.: pp. 749-753.

Simoneit, B.R.T. (1978b). The organic chemistry of marine sediments. In Chemical Oceanography, 2nd Edition, J.P. Riley and R. Chester, (eds.), Academic Press, New York, Vol. 7, Chap. 39: pp. 233-311.

Simoneit, B.R.T. (1980a). Organic geochemistry of the shales and sapropels of the Cretaceus Atlantic. In Advances in Organic Geochemistry 1977, USSR Acad. Sciences, Moscow (in press).

Simoneit, B.R.T. (1980b). Terrigenous and marine organic markers and their input to marine sediments. In Proceedings of Symp. on Organic Geochemistry of Deep Sea Drilling Project Sediments, E.W. Baker, (ed.), Science Press, Princeton, N.J., (in press).

Simoneit, B.R.T. (1980c). Organic geochemistry of Mesozoic sediments from the Falkland Plateau, DSDP Leg 36 Site 330. In Initial Reports of the Deep Sea Drilling Project, Vol. 50, Y. Lancelot, E. Winterer et al., U.S. Government Printing Office, Washington, D.C., (in press).

Simoneit, B. R.T. (1980d). The composition, sources and transport of organic matter to marine sediments--The organic geochemical approach. in Proc. Symp. Marine Chem. into the Eighties, J.A.J. Thompson, cd., Nat. Res. Board Canada, (in press).

Simoneit, B.R.T., Brenner, S.," Peters, K.E. and Kaplan, I.R. (1978). " Thermal alteration of Cretaceus black shale by basaltic intrusions in the Eastern Atlantic. Nature .273: 501-504.

Simoneit, B.R.T., Mazurek, M.A., Brenner, S., Crisp, P.T. and Kaplan, I.R. (1 979).. Organic geochemistry of recent sediments from Guaymas Basin, Gulf of Cal ifornia, Deep-Sea Res. 26A: 879-891.

Simoneit, B. R.T. and Kaplan, I.R. (1979). Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern. California Bight. Mar. Environ. Res., (in press).

Spyckerelle, C., Greiner, A.C., Albrecht P. and Ourisson, G. (1977a). Aromatic hydrocarbons from geological sources. Part III. A tetrahydrocrysene derived from triterpenes, in Recent and old sediments: 3,3,7-Trimethyl-1,2,3,4-tetrahydrochrysene, J. Chem: Res. (S): 330-331.

Spyckerelle, C., Greiner, A.C., Albrecht, P., and Ourisson, G. (1977b). ., Aromatic hydrocarbons from geological sources. Part IV. An Octahydrochrysene derived frcm triterpenes, in oil shale: 3,3,7,12a-tetramethyl-1,2,3,4,4a,11,1 2,12a-octahydrocJ.yChem. Res. (S): 332-333.

Stuermer, D.H., Peters, K.E. and Kaplan, I.R. (1978). Source indicators of humic substances and proto-kerogen. Stable isotope ratios, elemental compositions and electron spin resonance spectra. Geochim. Cosmochim. Acts, 42: 989-997.

Sweeney, R.E., Liu, K.K., and Kaplan, I.R. (1978). Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In Stable Isotopes in the Earth Sciences, B.W. Robinson, (ed.), DSIR Bull. 220, Wellington, N-Z.: pp. 9-26.

Stump, R.K., and Frazer, J.W. (1973). Simultaneous determination of carbon, hydrogen and nitrogen in organic compounds. Nucl. Sci. Abst. 28: 7848.

Thiede, J., and van Andel, T.H. (1977). The paleoenvironment of anaerobic sediments in the late Mesozoic South Atlantic Ocean, Earth Planet. Sci. Lett. 33: 301-309.

Tissot, B., Deroo, G., and Herbin, J.P. (1979). Organic matter in Cretaceous sediments of the North Atlantic: Contribution to sedimentology and paleogeography. (In preparation).

Tissot, B., Durand, B., Espitalié, J. and Combaz, A. (1974). Influence of nature and diagenesis of organic matter in formation of petroleum. Amer. Assoc. Petrol. Geol. Bull., 58: 499-506.

Waples, D.W. (1977). C/N ratios in source rock studies. Mineral Industries Bull. 20: 1-7.

TABLE 1

SAMPLE DESCRIPTIONS FOR DSDP 41-368 AND RESULTS OF ELEMENTAL AND STABLE ISOTOPE ANALYSES, AND LIPID COMPOSITIONS

Sample		Depth below seabed (m)[1]	Distance from major sill (m)	Carbon[2]		$CaCO_3$[2]	Nitrogen		Sulfur	Lipids								
												Hydrocarbons				Acids		
													n-alkanes				n-Fatty Acids	
No.	Designation DSDP 41-368			Total (%)	Organic (%)	(%)	Total (%)	C/N	Total (%)	Total (µg/g)	$\delta^{13}C$ (‰)[3]	Total (µg/g)	CPI[4]	Cmax[5]	Pr/Ph	Total (µg/g)	CPI[4]	Cmax[5]
1	38-2 (106-114 cm)	923.6	+32.90	1.00	0.66	3.0	0.07	11.0	1.05	7,300	-27.0	220	1.16	23,31	0.52	50	5.2	16
2	59-3 (composited)	~947.0 (~942.0)	~+9.50	11.71	11.61	1.0	-	-	-	48,500		250	1.23	19,31	0.48	866	2.1	18,26
3	60-1 (121-127 cm)	950.7	+5.80	7.45	3.03	38.2	-	-	-	26,300		1,600	1.17	17,25	1.26	310	7.1	16
4	60-2 (133-140 cm)	952.6	+4.18	1.50	1.32	0.7	-	-	-	23,200[6]		150	1.12	17,19,26	n.r.	33	3.3	16
5	60-3 (48-52 cm)	953.0	+3.50	0.39	0.33	0.5	0.08	4.8	2.29	7,150[6]		75	0.99	19,22	1.29	45	11.5	16
6	60-3 (122-126 cm)	953.7	+2.80	6.81	4.78	0.3	-	-	-	29,700[6]		60	1.07	17,19	2.84	18	13.7	16
7	60-4 (37-39, 48-51 cm)	954.6	+2.10	2.30	2.36	0.2	-	-	-	11,600[6]		50	1.04	17,22,26	1.86	56	10.6	16
8	60-5 (12-18 cm)	955.7	+0.60	8.60	8.11	6.5	0.11	85.5	2.70	34,300[6]		180	1.33	17	1.05	33	10.[illegible]	16
9[7]	62-3 (18-26 cm)	971.7	4.17				-	-	-	—				—	—			—
10	62-3 ([illegible] cm)	[illegible]	-0.25	0.32	0.07	3.0	0.03	2.7	0.56	37,000[6]		70	1.01	19,22	0.78	26	8.3	16
11[7]	62-3 (70-80 cm)	972.3	-0.75	2.46	0.55 0.33	16.0	0.04	14.1	-	420		[illegible]	1.03	18	1.20			—
12	62-3 (109-114 cm)	972.6	-1.[illegible]	1.50	1.33	0.3	0.22	10.2	1.43	9,400		172	0.92	19,22	0.73	26	10.3	16
13	62-3 (120-128 cm)	972.7	-1.22				-	-	-	—				—	—			—
14[7]	62-4 (44-52 cm)	973.5	-1.95	8.42	6.63	15.0	-	-	-	4,490		2,083	1.15	18	2.50			—
15	62-4 (106-110 cm)	974.1	-2.55	6.74	6.70	[illegible]	-	-	-	48,000	[illegible]	3,110	1.07	17,19,23,31	1.12	410	2.40	16
16[7]	62-4 (118-126 cm)	976.2	-2.65	2.33	1.93 11.72	3.3	0.12	19.2	-	6,930		2,066	1.28	17	1.50			—
17	63-1 (48-53 cm)	978.5 (975.5)	-6.95	4.77	4.26	4.4	0.26	20.7	2.52	18,300	-28.2	5,300	1.04	17,19,[illegible]	1.02	1,100	2.90	16
18	63-2 (14-19 cm)	979.7 (976.1)	-8.15	3.70	3.59	1.0	-	-	-	16,200	-28.4	1,350	1.18	17,31	0.92	396	2.50	16
19[7]	63-2 (44-52 cm)	980.0 (977.0)	-8.45		1.55		0.16	13.1	-	—				—	—			—
20	63-2 (127-132 cm)	980.8 (977.[illegible])	-9.25	6.64	6.56	0.7	-	-	-	19,800	-28.5	1,560	1.21	15,19,29	0.80	650	1.23	14,15,18,26
21	63-3 (110-114 cm)	982.1 (979.1)	-10.55	8.56	7.10	12.0	0.30	27.6	1.32	21,600	-28.4	3,250	1.11	17,27	0.53	1,160	2.30	16,26
22[6]	63-3 (147-150 cm)	982.5 (979.5)	-10.95		1.11		-	-	-	—				—	—			—
23[7]	63-4 (90-98 cm)	983.6 (980.4)	-11.30	3.79	3.43 2.91	3.0	0.28	20.3	-	3,560	[illegible]	590	1.56	17,27	0.53			—
Miscellaneous Samples																		
24[9]	58-4	925.5 to 927.0	+31.1 to +29.6	3.90	0.80	0.8	0.06	15.5	-	150	-23.7	25		18,31	—			—
25[10]	59-1 (97-107 cm)	944.0 (939.5)	+12.5	3.78	3.30	4.0	-	-	-	3,700		[illegible]	—	15,29	0.60			—
26[7]	59-2 (0-8 cm) (109-114 cm)	944.5 (940.0)	+12.0				-	-	-	—			—	—	—			—
27[7]	59-3 (98-103 cm)	947.0 (942.5)	+9.5				—	—	—	—			—	—	—			—
28[7]	60-2 (53-63 cm)	951.6	+4.9		0.97		0.53	18.4		—			—	—	—			—
29[7]	60-3 (25-33 cm)	952.8	+3.7		1.44		0.52	14.5		—			—	—	—			—
30[7]	60-3 (142-150 cm)	954.0	[illegible]				-	-		—			—	—	—			—
31[7]	60-4 (55-63 cm)	954.6	+1.9		5.09		0.14	42.7		—			—	—	—			—
32[7]	60-4 (110-118 cm)	955.1	+1.4		2.18		0.07	38.6		—			—	—	—			—
33[7]	60-5 (28-36 cm)	955.8	+0.7		3.73		0.24	18.2		—			—	—	—	—		—
34[7]	60-5 (88-96 cm)	956.4	+0.1		0.20		0.22	1.1		—			—	—	—			—
35[7]	63-1 (68-76 cm)	978.7 (975.7)	-7.15				-	-	-	—			—	—	—			—
36[10]	63-3 (17-27 cm)	981.2 (978.2)	-9.65	8.20	7.60	10.0	-	-		18,500		1,500	—	17,[illegible],23	0.47			—
37[9]	63-3 (30-40 cm)	981.3 (97[illegible].2)	-9.75	1.21	0.97	2.0	0.06	1[illegible].3		960	-28.1	179	—	18,31	-			—
38[7]	63-5 (161-164 cm)	982.6 (979.6)	-10.65	1.62	1.38	2.0				1,120		196	1.29	18,27	0.70			—
39[11]	58/59-2/3/4/3 (composite)	921.0 to 944.0	+35.0 to -9.8	2.70	1.33	3.0				1,330		680	1.41	17,19,23,29	0.68	297	1.30	16,26
40[11]	60-3/4/5 (composite)	953.0 to 956.5	+3.5 to +0.3	3.47	1.25	2.0				—		46	1.35	17,19	1.55	16	11.20	16,26
41[11]	63-3/4/cc (composite)	980.5 to 984.5	-9.0 to -13.0	[illegible]	[illegible]	7.0				7,000		2,500	1.66	17,23,29	0.32	670	2.50	16,26

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[1] Depths are calculated upward from the core catcher; these are probably more representative of the true (absolute) depths than those obtained by the DSDP convention of measuring downward from the top of each core (if different, the DSDP depth is given in parentheses).

[2] Data from this laboratory and Galbraith Laboratories, Knoxville, Tennessee.

[3] Values expressed versus standard PDB.

[4] CPI (carbon preference index) summed from C_{10} to C_{35} (odd-to-even for n-alkanes and even-to-odd for n-fatty acids).

[5] The distribution maximum is underscored.

[6] These total lipid yields contain elemental sulfur.

[7] Data from Dow (1977) and Bauer et al. (1977).

[8] Data from Kendrick et al. (1977).

[9] Data from Erdman and Schorno (1977).

[10] Data from Deroo et al. (1977).

[11] Composited samples used for laboratory thermal alteration experiments (Simoneit et al., in preparation).

n.r. - not resolvable

TABLE 2

RESULTS OF THE KEROGEN AND ASPHALTENE ANALYSES FOR DSDP 61-368 SAMPLES

SAMPLE		KEROGENS										ASPHALTENES		
		Elemental Ratio		Isotope Ratio		Reflectance	ESR Parameters			Sulfur				
No.	Designation DSDP 61-368	H/C	N/C (C/N)	$\delta^{13}C$ (‰)[1]	δD (‰)[1]	R_o (modal)[2]	Spins/g ($x10^{17}$)	Line Width (G)	g value	Presence in Lipids as S or org. S	$\delta^{34}S$ (‰)[1,3]	Yield (µg/g)	H/C	$\delta^{13}C$ (‰)[1]
1	58-2 (106-114 cm)	0.86	0.020 (33.3)	-25.01	-167	0.1s				0	-27.95			
2	$9-2 (composite)	1.12	0.032 (31.3)	-26.63	-329	0.22	22.0	6.60	2.0022	0	-20.24	5,400	1.02	-25.5
3	60-1 [2233.7 cm)	0.86	0.100 (10)	-24.62	-70	1.05				0	-3.16	1,300		
4	(133-140 cm)	0.32	0.032 (40)	-23.87		1.45				+	(-7.33)			
5	60-3 (48-52 cm)	0.13	0.020 (20)	-24.50	● U	2.29				+	(-11.44)			
6	60-3 (122-126 cm)	0.32	0.036 (38.5)	-24.27	-95	2.29	4.08	18.1	2.0020	+	-1.19 (-6.44)			
7	[illegible] (37-39, 48-51cm)	0.22	0.027 (279			2.65	0	0	0	●	-7.69 (-7.6S1			
8	60-5 (12-18 cm)	0.17	0.007 (143)	-13.87	-96	1.55	0	0	0	+	-8.38 (-6.40)			
9[4]	62-3 (18-26 cm)		—			s. 22								
Lo	62-3 (28-34 cm)			-24.71	-72					●	-6.88 (-6.411			
11[4]	62-3 (70-90 cm)					1.95						60		
32	62-3 (109-114 cm)	0.27	0.014 (71.4)	-26.62	-229	2.26	2.89	3.78	2.0024	·	(-10.11)			
13[4]	62-3 (120-128 cm)					0.99		5.52	2.0030					
14[4]	62-4 (44-52 cm)					2.60 1.42		6.69	2.0030			247		
32	62-4 (106-110 cm)	0.65	0.052 (19.2)	-37.65		0.95	66.7	7.40	2.0024	0	-1.49	4,800		-27.0
16[4]	62-4 (118-126 cm)					1.64 0.68		6.40	z.0031			375		
17	63-1 (u-32 cm)	0.62	0.029 (34.5)	-27.16	-223	0.45	80.4	6.19	2.0025	0	-13.93			
18	63-2 (14-19 cm)	1.09	0.038 (26.3)	-27.75		0.63	33.8	6.24	2.0022	0	-11.23	820	0.98	-27.6
19[4]	63-2 (44-52 cm)		—	—		0.48		0.36	2.0033	0				
20	63-2 (127-132 cm)	1.88	0.060 (16.7)	-28.40	-32s	0.22	12.4	6.72	.7.0027		-LO. 03			
21	63-3 (110-116 cm)	1.06	0.026 (38.5)	-27.44	-147	0.35	27.5	?. 23	z.0025	0	-u. 25			
22[5]	63-3 (147-150 cm)		-	-		0.64		6.12	2.0031			—		
23[4]	63-4 (90-98 cm)		—	—		0.23 0.50		10.22	2.00'39			915		
Miscell— Samples														
24[6]	58-4			-31.3						2.3% S org.		59		
25[7]	59-1 (97-107 cm)	1.16	0.027 (37)	-								—		
26[4]	59-2 (0-8 cm)							10.23	z.0037			—		
27[4]	59-3 (98-103 cm)							9.46	2.0033					
28[4]	60-2 (55-63 cm)							6.46	2.0029					
29[4]	60-3 (25-33 cm)							3.25	2.0030					
30[4]	60-3 (142-150 cm)							19.32	2.0034					
35[4]	63-1 (68-76 cm)							7.34	2.0031					
36[7]	63-3 (17-27 cm)	1.17	0.023 (32.3)											
37[6]	63-3 (30-40 cm)	—		-29.6						2.5% S org.		261		
38[4]	63-3 (141-144 cm)	—				1.03						170		
40[8]	60-3/4/5 compos	—								+	-5.51			

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[1] Values expressed versus standard PDB, SMOW and CD troilite for C, H and S, respectively.

[2] Vitrinite reflectance expressed as modal percentage reflectance under oil immersion of incident light from about 100 randomly-oriented vitrinite particles per sample.

[3] Values are for kerogenous and pyritic sulfur, values in parentheses are for elemental sulfur from the lipid fractions.

[4] Data from Dow (1977) and Baker *et al.* (1977).

[5] Data from Kendrick *et al.* (1977).

[6] Data from Erdman and Schorno(1977).

[7] Data from Deroo *et al.* (1977).

[8] Data from Simoneit *et al.* (in preparation).

FIGURE LEGENDS

Figure 1: Location map of DSDP Holes 367 and 368.

Figure 2: Lithologic column showing the locations of samples 1-23 in the Cretaceus black shale sequence in the proximity of the sill intrusions.

Figure 3: Experimental flow chart for the sample preparation, fractionation, and analyses.

Figure 4: Distributions of organic carbon, hydrocarbons, atomic H/C, and stable sulfur isotopes with depth. (a) Total organic carbon content; (b) upper scale--total hydrocarbon content (●——●) and lower scale--pristane to phytane ratio (Pr/Ph, o. . . . . .o)(✦ data from Deroo et al., 1977; ✧ Erdman and Schorno, 1977; ▲ Dow, 1977, ◆ and ◇, averaged data from composite samples); (c) atomic H/C (✦ Deroo *et al.*, 1977); (d) δ^{34}S (● total kerogenous sulfur, ■ extracted elemental sulfur).

Figure 5: Analytical capillary gas chromatographic traces for lipid fractions from sample 41-368-63-3, 110-114 cm, an unaltered example (GC conditions as cited in the text) (a) total hydrocarbon fraction, (b) n-alkanes, (c) branched and cyclic hydrocarbons, 1-pristane, 2-phytane, (d) alkylarene fraction., (e) polynuclear aromatic hydrocarbon fraction, 1--norsimonellite, 2--3,3,7,13-tetramethyloctahydro(1,2,3,4,11,12,13,14)-chrysene (XVI), 3--14,18-bisnormethyladianta-13,15,17-triene (XIV), 4--3,3,7-trimethyltetrahydro(1,2,3,4)chrysene (XV), 5--8,14,18-trisnormethyladianta-8,11,13,T5Y17-pentaene (XIII), 6--(3'-ethylcyclopenteno-7,8)1,1-dimethyltetrahydro(1,2,3,4)-chrysene (XII), 7--(3'-ethylcyclopenteno-7,8)-1-methylchrysene (XI), (f) total fatty acid (as methyl esters) and ketone fraction.

Figure 6: Analytical GC traces for the lipid fractions from sample 41-368-60-1, 121-127 cm, an altered example (GC conditions cited in the text (a) total hydrocarbon fraction, (b) n-alkanes, (c) branched and cyclic hydrocarbons, (d) alkylarene fraction, (e) polynuclear aromatic hydrocarbon fraction.

Figure 7: Distribution diagrams of the normal and isoprenoid alkanes (concentration versus carbon number). The sample numbers are also given on each diagram: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, (f) sample 6, (g) sample 7, (h) sample 8, (i) sample 10, (j) sample 12, (k) sample 15, (l) sample 17, (m) sample 18, (n) sample 20, (o) sample 21.

Figure 8: Distribution diagrams of n-fatty acids, alkylcyclohexanes and steranes: n-fatty acids: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 15, (e). sample 18, (f) sample 20, (g) sample 21; alkylcyclohexanes: (h) sample 12, (i) sample 20, (j) sample 21, (k) sample 36-330-10-1, 95-102 cm

(Simoneit, 1979c); steranes (5αH —, 5βH —·—·—): (l) sample 1, (m) sample 12, (n) sample 18, (o) sample 36-330-10-1, 95-102 cm (Simoneit, 1979c).

Figure 9: Relative distribution histograms for extended diterpanes and triterpanes (based on the m/z 191 mass chromatograms) in the hole 368 samples: (a) sample 2, (b) sample 39 (Table 1), (c) sample 21, (d) sample 10, (e) sample 15, (f) sample 20.

Figure 10: Total ion current trace of the GC/MS analysis of the total branched and cyclic hydrocarbon fraction from sample 4. Peaks labeled are: 1--dimethyltetrahydronaphthalene; 2,3,4--dimethylnaphthalenes; 5 to 8,11--C_3-naphthalenes; 10--fluorene; 12,14--methyldibenzofuran; 13--*n*-hexadecane; 15,16--C_2-biphenyl; 17 to 20--methylfluorene; 21--*n*-heptadecane; 22--dibenzothiophene; 23--phenanthrene; 24,25,28--methyldibenzothiophene; 26,27,29--methylphenanthrene; 30--dimethylphenanthrene; 31--fluoranthene; 32--pyrene; 33--methylpyrene; 34--chrysene.

Figure 11: Correlation plot of atomic N/C versus H/C for the kerogens from site 368, compared with some kerogens and humic acids from Recent environments.

Figure 12: Temperature (°C) of country rock, determined after Bostik (1971), versus distance above (A) or below (=) the sill. The temperature range below the sill was predicted from porphyrin and kerogen rate assumptions (I) (Baker *et al.*, 1977a). Data of Baker *et al.* (1979b) for samples below the sill were also converted to temperature (●). The theoretical line after Jaeger (1959) is indicated (........).

Figure 13: Correlation plots of kerogen parameters: (a) R_o value versus atomic H/C, (b) R_o value versus $\delta^{13}C$, (c) R_o value versus EESR spin density ($N \times 10^{17}$ spins/g), (d) atomic H/C versus $\delta^{13}C$, ■ samples this work, ▲ samples in Stuermer *et al.*, 1978.

Appendix I - Chemical Structures Cited.

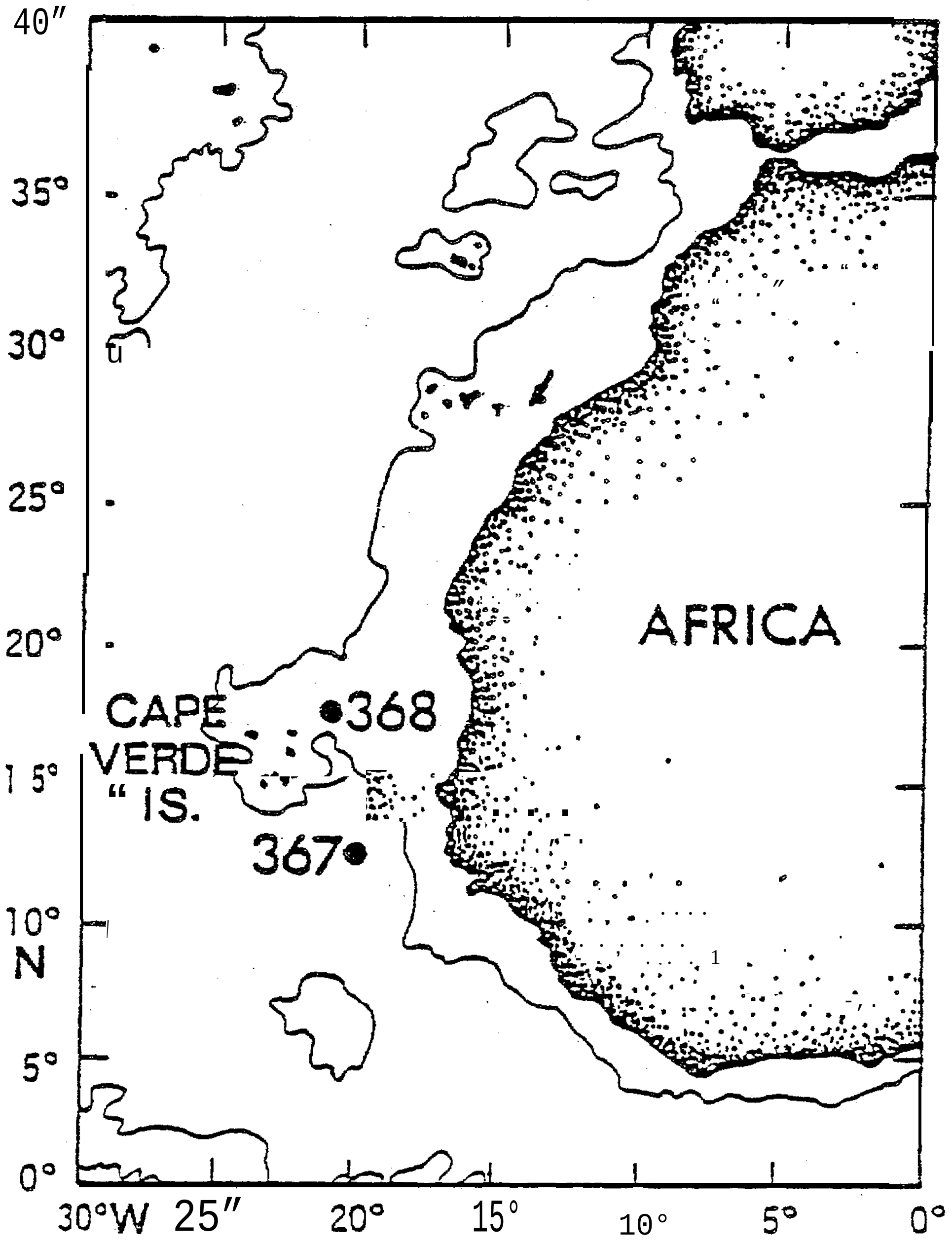
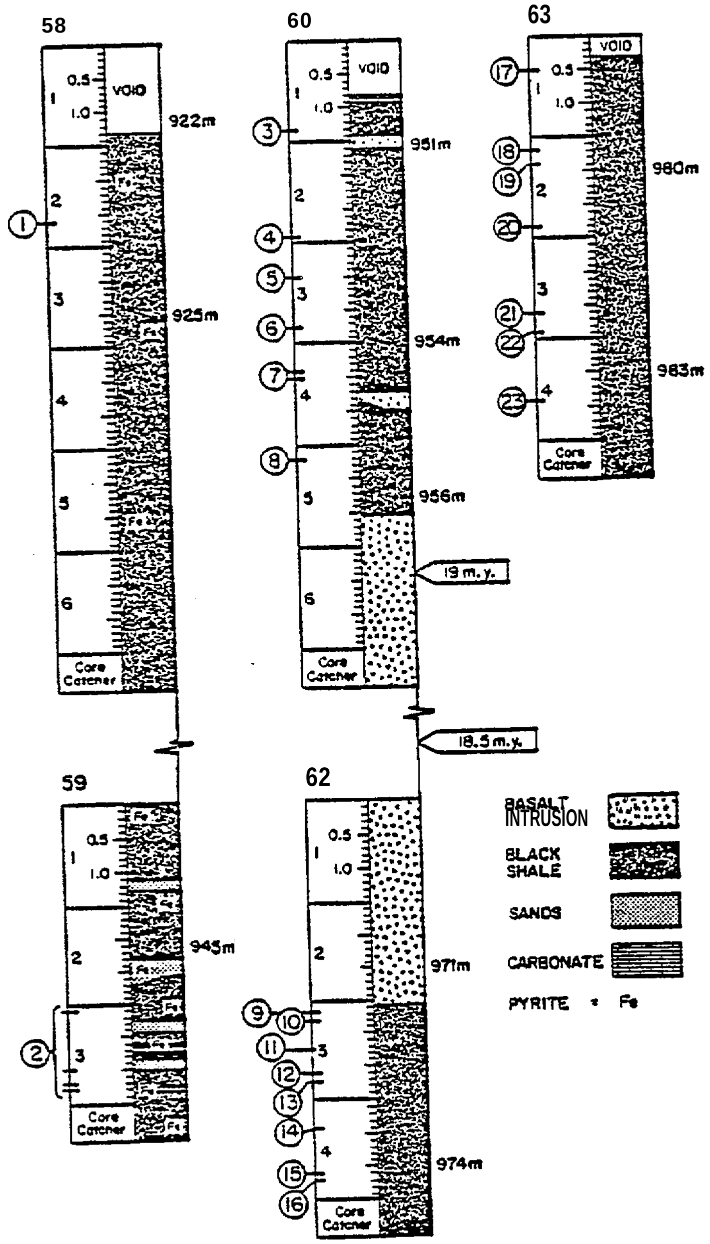

40″
35°
30°
25°
20°
15°
10°
N
5°
0°
30°W 25″
20°
15°
10°
5°
0°
AFRICA
CAPE VERDE IS.
368
367

Fig. 1



58
60
63
59
62
VOID
0.5
1.0
922m
925m
951m
954m
956m
945m
971m
974m
980m
983m
19 m.y.
18.5 m.y.
Core Catcher
Fe
BASALT INTRUSION
BLACK SHALE
SANDS
CARBONATE
PYRITE = Fe

Fig. 2

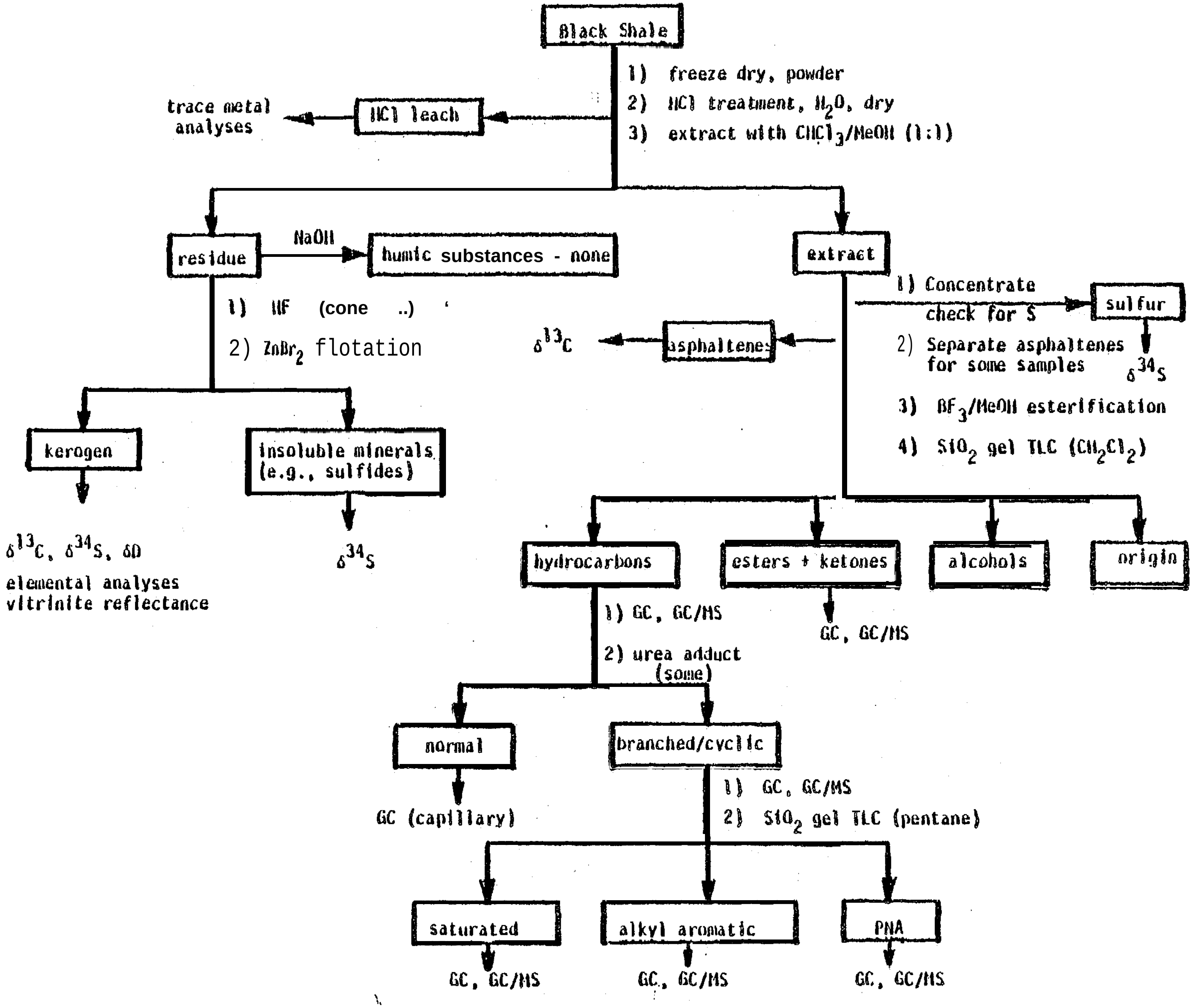

Black Shale
1) freeze dry, powder
2) HCl treatment, H2O, dry
3) extract with CHCl3/MeOH (1:1)
trace metal analyses
HCl leach
residue
NaOH
humic substances - none
extract
1) HF (conc.)
2) ZnBr2 flotation
kerogen
insoluble minerals (e.g., sulfides)
δ13C, δ34S, δD
elemental analyses
vitrinite reflectance
δ34S
δ13C
asphaltenes
1) Concentrate check for S
sulfur
δ34S
2) Separate asphaltenes for some samples
3) BF3/MeOH esterification
4) SiO2 gel TLC (CH2Cl2)
hydrocarbons
esters + ketones
alcohols
origin
GC, GC/MS
1) GC, GC/MS
2) urea adduct (some)
normal
branched/cyclic
GC (capillary)
1) GC, GC/MS
2) SiO2 gel TLC (pentane)
saturated
alkyl aromatic
PNA
GC, GC/MS
GC, GC/MS
GC, GC/MS

Fig. 3

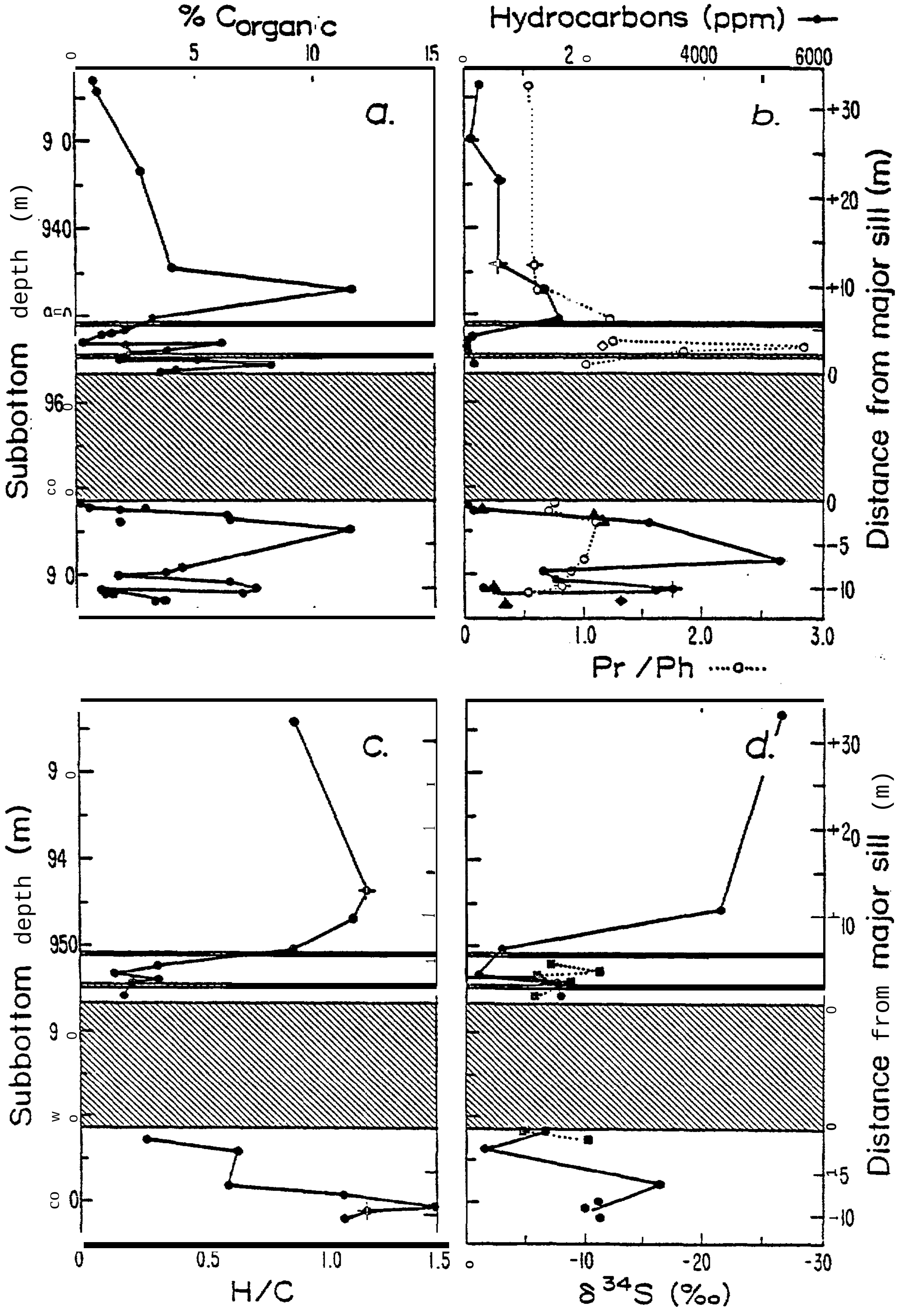
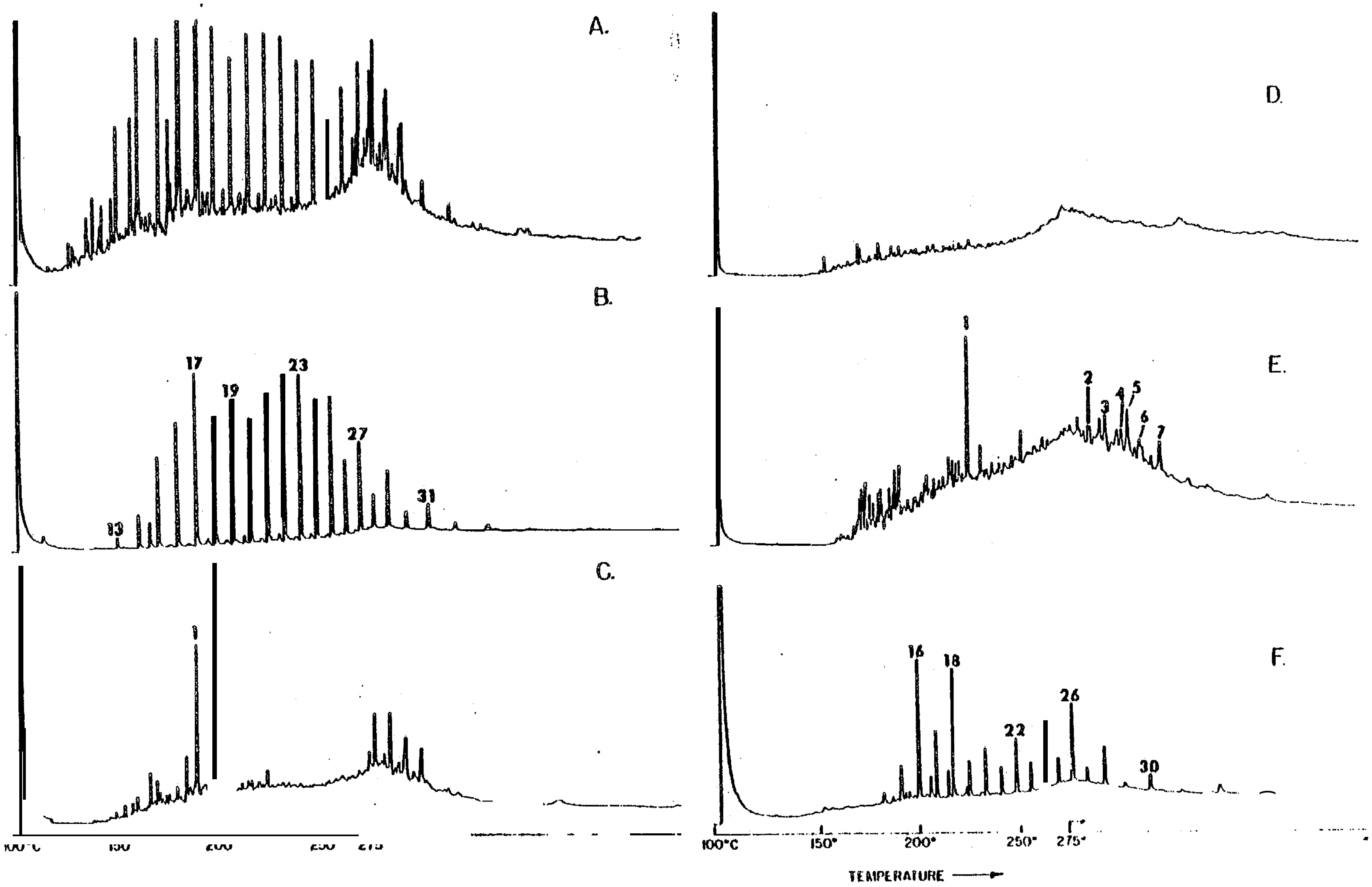

% Corganic
0
5
10
15
Hydrocarbons (ppm)
2
4000
6000
a.
b.
Subbottom depth (m)
940
96
9 0
Distance from major sill (m)
+30
+20
+10
0
-5
-10
0
1.0
2.0
3.0
Pr / Ph
c.
d.
Subbottom depth (m)
9 0
94
950
Distance from major sill (m)
+30
+20
+10
0
-5
-10
0
0.5
1.0
1.5
H/C
0
-10
-20
-30
δ³⁴S (‰)

Fig. 4


A.
B.
C.
D.
E.
F.
13
17
19
23
27
31
1
2
3
4
5
6
7
16
18
22
26
30
100°C
150°
200°
250°
275°
TEMPERATURE

Fi 5

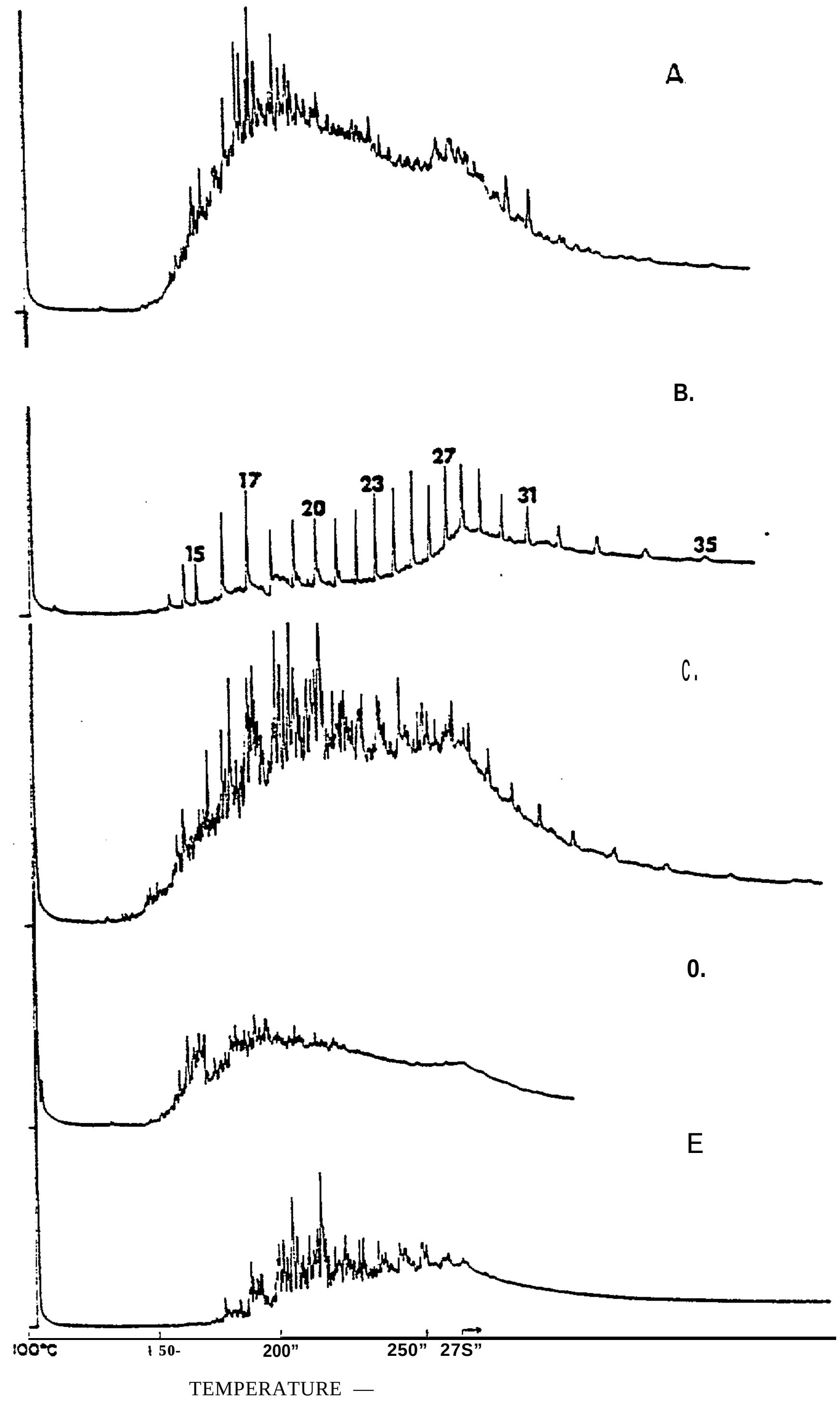


Fig. 6

Alkanes ⟶

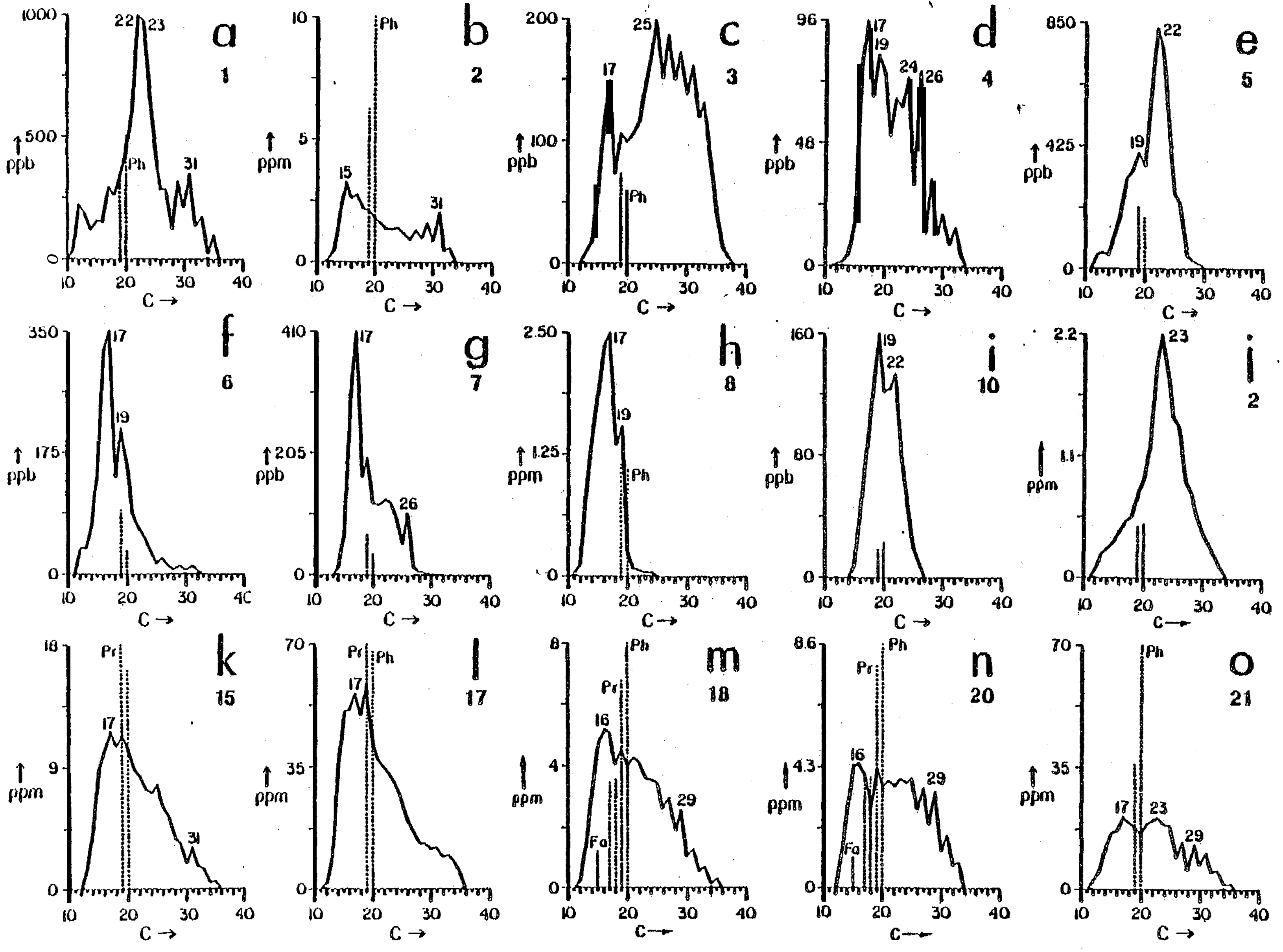


Fig. 7

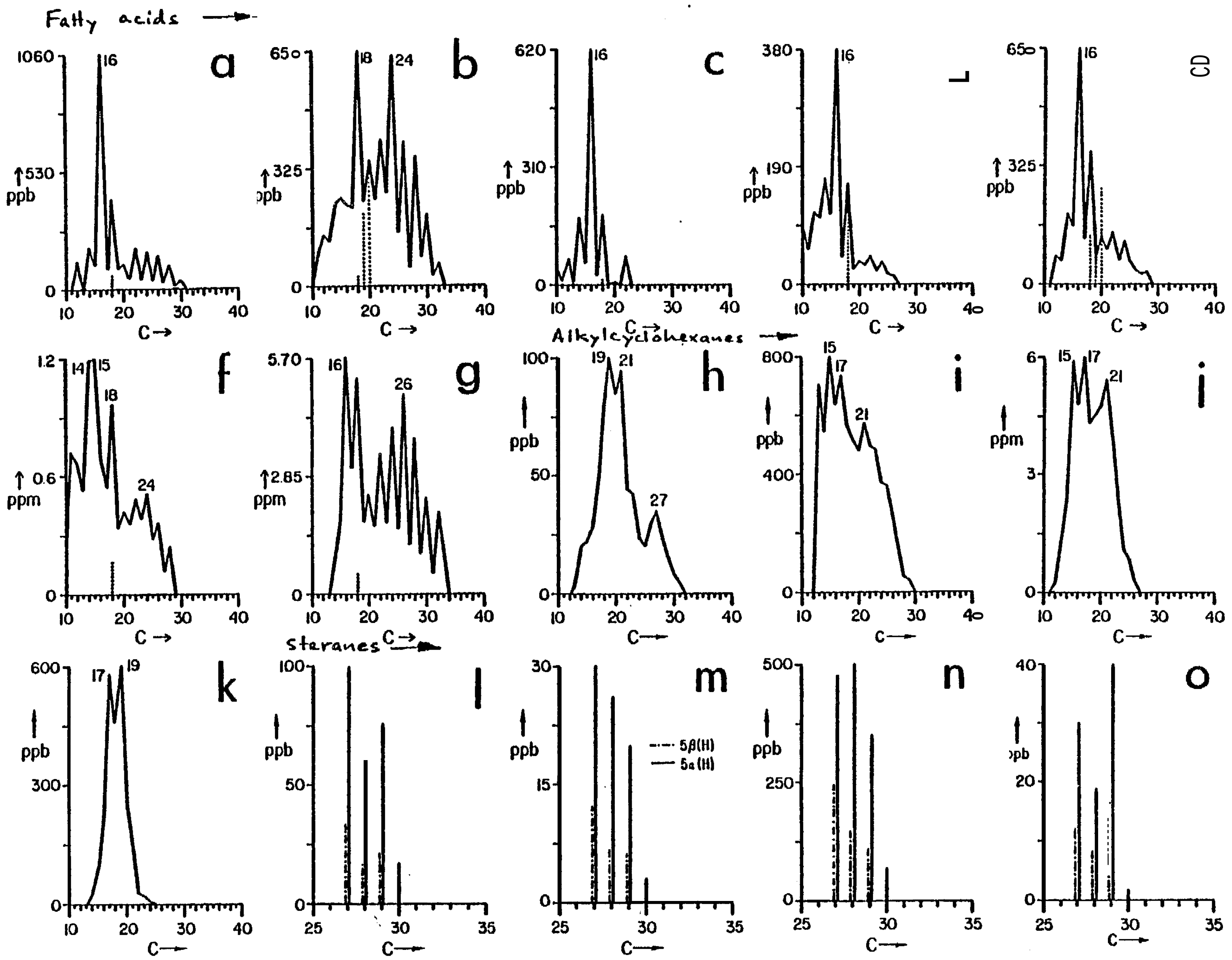

Fatty acids
a
1060
530
ppb
0
16
10
20
30
40
C →
b
650
325
ppb
18
24
c
620
310
16
L
380
190
16
CD
650
325
16
f
1.2
0.6
ppm
14
15
18
24
g
5.70
2.85
16
26
Alkylcyclohexanes
h
100
50
19
21
27
i
800
400
15
17
21
j
6
3
15
17
21
steranes
k
600
300
17
19
l
100
50
25
30
35
m
30
15
5β(H)
5α(H)
n
500
250
o
40
20

Fig. 8

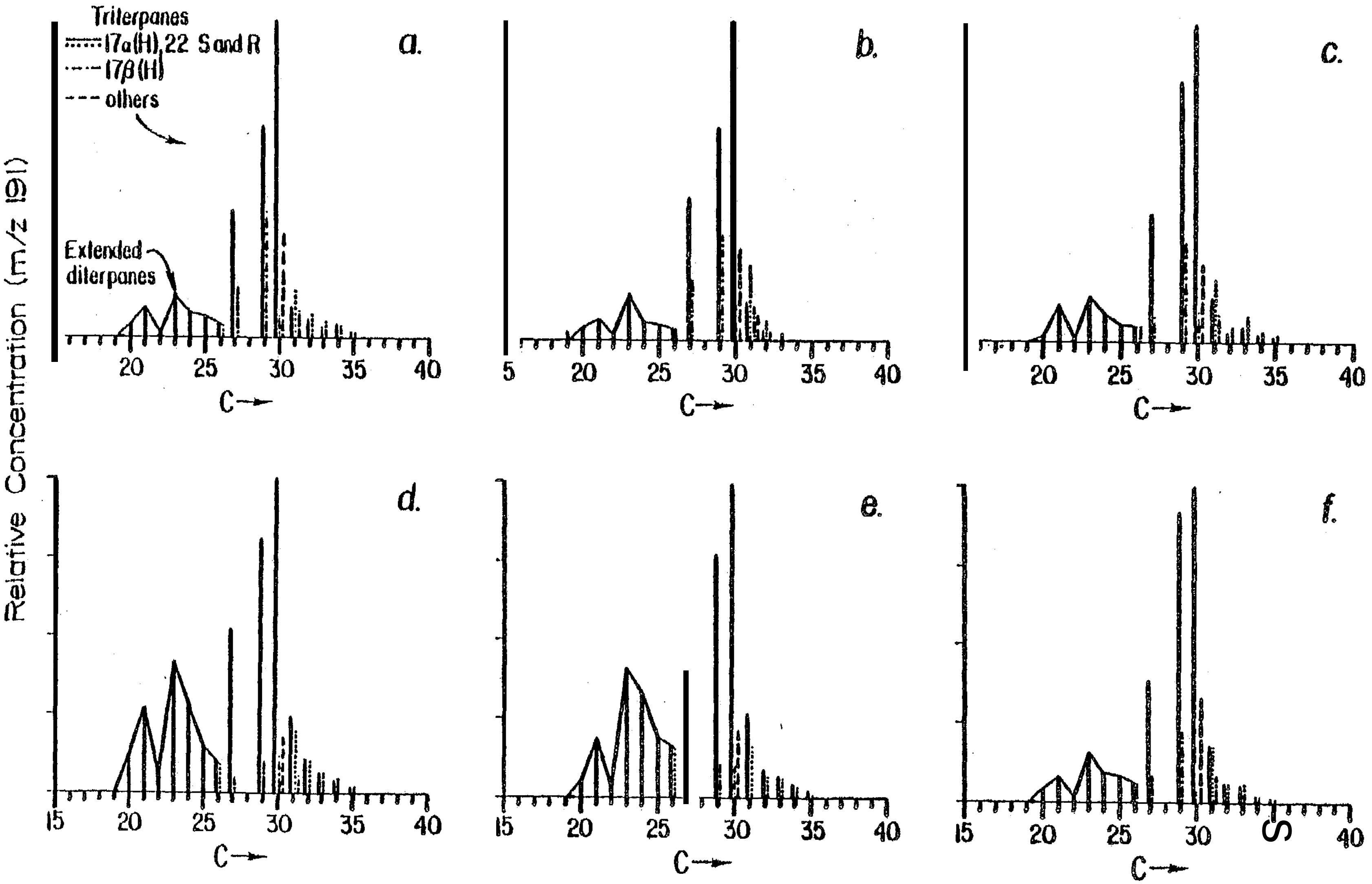

Triterpanes
17α(H), 22 S and R
17β(H)
others
Extended diterpanes
Relative Concentration (m/z 191)
a.
b.
c.
d.
e.
f.
5
15
20
25
30
35
40
C→

Fig. 9

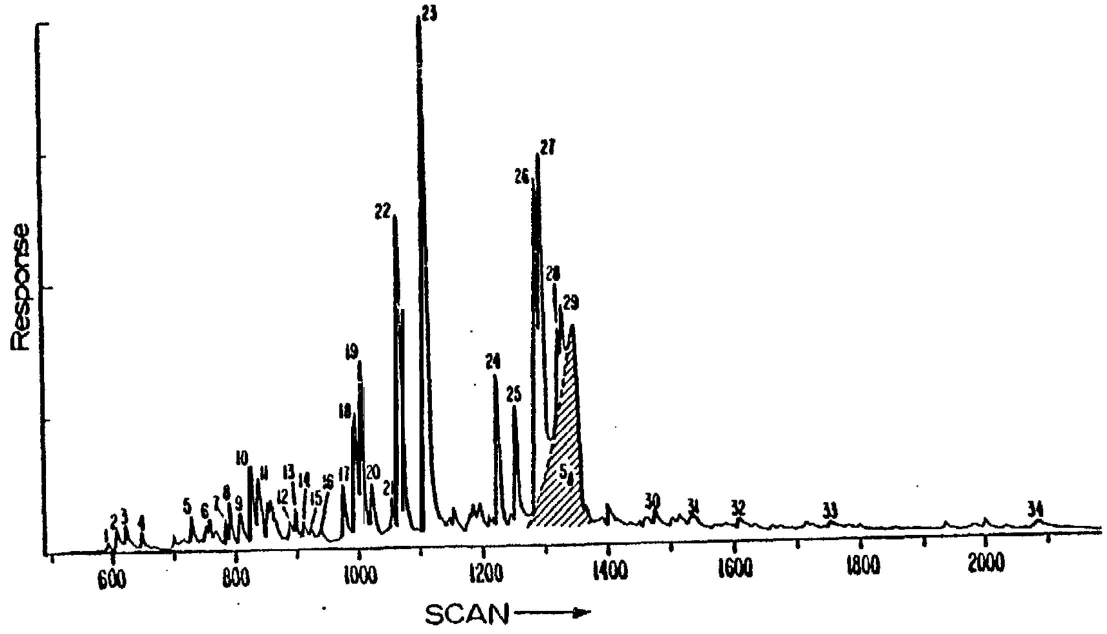

Response
SCAN
600
800
1000
1200
1400
1600
1800
2000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

Fig. 10

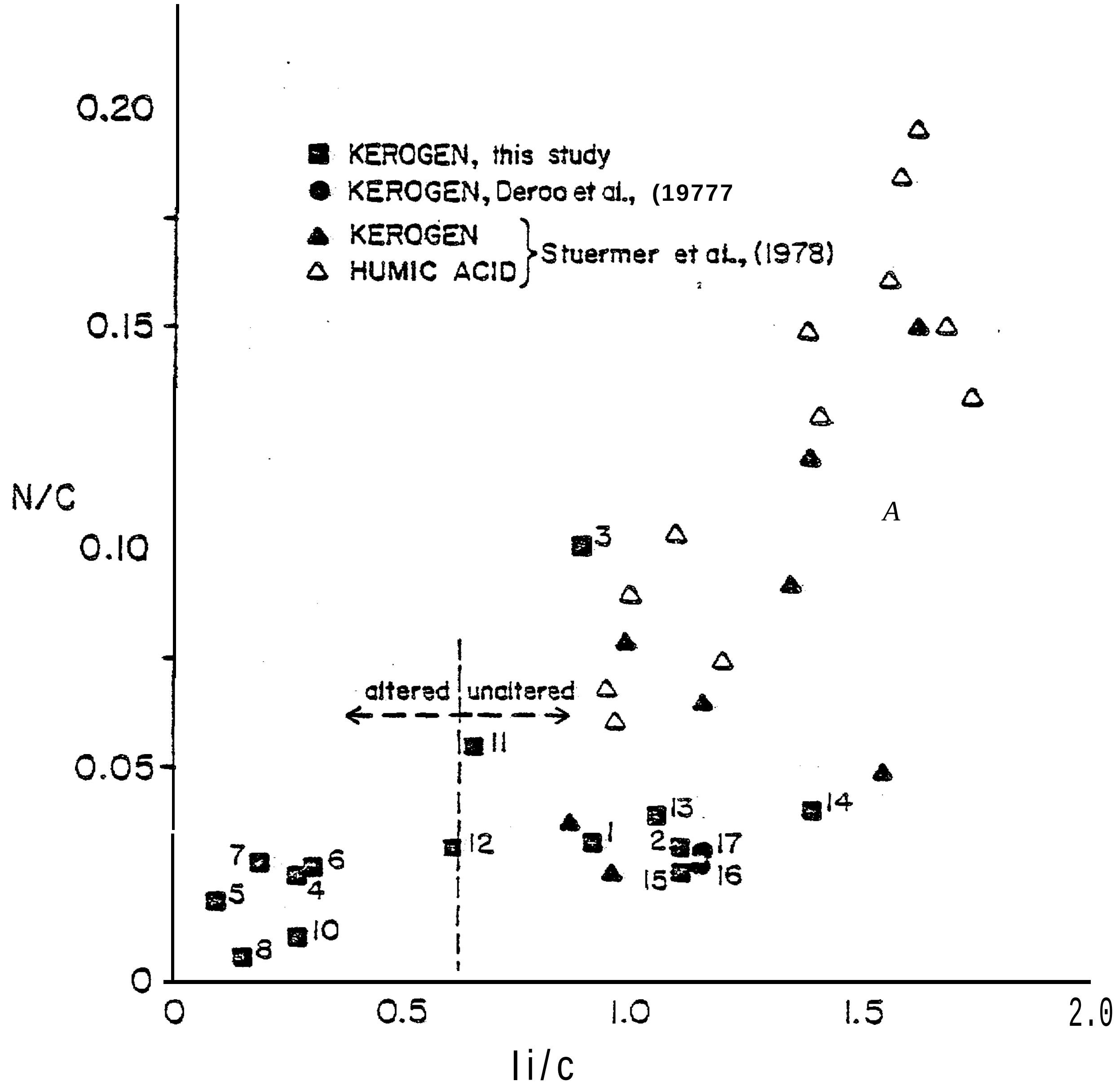

0.20
0.15
0.10
0.05
0
N/C
■ KEROGEN, this study
● KEROGEN, Deroo et al., (19777
▲ KEROGEN
△ HUMIC ACID
Stuermer et al., (1978)
altered
unaltered
A
1
2
3
4
5
6
7
8
10
11
12
13
14
15
16
17
0
0.5
1.0
1.5
2.0
Ii/c

Fig. 11

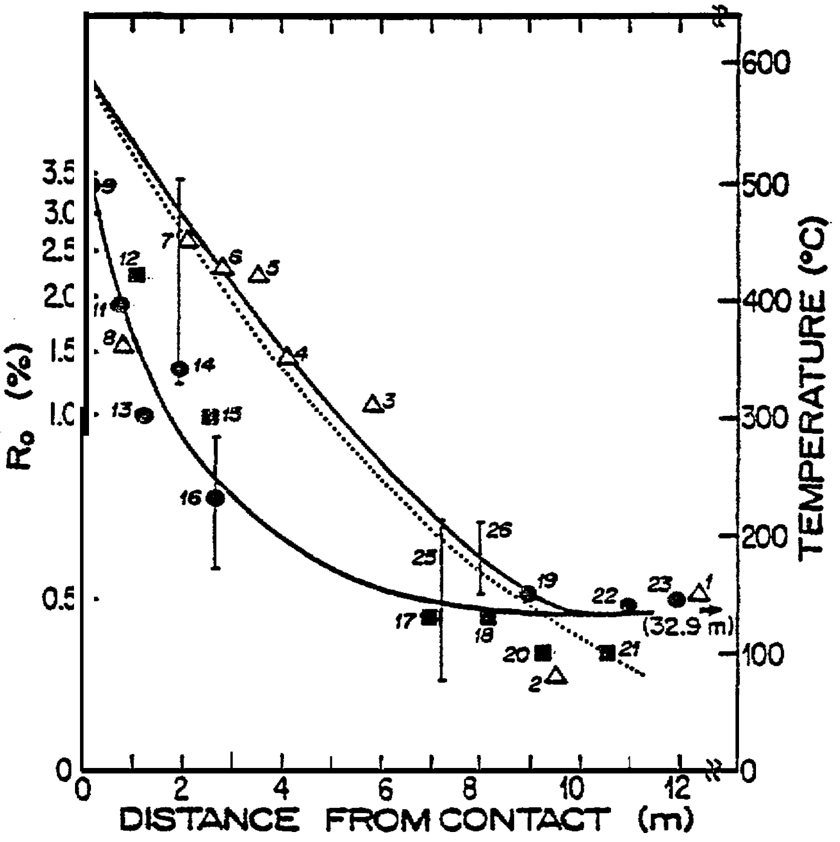

Ro (%)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
TEMPERATURE (°C)
600
500
400
300
200
100
0
0
2
4
6
8
10
12
DISTANCE FROM CONTACT (m)
1
2
3
4
5
6
7
8
9
11
12
13
14
15
16
17
18
19
20
21
22
23
25
26
(32.9 m)

Fig. 12

DIFFERENCES IN ANIMAL ^{13}C, ^{15}N and D ABUNDANCE BETWEEN A POLLUTED AND AN UNPOLLUTED COASTAL SITE:

LIKELY INDICATORS OF SEWAGE UPTAKE BY A MARINE FOOD WEB

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ABSTRACT

In comparing a control versus a sewage-affected near-shore site off Southern California, the natural relative abundances of ^{13}C, ^{15}N and D in Dover sole and Ridgeback prawn muscle were found to be significantly different. This between-site shift in animal isotope abundance is of the type expected if sewage organic materials were an important food source for animals in the latter site. Use of stable isotope natural abundance to trace the incorporation and movement of sewage-derived organics in marine food webs is suggested.

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INTRODUCTION

Large areas of the Southern California nearshore marine environment are exposed to municipal and industrial sewage. This effluent represents a significant amendment of organic material to sites in close proximity to sewage outfalls, and it is of interest to determine to what extent this material is being incorporated into marine food webs. By measuring the natural stable isotope abundances in animals from polluted and unpolluted sites, we herein present a preliminary attempt to demonstrate the uptake of sewage C, N and H by two marine animal species.

A number of recent studies of aquatic food webs have successfully used naturally-occurring stable carbon isotope ratios, $^{13}C/^{12}C$, in animal tissue to determine the primary carbon/food sources they are using (e.g., Fry *et al*., 1977; Thayer *et al*., 1978; Haines and Montague, 1979; McConnaughey and McRoy, 1979a,b; Rau and Hedges, 1979; Rau, 1980;1981). Because animal metabolism little alters the $^{13}C/^{12}C$ of the food assimilated, the $^{13}C/^{12}C$ of an animal's tissue can be matched to the $^{13}C/^{12}C$ of a food source or mixture of food sources that are in question (DeNiro and Epstein, 1978; Teeri and Schoeler, 1979). Similarity, $^{15}N/^{14}N$ and D/H have also been proposed as food web tracers (DeNiro and Epstein, 1981; Estep and Hoering, 1980; Estep and Dabrowski, 1980). Thus, if sewage material was isotonically distinct from marine-derived material, animals using sewage directly or indirectly as a C, N, and H source. should, as a result, be isotonically discernible from animals feeding exclusively on marine-produced food sources

That land-produced organic material is isotonically different from marine sources has been reported in a number of studies. A 1‰ to 10‰

difference in both $^{13}C/^{12}C$ and $^{15}N/^{14}N$ can b-e expected when comparing terrestrial or sewage versus marine organics (Nissenbaum, 1973; Myers, 1974; Wada *et al.*, 1975; Peters *et al.*, 1978; Sweeney *et al.*, 1978, 1980; Burnett and Schaeffer, 1980; Sweeney and Kaplan, 1980a,b; Venkatesan *et aT.*, 1980), with marine material having the higher isotope rat'iOs. Whereas the range of values is much larger, the D/H ratio of marine organ'ics is commonly Tower-than in temperate-latitude terrestrial counterparts (Schiegl and Vogel, 1970; Nissenbaum, 1973; Hoering, 1974; Stuermer *et al.*, 1978; Estep and Hoering, 1980). Accordingly, members of a marine" food web utilizing sewage-derived organic material as a portion of their diet would be expected to have lower relative concentrations of ^{13}C and ^{15}N, and higher D than the same species of animals having access only to marine-produced food sources.

MATERIALS AND METHODS

Specimens of Ridgeback prawn (*Sicyonia ingentis*) and Dover sole (*Microstomus pacificus*) were taken from a control station and a sewage-affected station as part of a sampling program conducted by the Southern California Coastal Water Research Project (Word and Mearns, 1979). Station 34, located off the Pales Verdes peninsula at a water depth of 61 meters, lies less than a kilometer "downstream" from the Whites Point sewage outfall, one of the largest" in the world. Measurements of BOD, COD and TOC, among other parameters., clearly indicates that this site is significantly affected by sewage effluent (Word and Mearns, 1979). In contrast, " values of the same analyses from the control station (11), are some one to two orders of magnitude lower than those of Station 34 (Word and Mearns, 1979). Station 11 lies at a water depth of

58 m near Ventura, California, some 130 km NW of the Pales Verdes station. No sewage or terrestrial inputs, or oil seepage are known to occur in the immediate vicinity of this site.

Muscle tissue from 5 to 6 sole and 3 prawns were taken from the collected specimens from each of the two stations and dried at 60°C for several days. Further dehydration of the samples was accomplished by heating ($<100^\circ$C) under vacuum for 6-12 hours. Five to ten milligram subsamples of these tissues were then combusted, and the resultant CO_2, N_2 and H_2O (ultimately H_2) gases were separated, purified and collected using methods described by Stump and Frazer (1973). The stable isotope ratios in these gases (equivalent to the ratios in the original animal tissue) were measured using a Varian MAT 250 mass spectrometer. By convention, the "δ" notation is used to report these ratios as follows:

$$\delta X = \{(R_{sample}/R_{standard})-1\}\cdot 10^3 \text{ ‰ (per mil)}$$

where X = ^{13}C, ^{15}N, or D,

R = $^{13}C/^{12}C$, $^{15}N/^{14}N$, or D/H

and standard = Peedee Belemnite, Air, or Standard Mean Ocean Water, respectively.

RESULTS AND DISCUSSION

As shown in Table 1 and Figure 1, the mean and range of $\delta^{13}C$, $\delta^{15}N$, and δD values for both sole and prawn are significantly different between stations. The $\delta^{13}C$ of polluted site individuals averaged 0.7 ‰ to 1.4 ‰ lower than their counterparts from Station 11. Because $^{13}C/^{12}C$ in animal tissue is largely determined by the $^{13}C/^{12}C$ of the animals' diet (DeNiro and Epstein 1978; Teeri and Schoeller 1979), the lower $\delta^{13}C$ found in animals from the Pales Verdes station likely reflects the utilization of food/carbon sources possessing lower

$\delta^{13}C$ values than those normally found in unpolluted marine settings. Whites Point sewage detritus is such a ^{13}C-depleted source of organic material at Station 34. Its $\delta^{13}C$ is approximately 2 ‰ lower than those of plankton and benthic algae sampled from waters off the Pales Verdes peninsula (Myers, 1974). Thus, a significant uptake and incorporation of sewage organic carbon by Station 34 animals may explain the more negative animal $\delta^{13}C$ values observed there.

While the shift in animal carbon isotope abundance in polluted-site animals is of the appropriate size and direction if sewage organics were being utilized, it must be pointed out that all of the animal $\delta^{13}C$ values were somewhat higher than the $\delta^{13}C$ values previously reported for the assumed primary food sources at either station. Some ^{13}C enrichment in marine animals relative to food sources has been noted elsewhere by McConnaughey and McRoy (1979a). They attribute such isotopic enrichment or biomagnification to heterotrophic effects whereby ^{13}C is preferentially retained (and ^{12}C is preferentially lost) as plant carbon is consumed, processed, and transferred through aquatic food chains. Indeed, both the prawn and the sole species we analyzed are known to be predators of benthic invertebrates in sewage outfall and non-outfall environments (Kleppel *et al.*, 1980; P. Striplin, Southern California Water Research Project, unpublished data). The relatively elevated $\delta^{13}C$ values of prawn and sole may therefore reflect their indirect utilization of marine primary production or sewage organics; a utilization that requires intermediate consumers.

As in the case of carbon isotopes, the $\delta^{15}N$ of polluted-site animals is lower than the $\delta^{15}N$ of animals from Station 34 (Table 1, Figure 1). Again, these differences are in concordance with the $\delta^{15}N$ differences found in terrestrial/sewage versus marine organics (Wada *et al.*, 1975; Sweeney *et al.*, 1978, 1980; Sweeney and Kaplan, 1980a,b; Venkatesan *et al.*, 1980). The higher $\delta^{15}N$ in the latter material (commonly 8 ‰ to 12 ‰) is thought to reflect fundamental differences in the sources and cycling of nitrogen in the marine environment which ultimately results in a significant enrichment of ^{15}N in marine animal biomass.

The contention that residual organic $^{15}N/^{14}N$ increases as a function of heterotrophic nitrogen cycling and metabolism (Gaebler et al., 1966; Miyake and Wada, 1967; Saino and Hattori, 1980; Rau, 1981) is supported by the data in Figure 2. Here, sole $\delta^{15}N$ is positively correlated with individual fish biomass, an indication that growth and/or metabolism over time can significantly modify the $^{15}N/^{14}N$ in animal tissue. However, a large difference in the $\delta^{15}N$ of food sources between the two sites apparently is the primary factor maintaining significant between-site differences in animal $\delta^{15}N$. Metabolic and trophic level effects in addition to food source effects, however, will need to be considered in future food web tracer studies using $^{15}N/^{14}N$ as well as $^{13}C/^{12}C$.

The δD values of animals from the unpolluted station (11) are significantly lower than those from Pales Verdes. Assuming animal D/H is largely determined by food D/H (Estep and Dabrowski, 1980), the higher animal δD at Station 34 is indicative of the utilization of a non-marine and deuterium-rich hydrogen source. Temperate/arid terrestrial organic materials, presumably the primary constituent of Whites Point sewage, have δD values ($\geq -100‰$) that are commonly higher than those found in marine organic material ($\leq -100‰$; Schiegl and Vogel, 1970; Nissenbuam, 1973; Hoering, 1974; Estep and Hoering, 1980). In support of this relationship, Eganhouse et al. (in preparation) found the δD of insoluble organic matter from the Los Angeles River to range from -62.4 ‰ to -77.4 ‰, in contrast to California offshore sediment values of -105 ‰ to -139 ‰ (Stuermer et al., 1978). Assimilation of terrestrially-derived sewage detritus, having higher δD values than marine food sources, may thus be the cause of the hydrogen isotope discrepancy observed between Station 34 and Station 11 animals.

In conclusion, it has been shown that the natural relative abundances of ^{13}C, ^{15}N and D in two species of marine animals were significantly different when comparisons between a sewage-affected and non-sewage-affected site were made. These site differences in animal isotope abundance appear to be due to the incorporation of isotonically distinct sewage organics into the animal biomass produced in the sewage-affected environment. Refinements in the site selection, animal and detritus sampling, and analytical methods should provide a more accurate method of determining not only the presence, but also the quality and movement of sewage- and terrestrially-derived materials in marine food webs.

ACKNOWLEDGEMENTS

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REFERENCES

Burnett, W.C. and Schaeffer, O.A. 1980. Effect of ocean dumping on $^{13}C/^{12}C$ ratios in marine sediments from the New York Bight. Estuar. Coast. Mar. Sci. 11: 605-611.

DeNiro,M.J. and Epstein, S. 1978. Influence of diet on the distribution of carbon isotopes in animals. Geochim.Cosmochim. Acts 42: 495-506.

DeNiro,M.J. and Epstein, S. 1981. Influence of diet on the distribution of nitrogen isotopes in animals. Geochim.Cosmochim. Acts (in press).

Estep, M.F. and Dabrowski, H. 1980. Tracing food webs with stable hydrogen isotopes. Science 209: 1537-?538.

Estep, M.F. and Hoering, T.C. 1980. Biogeochemistry of the stable hydrogen isotopes. Geochim. Cosmochim. Acts 44: 1197-1206.

Fry, B., Scanlan, R.S., Parker, P.L. 1977. Stable carbon isotope evidence for two sources of organic matter in coastal sediments: Seagrasses and plankton. Geochim.Cosmochim.Acts 41: 1875-1877.

Gaebler, O.H., Vitti, T.G. and Vukmirovich, R. 1966. Isotope effects in metabolism of ^{14}N and ^{15}N from unlabeled dietary proteins. Can. J. Biochem. 44: 1149-1257.

Haines. E.B. and Montaque,C.L.1979. Food sources of estuarine invertebrates analyzed using $^{13}C/^{12}C$ ratios. Ecology 60: 48-56.

Kleppel, G.S., J.Q. Word, and J. Roney. 1980. Demersal fish feeding in Santa Monica Bay and off Pales Verdes. 309-318. In: Coastal" Water Research Project Biennial Report, 1979-80. So. Cal If. Coastal Wat.Res.Proj.,Long Beach, CA; 363 pp.

McConnaughey,T. and McRoy,C.P. 1979a. Food web structure and the fractionation of carbon isotopes in the Bering Sea. Mar.Biol. 53: 257-262.

McConnaughey, T. and McRoy,C.P.1979b. ^{13}C label identifies eelgrass, Zostera marina, carbon in an Alaskan estuarine food web. Mar. Biol. 53: 263-269.

Miyake, Y. and Wada, E. 1967. The abundance ratio of $^{15}N/^{14}N$ in marine environments. Records Oceanogr. Works Japan 9: 3753.

Myers, E.P. 1974. The concentration and isotopic composition of carbon in marine sediments affected by a sewage discharge. Ph.D. Thesis, Cal. Tech.

Nissenbuam, A. 1973. The organic geochemistry of marine and terrestrial humic substances: Implications of carbon and hydrogen isotope studies. Advances Org. Geochem.1973: 39-52.

Peters, K.E., Sweeney, R.E., and Kaplan, I.R.1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23: 598-604.

Rau, G.H. 1980. Carbon-13/carbon-12 variation in subalpine lake aquatic insects: Food source implications. Can. J. Fish. Aquat. Sci. 37: 742-746.

Rau, G.H. 1981a. Carbon-13/carbon-12 in clam and tube worm tissue from hydrothermal vents.: Further evidence of non-photosynthetic food sources. Science (in press).

Rau, G.H. 1981b. Low $^{15}N/^{14}N$ of hydrothermal vent animals: Ecological implications. Nature 289: 484-485.

Rau, G.H. and Hedges, J.I. 1979. Carbon-13. depletion in a hydrothermal vent mussel: Suggestion of a chemosynthetic food source. Science 203: 648-649.

Saino, T. and Hattori, A. 1980. ^{15}N natural abundance in oceanic suspended particulate matter. Nature 283: 752-754.

Schiegl, W.E. and Vogel, J.C. 1970. Deuterium content of organic matter. Earth Planet. Sci. Lett. 7: 307-313.

Stuermer, D.H., Peters, K.E. and Kaplan, I.R. 1978. Source Indicators of humic substances and proto-kerogen. Stable isotopic ratios, elemental compositions and electron spin resonance spectra. Geochim. Cosmochim. Acts 42: 989-997.

Stump, R.K. and Frazer, J.W. 1973. Simultaneous determination of carbon, hydrogen and nitrogen in organic compounds. Nucl. Sci. Abs. 28: 746.

Sweeney, R.E., Liu, K.K., and Kaplan, I.R. 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: Robinson, B.W. (cd.), Stable Isotopes in the Earth Sciences; pp. 9-26, (DSIRO, Wellington).

Sweeney, R.E. and Kaplan, I.R. 1980a. Natural abundance of ^{15}N as a source indicator for near--shore marine sedimentary and dissolved nitrogen. Mar. Chem. 9: 81-94.

Sweeney, R.E. and Kaplan, I.R. 1980b. Tracing flocculent industrial and domestic sewage transport on San Pedro Shelf, Southern California, by nitrogen and sulphur isotope ratios. Mar. Environ. Res. 3: 215-224.

Sweeney, R.E., Kalil, E.K. and Kaplan, I.R. 1980. Characterization of domestic and industrial sewage in Southern California coastal sediments using nitrogen, carbon, sulphur and uranium tracers. Mar. Environ. Res. 3: 225-243.

Teeri, J.A. and Schoeller, D.A. 1979. $\delta^{13}C$ values of an herbivore and the ratio of C_3 and C_4 plant carbon in its diet. Oecologia 39: 197-200. .

Thayer, G.W., Parker, P.L., LaCroix, M.W., and Fry, B. 1978. The stable carbon isotope ratio of some components of an eel grass, Zostera marina; bed. Oecologia 35: 1-25.

Venkatesan, M.I., Brenner, S., Ruth, E., Bonilla, J. and Kaplan, I.R. 1980. Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochim. Cosmochim. Acts 44: '789-802.

Wada, E., Kadonaga, T., and Matsuo, S. 1975. ^{15}N abundance in nitrogen of naturally occurring substances and global assessment of denitrification from isotopic viewpoint. Geochemical J. 9: 139-148.

Word, J.Q. and Mearns, A.J. 1979. 60-Meter control survey off Southern California.. S.C.C.W.R.P. , Long Beach; 58 pp.

Table . The individual and mean $\delta^{13}C$, $\delta^{15}N$, and δD values for Dover Sole and Ridgeback Prawn taken from a polluted and an unpolluted site off the Southern California coast. The analytical precision of these measurements are, respectively, ± 0.2‰, ± 0.5‰, and ± 3.0‰.

Animal	Station No.	Sample No.	Wet weight (grams)		$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	δD (‰)
Dover Sole	34 Polluted site)	143	52.0		-18.1	+11.4	-55.7
		144	41.8		-18.2	+10.8	-61.9
		145	37.3		-18.2	+ 9.5	-60.9
		146	20.0		-17.7	+ 0.0	-54.6
		147	14.5		-18.0	+ 8.7	-56.6
		148	10.4		-17.9	--	-52.2
				$\overline{X}_{34}$ (S.D.) =	-18.0 (0.2)	+ 0.1 (1.1)	-57.0 (3.7)
	11 (Unpolluted site)	167	21.5		-16.9	+ 14.7	-75.8
		168	39.9		-16.5	+ 16.7	-78.5
		169	32.7		-16.3	+ 15.3	-78.6
		170	57.5		-16.3	+ 15.5	-74.4
		171	10.2		-17.0	+ 11.6	-70.8
				$\overline{X}_{11}$ (S.D.) =	-16.6 (0.3)	+ 14.8 (1.9)	-75.[illegible] (3.2)
				$\overline{X}_{11} - \overline{X}_{34}$ =	+ .4*	+ [illegible].7*	- 8.[illegible]*
Ridgeback Prawn	34 (Polluted site)	197	--		-16.7	+11.8	-56.9
		198	--		-17.6	+ 8.6	-61.5
		199	--		-17.3	+ 8.5	-56.0
				$\overline{X}_{34}$ (S.D.) =	-17.2 (0.5)	+ 9.6 (1.9)	-58.1 (3.0)
	11 Unpolluted site)	200	--		-16.5	+ 3.2	-63.1
		201	--		-16.4	+ 5.3	-72.1
		202	--		-16.5	+ 4.0	-64.6
				$\overline{X}_{11}$ (S.D.) =	-16.5 (0.1)	+14.2 (1.1)	-66.6 (4.8)
				$\overline{X}_{11} - \overline{X}_{34}$ =	+ 0.7*	+ 4.6*	- 8.5*
Detritus Sources			$\overline{X}_{\text{Marine Organics}} - \overline{X}_{\text{Sewage Organics}}$ =		$+ 2^{a}$	$+ 8^{b}$	$< 0^{c}$

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a, Myers (1974); b, Sweeney et al., (1980); c, Schiegl and Vogel (1970), Nissenbaum (1973), Hoering (1974), Estep and Hoering (1980).

* ≠ 0, α ≤ 0.1.

FIGURE LEGENDS

Figure 1: The range of $\delta^{13}C$, $\delta^{15}N$, and δD values for Ridgeback prawn and Dover sole taken from a polluted and a non-polluted site off the Southern California coast.

Figure 2: Individual Dover sole $\delta^{15}N$ versus individual sole wet weight. Both the correlation coefficient, r, and the slope of the linear regression of both sets of data are not equal to zero (significance level = 0.05). The hypothesis that the two slopes are equal is not rejected at the same significance level, 0.05.

a

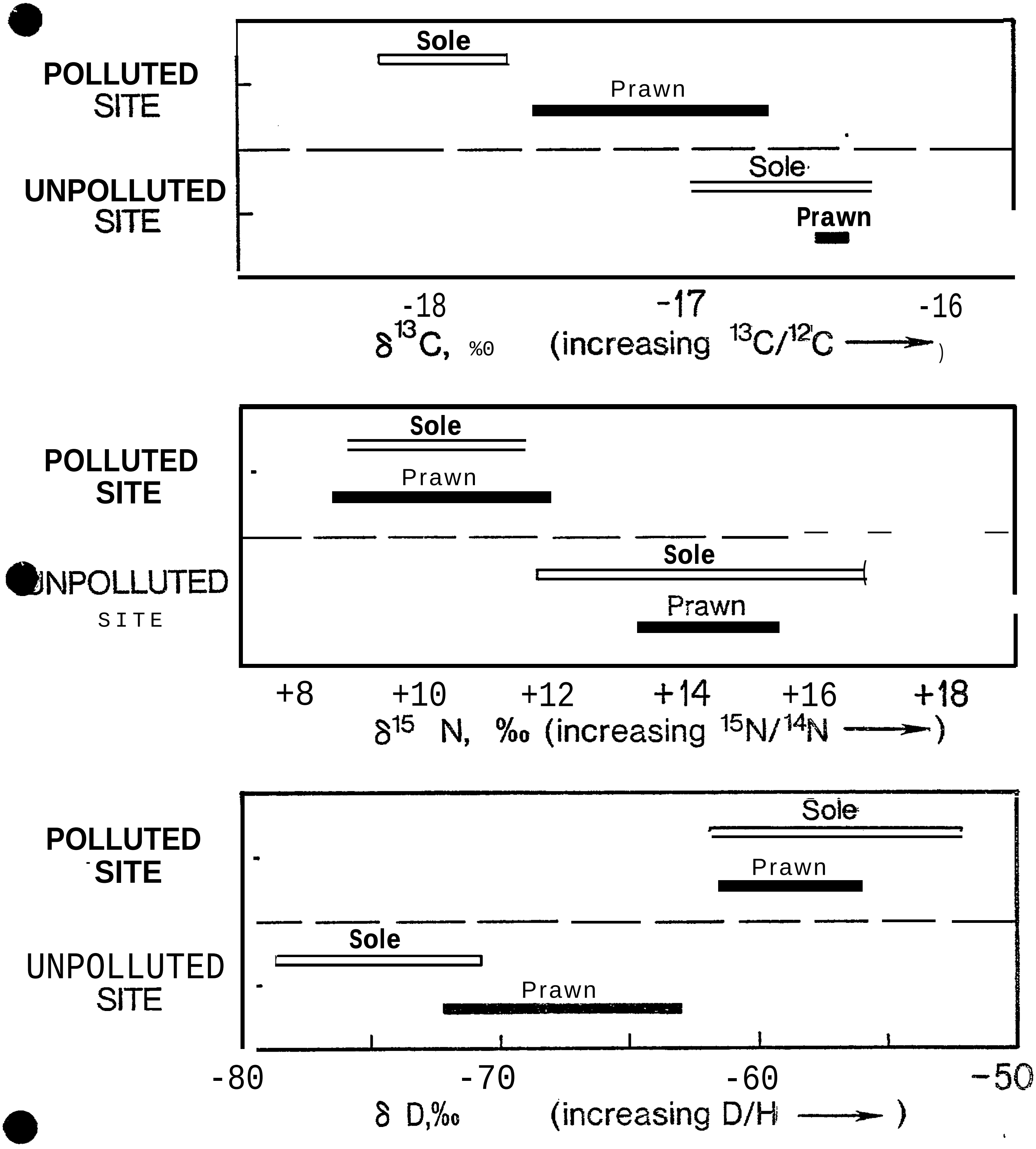

Fig. 1 Rau et al.

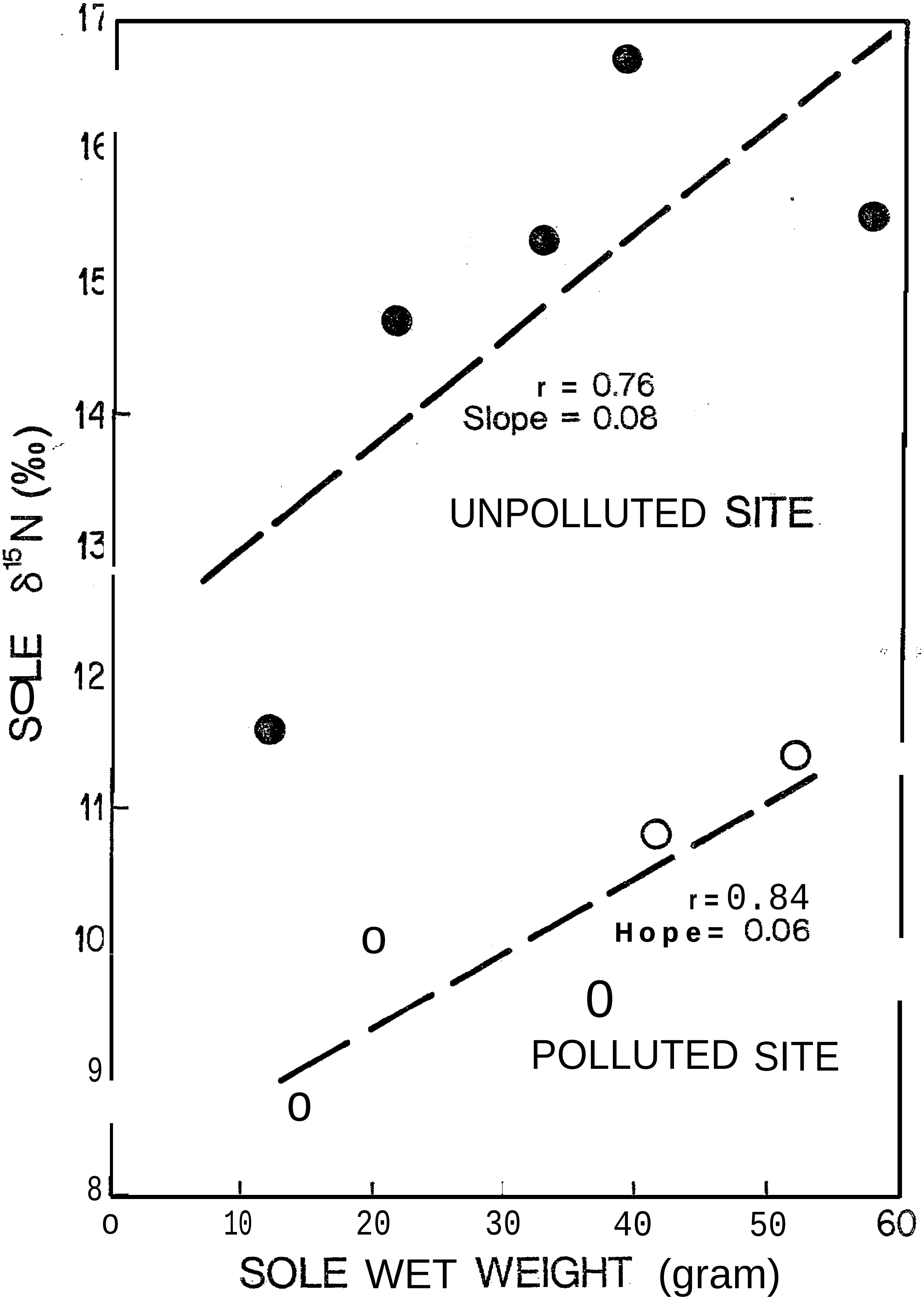

Fig 2 Ram et al

May 18 '81

Plankton $^{13}C/^{12}C$ Change with Latitude: Differences Between Northern and Southern Oceans[1]

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ABSTRACT

Latitudinal trends in plankton $\delta^{13}C$ were found to significantly differ between northern and southern oceans. Apparently factors other than water temperature and dissolved inorganic carbon $\delta^{13}C$ are important in producing the marked ^{13}C depletion observed in antarctic plankton.

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INTRODUCTION

In 1965, a paper by Sackett and others reported that the $^{13}C/^{12}C$ of both Atlantic and Pacific Ocean plankton decreased toward the Antarctic. The cause of this plankton $^{13}C/^{12}C$ decrease in southern latitude waters was attributed to carbon isotope fractionation effects (associated with phytoplankton carbon fixation processes) that were directly affected by latitude vis-a-vis water temperature. However, further sampling and analysis of southern hemisphere plankton (Sackett et al., 1973; Fontugue and Duplessy, 1978) as well as controlled laboratory experimentation (Degens, et al., 1968a; Wong and Sackett, 1976; Falkowski, unpublished} indicated that factors other than water temperature were most responsible for the observed isotopic variations in open ocean plankton. In our research it was reasoned that if temperature were not important in determining the carbon isotope abundances in plankton, then the $^{13}C/^{12}C$ of plankton from arctic waters might not reflect the ratios previously found at similar latitudes *in* the antarctic. As described below, such circumstances were found.

MATERIALS AND METHODS

Samples of near-surface ocean plankton were collected by water filtration or netting at a number of North Pacific and Arctic Ocean stations ranging from 28°N latitude to 71°N latitude as noted in Table 1. In the case of samples derived from seawater filtration, the contents retained on glass fiber filters were dried and stored. Samples collected from net tows (bongo, 333µ mesh) were either stored frozen or in formal in. Subsamples of two of the formalin preserved samples were allowed to leach in 1°C, distilled water that was changed daily during a five-day period. This was an attempt to remove residual formalin carbon whose effect on plankton isotope abundance could then be estimated by comparison with preserved, but unleached, plankton. All of the above samples were then submerged for several hours in 1N HC1 to remove carbonates, washed in distilled water, and dried at 50°C for several days. The carbon present in 5-10 mg subsamples of the above materials was subsequently converted to CO_2 gas and collected as described by Stump and Frazer (1973). The relative $^{13}C/^{12}C$ of each of these CO_2 gas samples (derived from the original plankton organic carbon) was measured on a Varian 250 MAT ratio mass spectrometer. By convention, the Isotope ratios are reported as $\delta^{13}C$, the parts-per-thousand (‰) difference between the $^{13}C/^{12}C$ of the sample and the $^{13}C/^{12}C$ of the PDB carbonate standard (Table 1 legend).

RESULTS AND DISCUSSION

Thus analyzed, northern latitude plankton $\delta^{13}C$ values ranged from -18.4 to -23.3°/00 with the lowest values belonging to the formal in-preserved samples (PS-21 and N-31, Table 1). Indeed, by comparison with their formal in-preserved, distilled-water-leached subsamples, residual formalin contamination appears to have caused a slight $\delta^{13}C$ decrease in the preserved plankton material of less than 1‰.

Even with this negative bias in three of our plankton samples, however, none of our arctic plankton $\delta^{13}C$ values are as low as those found below 40°S '(Figure 1).

South of the equator, thee correlation between "latitude and previously-reported plankton $\delta^{13}C$ is significant ($r = -0.917$), whereas a much weaker relationship exists in northern waters ($r = 0.405$). Linear regression of the northern and southern hemisphere data separately produces lines whose slopes are significantly different from zero as well as being significantly different from each other ($\alpha = 0.05$). These differences between the northern and southern hemisphere exist despite rather symmetrical latitudinal trends (about the equator) in surface water temperature and dissolved inorganic carbon (DIC) $\delta^{13}C$

Should state either here or in Figure legend the criterion for including points in the "northern" or the "southern" regression. Presumably it's whether or not the points are N or S of the equator, but the lines in the Figure appear to be separated at about 10°S. State criterion.

(Figure 1). We conclude, that while plankton $\delta^{13}C$ does significantly decrease toward both poles, the amount and nature of this decrease is quite different between northern and southern waters. These circumstances argue against a strict temperature-plankton $\delta^{13}C$ relationship common to all oceans. Rather, factors other than temperature and $\delta^{13}C$(DIC) must play a significant role in determining plankton $\delta^{13}C$.

of

Perhaps the significant dark CO_2 fixation recently discovered in high latitude antarctic waters (Horrigan, 1981) is the ultimate source of the low plankton $\delta^{13}C$ observed there. A number of marine organisms whose metabolism is based upon dark chemoautotrophic rather than photosynthetic primary production have been shown to possess $\delta^{13}C$ values near or below -30 ‰ (Degens et al., 1968a; Fuchs et al., 1979; Rau and Hedges, 1979; Rau, 1981; Rau et al., 1981; Rau, unpublished data). In any case, a ^{13}C depletion similar to that found in antarctic plankton has not been found in their northern-latitude counterparts. This isotopic discrepancy apparently has a biological or biochemical basis rather than a ~~direct~~ purely physical/chemical cause.

I talked with Horrigan, she says data are scanty, insufficient to say either 1) ~~dark~~ CO2 fixation is ~~[illegible]~~ widespread in Antarctica or 2) dark CO2 fixation is higher in the Antarctic than in the Arctic.

ACKNOWLEDGEMENTS

We gratefully acknowledge the help of Dr. David Shaw (University of Alaska) and Dr. Rita Homer (University of Washington) in obtaining the samples we analyzed. Most of the samples were collected during oceanographic cruises sponsored by the Outer Continental Shelf Environmental Assessment Program (NOAA). Isotopic analyses were supported by DOE/BLM Contract No. EY-76-3-03-0034 with UCLA.

REFERENCES

Degens, E.T., R.R.L. Guillard, W.M. Sackett and J.A.Hellebust (1968a). Metabolic fractionation of carbon isotopes in marine plankton--i. Temperature and respiration experiments. Deep-Sea Research 15;1-9.

Degens, E.T., M. Behrendt, B. Gotthardt and E. Reppmann (1968b). Metabolic fractionation of carbon isotopes in marine plankton--n. Data on samples collected off the coasts of Peru and Ecuador'. Deep-Sea Research 15;11-20.

Eadie, B.J. arid L.M. Jeffrey (1973). $\delta^{13}C$ analyses of oceanic particulate organic matter. Marine Chemistry 1; 199-209.

Falkowski, P.G. (19) Fractionation of ^{13}C and ^{12}C by marine phytoplankton: Evidence for multiple paths of carbon in photosynthesis. (Unpublished manuscript).

Fontugne, M. and J.C. Duplessy (1978). Carbon isotope ratio of marine plankton related to surface water masses. Earth Planetary Science Letters 41; 365-371.

Fuchs, G., R. Thauer, H. Ziegler and W. Stichler (1979). Carbon isotope fractionation by Methanobacterium thermoautotrophicum. Archives of Microbiology 120;135-139.

9 Harrigan, S.G. (1981). Primary production under the Ross Ice Shelf, Antarctica. Limnology and Oceanography 26;378-382.

Kroopnick, P.M., S.U. Margolis, and C.S. Wong (1977). $\delta^{13}C$ variations in marine carbonate sediments as indicators of the CO_2 balance between the atmosphere and oceans. In: The Fate of Fossil Fuel CO_2 in the Oceans, (N.R. Anderson and A. Malahoff, Eds.), Plenum Press, N.Y.; 295-321.

McConnaughey, T. and C.P. McRoy (1979). ^{13}C label identifies eelgrass (Zostera marina) carbon in an Alaskan estuarine food web. Marine Biology 53; 263-269.

Rau, G.H. (1981). Hydrothermal vent clam and tube worm $^{13}C/^{12}C$: Further evidence of nonphotosynthetic food sources. Science, in press.

Rau, G.H. and T.I. Hedges (1979). Carbon-13 depletion in a hydrothermal vent mussel: Suggestion of a chemosynthetic food source. Science 203; 648-649.

Rau, G.H. A.J. Southward and E.C. Southward (1981). Low $^{13}C/^{12}C$ in the pogonophore Siboglinum atlanticum: Carbon source implications. Nature, in review.

Sackett, W.M., W.R. Eckelmann, M.L. Bender and A.W.H. Bé (1965). Temperature dependence of carbon isotope composition in marine plankton and sediments. 'Science 148; 235-237.

Sackett, W.M., B.J. Eadie, and M.E. Exner (1974). Stable isotope composition of organic carbon in recent antarctic sediments. In: Advances in Organic Chemistry 1973, (B. Bienner, Eds.), Editions Technip, Paris; 661-671. "issot and '*

Stump, R.K. and J.W. Frazer (1973). Simultaneous determinations of carbon, hydrogen and nitrogen in organic compounds. Nuclear Science Abstracts 28; 746.

Sweeney, R.E. (1979). Carbon and nitrogen isotopic composition in marine plankton. Annual Report, BLM/DOE Contract No. EY-76-S-03-0034

Wong, W.W. and W.M. Sackett (1978). Fractionation of stable carbon isotopes by marine phytoplankton. Geochimica et Cosmochimica Acts 42; 809-1815.

Table 1: The $\delta^{13}C$ of bulk surface water plankton collected from various locations in the Pacific-Arctic Ocean where:

$$\delta^{13}C = \{[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB}] - 1\} \times 10^3 ‰.$$

The plankton was collected either by seawater filtration or plankton net tows and were stored frozen, dried, or in formalin prior to isotope analysis, as noted.

Sample #	Latitude	Longitude	Collection & Storage	$\delta^{13}C$ (‰)
S-1	28°N	155°1d	Filtered, Dried	-20.3
S-2	33*N	120°W	Filtered, Dried	-20.5
S-3	34°N	119°W	Filtered, Dried	-20.1
PS-21	55°N	170°W	Netted, Formalin	-23.3
PS-21	55°N	170°W	Netted, Formalin*	-22.9
S-4	59°N	142°W	Filtered, Dried	-20.8, -21.1
PS-15	60°N	175°W	Netted, Frozen	-20.3, -20.7
PS-30	62°N	167°W	Netted, Frozen	-18.4, -18.5
WP-014	63°N	171°W	Netted, Formalin	-21.4
N-13	71°N	150”W	Netted, Formalin	-22.4
N-13	71°N	150°W	Netted, Formalin*	-21.5

* Sample leached in cold distilled water prior to analysis.

Figure 1: Surface water temperature, ΣCO_2 $\delta^{13}C$ and surface and near-surface water plankton $\delta^{13}C$ versus latitude as compiled from the sourced cited. The hypothsis that the slopes of the. lines relating plankton $\delta^{13}C$ witl latitude are equal to zero is rejected (significance level = 0.05), as is the hypothesis that the two slopes are equa .

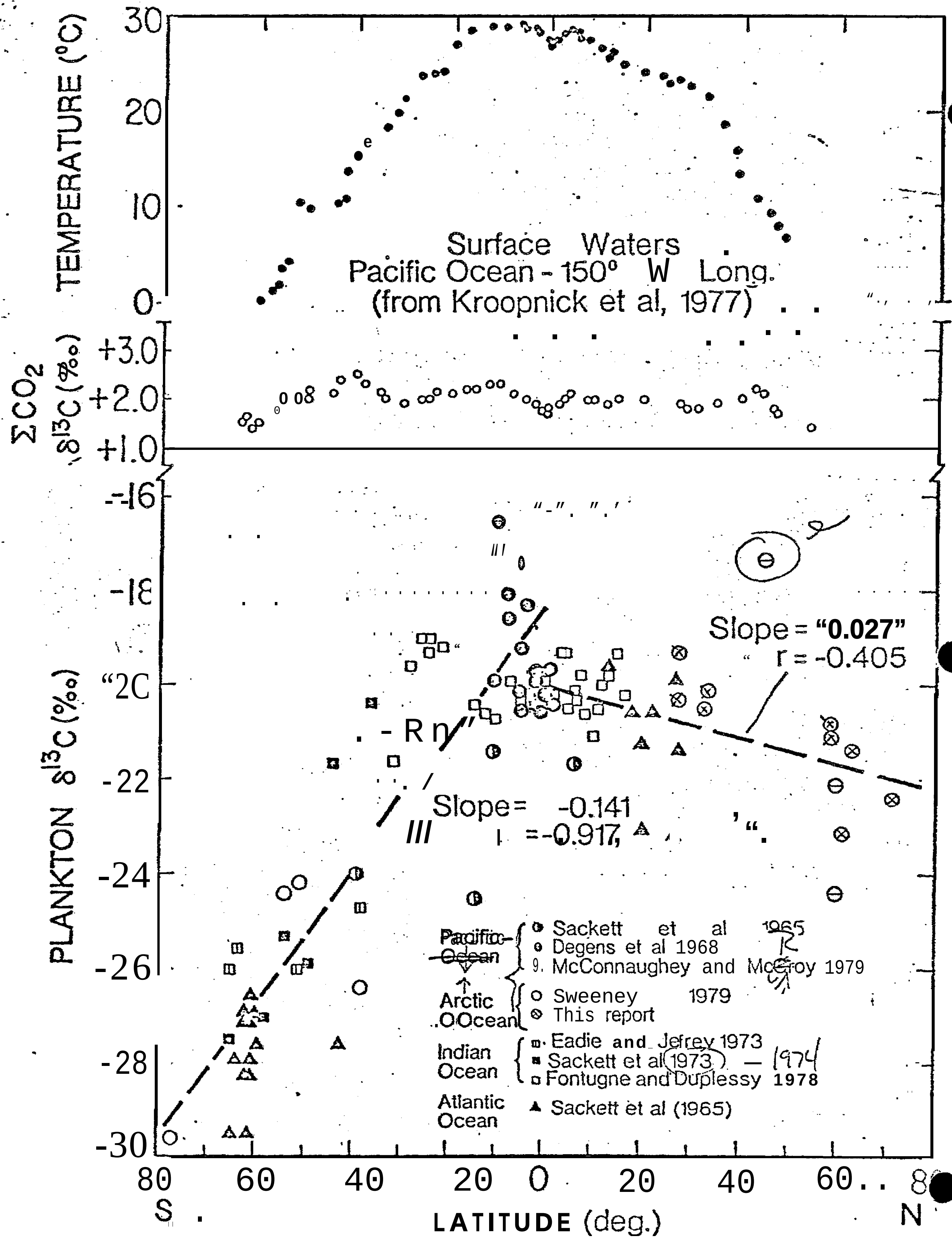
TEMPERATURE (°C)
30
20
10
0
Surface Waters
Pacific Ocean - 150° W Long.
(from Kroopnick et al, 1977)
ΣCO2 δ13C (‰)
+3.0
+2.0
+1.0
PLANKTON δ13C (‰)
-16
-18
-20
-22
-24
-26
-28
-30
Slope = "0.027"
r = -0.405
Slope = -0.141
r = -0.917
Pacific Ocean
Sackett et al 1965
Degens et al 1968
McConnaughey and McRoy 1979
Arctic Ocean
Sweeney 1979
This report
Indian Ocean
Eadie and Jefrey 1973
Sackett et al 1973 — 1974
Fontugne and Duplessy 1978
Atlantic Ocean
Sackett et al (1965)
80
60
40
20
0
20
40
60
80
S
N
LATITUDE (deg.)

Figure 3

DETERMINATION OF PETROLEUM CONTAMINATION IN MARINE SEDIMENTS BY ORGANIC GEOCHEMICAL AND STABLE SULFUR ISOTOPE ANALYSES[1]

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Chapter 5

ABSTRACT

Sediment samples from pristine and polluted marine environments were analyzed for their hydrocarbon distributions. Stable isotope ratios of sulfur in the extractable organic matter were also determined for the same samples. $\delta^{34}S$ values could be correlated with petroleum contamination indicated by the hydrocarbon profiles.

In the pristine marine environment, extractable sulfur is derived mainly from bacterial reduction of sea water sulfate. In both reducing and oxidizing sediment, the $\delta^{34}S$ value of extractable sulfur is ≤ -15 ‰. Petroleum-derived sulfur, concentrated in the refractory compounds resistant to weathering and transported to marine sediment, is isotopically heavier than bacterial sulfur: $\simeq 0$ ‰ for Prudhoe Bay, Alaska; -5 to +5 ‰ for the Gulf Coast oils and +8 to +15 ‰ for the Southern California natural seeps. In marine environments adjacent to each of these areas, abnormally positive $\delta^{34}S$ values were measured in certain sediments. These sediments are the same as those shown by organic geochemical analyses to be contaminated by crude oil.

Extractable sulfur from sediment-trap particulates does not appear to originate from *in situ* bacterial processes and the $\delta^{34}S$ may therefore be directly related to the $\delta^{34}S$ value of petroleum contaminants,

INTRODUCTION

Frequently, normal alkanes are useful indicators of hydrocarbon sources; marine organisms, land plants and petroleum each have characteristic distributions of n-alkanes which can be distinguished for correlation purposes (Clark and Blumer, 1967; Kollatukudy and Walton, 1972; Eglinton and Hamilton, 1963; Speers and Whitehead, 1969). However, weathering processes may extensively alter the composition of petroleum hydrocarbons introduced into the marine sedimentary environment, often resulting in an "unresolved complex mixture" (Farrington et al., 1977). Therefore, identifying the predominant source of hydrocarbons requires other correlations. The branched and especially the cyclic hydrocarbons, more resistant than n-alkanes can yield information correlating sediment chemistry with sources (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980). Stable isotopic fractionation studies of carbon, nitrogen and sulfur, which may be less affected by weathering, could also be useful as source indicators. Particularly, petrogenic sulfur, concentrated in the refractory compounds, can yield information independent of the compositional complexity of the sample. The range of $\delta^{34}S$ values (stable isotope ratio of sulfur) for a series of oils studied by Sweeney and Kaplan (1978) were significantly different from those of the various sulfur species present in the offshore sediments (Kaplan et al., 1963). In fact, the isotopic ratio was so characteristic for some oils that they could be distinguished from one another. However, $\delta^{13}C$ and $\delta^{15}N$ were not helpful for tracing petrogenic pollution in the marine environment due to the similar ranges of values measured for the local oils. Based on these observations, an attempt was made to correlate the hydrocarbon data of sediments from different environments with the stable isotope composition of sulfur. The southern California Bight region known to be contaminated by crude oil (Reed et al., 1977; Crisp et al., 1979; Venkatesan et al., 1980a) Simoneit and Kaplan, 1980) was chosen as the primary site of study. Sediments and trap particulate were analyzed from the area. The main alternative source of organic sulfur in marine sediments is bacterially produced hydrogen sulfide from in situ sulfate reduction. Therefore, sediments from pristine environments such as Gulf of Alaska, eastern Bering Sea and Walvis Bay, were collected to document the distribution of $\delta^{34}S$ values in non-contaminated samples.

Pertinent data were also obtained on the potential sources of oil pollution such as beach tars and imported oils to the Los Angeles Harbor in the southern California Bight to compare with the natural seeps and sediments of this area. The locations of the natural seeps previously measured for $\delta^{34}S$ (Sweeney and Kaplan, 1978) from southern California Bight are shown in Fig. 5-1. Coal Oil Point (+14 to +15 ‰) and Carpenteria (+10 ‰) seeps were shown to have different isotopic ratios and several beach tars collected along the shore from Jalama to Venice Beach *were* shown by isotope comparison to have been derived from Coal Oil Point (Sweeney and Kaplan, 1978). The beach tars in the Santa Monica Bay region were also reported to come mainly from the Coal Oil Point seepage or from a submarine seepage in the Redondo Canyon ($\delta^{34}S$, +8 to+12 ‰) by Hartman (1978) after his detailed study of the $\delta^{34}S$ values.

Fig 5-1

The transport of the Coal Oil Point material was considered to occur via the counterclockwise California current that travels around offshore islands before returning to the coast near Santa Monica Bay. Hartman (1978) compared the rate of seep discharge at Coal Oil Point to the rate of accumulation of beach tars (with this isotopic label) along the coast. Using suitable corrections for -evaporation and weathering, he estimated that most of the refractory portion of the seep discharged material was ultimately transported to the beaches. Tars on the beaches are soon agglomerated with sand grains and transported back to the ocean by tidal action and bottom currents. The ultimate fate of the natural marine seep material off southern. California,' thereforei appears to be the marine sediments of the continental shelf.

A study of hydrocarbon distributions and sulfur" isotope ratio measurements of sulfur in the extractable organic matter from these sediments were carried out to test if crude oil contamination can be determined by using ^{34}S measurements.

EXPERIMENTAL

Freeze-dried sediments were extracted using a toluene:methanol (3:7) azeotropic mixture in a Soxhlet apparatus for 100 hours with one solvent." change after 24 hours (Venkatesan et al., 1980b). The total extracts were washed down a copper column to purify the samples of elemental sulfur, saponified and then chromatographed on a column packed with 1:2 alumina over silica gel, successively eluting with 2 column volumes each of hexane, benzene and methanol. The three solvents eluted the n-alkanes and olefins, aromatic compounds and olefins, and polar compounds, respectively.

Gas chromatographic analyses of the hexane and benzene fractions were conducted using a Hewlett Packard Model 5840A instrument, equipped with a linear temperature programmer, flame ionization detector and an electronic integrator. A 30m x 0.25 mm glass capillary column wall-coated with OV-101 (J&W, Inc.) was used and programmed at 4°C/min from 35° to 260°C, then held isothermal for about 2 hours, with a flow rate of' 4 ml/min of helium".

The GC/MS analyses of the hexane and benzene fractions were carried out on a Finnigan Model 4000 Quadruple Mass Spectrometer interfaced directly witha Finnigan Model 9610 Gas Chromatography. The GC was equipped with a 30m x 0.25 mm glass capillary column wall-coated with OY-101 (J&W, Inc.). The mass spectrometric data was acquired and processed using a Finnigan Incos Model 2300 data system with 3.1 software.

The methanol fraction was combusted in a Parr bomb with 30 atmospheres oxygen pressure and the produced sulfate was precipitated with barium chloride and converted to sulfur dioxide by the method of Bailey and Smith , (? 972). A minimum of 0.1 mg of sulfur was necessary for the isotope preparation technique. Therefore, 20 mg of sample had to be used for a typical sulfur content of 0.5%. Though' organic sulfur compounds are present to a lesser extent in the hexane and benzene fractions, the methanol fraction, for simplicity, will be termed extractable sulfur in this paper. The methanol fraction is seldom used for gas chromatographic identification and so is readily available from sediments analyzed in organic geochemical studies. Stable isotope ratios were determined following the method of Kaplan <u>et al</u>., (1970) and are. presented in the standard "δ" notation relative to Canyon Diablo troilite (FeS) with a precision of 0.1 ‰ .

$$\delta = \left[\frac{'sample\ \ 'standard}{R_{standard}} - 1\right] \times 1000$$

where: $R = {}^{34}S/{}^{32}S$ for sulfur.

RESULTS AND DISCUSSION

Table 5-1 lists the contents and $\delta^{34}S$ values of extractable sulfur of various sediment and trap particulate samples. All sediment samples were collected at the sediment surface except for two sections of core from the Santa Barbara Basin.

[Table 5-1]

The sediment from Walvis Bay, off the west. coast of Africa, consists predominantly of diatomaceous ooze. The bottom waters have low oxygen concentrations and aid in the preservation of this algal organic detritus. The n-alkanes and n-fatty acids of the samples exhibit a predominantly marine autochthonous origin (Simoneit et al., 1978). No petroleum residues were detected and only trace amounts of terrigenous lipids are present. The sediments from this area represent a typical example of a marine end member environment. Hydrogen sulfide exists in the surface pore water of this reducing basin. The $\delta^{34}S$ value of the organic sulfur (-21 ‰) is typical of nearshore reducing marine sediments (Goldhaber and Kaplan, 1974).

The Gulf of Alaska and eastern Bering Sea samples are from oxidizing sedimentary environments and contain 1-2% organic carbon.. Hydrocarbons in the Gulf of Alaska sediments appear to be derived approximately in equal abundance from marine and terrigenous sources, while in Bering Sea, a terrigenous source predominates. The sediments show no indication of petroleum input. Sulfate reduction may occur in micro-reducing environments of oxidizing sediment (Kaplan et al., 1963) and the sulfur in the extractable organic matter, as denoted by the $\delta^{34}S$ value of -170/00, appears to be of this origin.

Of the 40 samples analyzed from the eastern Bering Sea and Gulf of Alaska areas, only one sample at station 35 (EBBS 35, 56° 12.4'N; 168° 20.4'W) shows anomalous data on hydrocarbons. The total hydrocarbon contents range from 2 to 27 μg/g in all of the stations typical of unpolluted Recent marine sediments, whereas at station 35, the total extractable hydrocarbons were measured to be 241 μg/g dry sediment. The gas chromatographic profile of n-alkanes also substantiates that this station has been exposed to weathered petroleum hydrocarbons similar to southern California Bight sediments while the other stations are not (Fig. 5-2). As a comparison, a chromatogram of a clean sediment (EBBS 37) is also included...

[Fig. 5-2] The extended triterpanes ($\geq C_{31}$), analyzed by GC/MS exist as two diastereomers at position 22 in EBBS 35, also indicating petroleum input (Dastillung and Albrecht, 1976). The preponderance of the 17α(H)-hopanes in this station further corroborates a petroleum source for these compounds (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980). The δ^{34}S value of this sample is 10 ‰ more positive than other samples from the Alaska offshore. Alaskan oil at Prudhoe Bay has a δ^{34}S value of about 0 ‰ (Grizzle et al., 1979). Petroleum from this source or from an unidentified oil seep on the eastern Bering sea shelf could be the contaminant in EBBS 35. GC/MS analyses of other samples in this area such as at stations 8, 59 and 65 (for exact locations, see Venkatesan et al., 1980b) indicate that the triterpenoids consist of predominantly the 17β(H),21β(H)-hopanes and hopenes with only traces of the 17α(H),21β(H)-hopanes. The extended hopanes ($\geq C_{31}$) are present as single C-22 diastereomers. The presence of 17β(H) stereomers and of the triterpenes suggests a recent biogenic source for these compounds, originating directly from the regional biota.

Three nearshore sediment samples from the Gulf of Mexico were selected at sites which *were* considered to have different degrees of petroleum contamination (Shokes and Mankiewicz, 1978). A direct correlation exists between the δ^{34}S value of organic sulfur and the methylated/condensed ratio of the polynuclear aromatic series. The low methylated/condensed ratio, (Big Hill) indicative of low level petroleum contamination., corresponds to a δ^{34}S of -16 ‰, similar to that of many other non-contaminated marine environments. The δ^{34}S value becomes progressively more positive as the petroleum hydrocarbon contamination increases (Table 5-1). The set of data comparing methyl/condensed phenanthrenes and δ^{34}S: 0.4, -1.5.7°/00 , 0.7,

-12.7‰ and 11.6, -6.1‰, for the three stations illustrates this argument. Several Gulf Coast oils have $\delta^{34}S$ values (UCLA, unpublished data) ranging from -5 to +5‰ and could be the source of contamination. However, Big Hill sample has a higher concentration of extractable hydrocarbons (35ppm), compared to the two west Hackberry samples (9 and 13. ppm). The hydrocarbon contamination in the former sample is indicated, by the unresolved complex mixture on the gas chromatograms, which is 80% of the total hydrocarbons. This is attributed to a combination of finer sediment texture and higher input of pyrolytic hydrocarbons transported via atmospheric fallout and urban runoff rather than to crude oil hydrocarbons from sea water. This is also supported by our observation that benzopyrene, a combustion product, is more predominant in the Big Hill than in the West Hackberry samples (Mankiewicz, 1980). Therefore, the possible important implication is that the sulfur isotope data here may indicate that crude petroleum is not the direct source of hydrocarbons in the Big Hill sample, unlike the West Hackberry samples, which exhibit sulfur isotopic data characteristic of direct petroleum pollution.

The above results indicate that extractable sulfur in marine sediments which have not been contaminated by petroleum hydrocarbons has a $\delta^{34}S$ value similar to that of bacterially produced hydrogen sulfide, or generally; in the range of -15 to -22‰. Although only a few samples were analyzed, the sediments chosen in uncontaminated areas represented both oxidizing and reducing conditions and seem to show little differences in $\delta^{34}S$ values.

The extractable sulfur in petroleum-contaminated sediments has $\delta^{34}S$ values intermediate between that of the uncontaminated sediment (-15 to -22‰) and values of sulfur in petroleum-rich source areas. In areas off the western coast of Alaska and in the Gulf of Mexico, the $\delta^{34}S$ value of the sulfur in the petroleum contaminant is more positive than the bacterially-produced sulfur. Protein-bound sulfur in marine organisms have-been reported to have $\delta^{34}S$ values around +20‰ (Kaplan et al., 1963). However, under the experimental conditions employed here, only lipid-related sulfur is extracted into the hexane fraction which is used in the column chromatography and subsequent sulfur isotopic analysis. Any protein-bound sulfur if at all extracted by the initial toluene:methanol soxhlet extraction would be hydrolyzed and. remain in the aqueous phase in the saponification step. Therefore, the relatively positive $\delta^{34}S$ values would indicate only petroleum input in these areas.

Sediment samples from the southern California Bight have $\delta^{34}S$ values in the methanol extracted sulfur between -6.8 and +13.5‰ (Table ~~7~~ 5). The most positive value (+13.5‰) is for Coal Oil Point sediment, about 500 meters from the seep. Trap particulate from the Santa Monica Basin and the San Pedro Basin have $\delta^{34}S$ values more positive than those for the underlying sediment; +7.3, compared to +0.3‰ and +3.0, compared to -6.8‰, respectively. Although isotonically light sulfur (pyrite) existed in these trap particulate (Crisp et al., 1979), the humic acid fraction contained no measurable sulfur. Humic acids in marine sediment commonly contain about 1% bacterial sulfur (Nissenbaum and Kaplan, 1972) and it could be argued that extractable organic sulfur in the trap particulate is not of a bacterial origin. The more negative values. observed in the sediments are probably due to the incorporation of bacterial sulfur. For the San Pedro Basin, the hydrocarbon distribution pattern indicates a mixed petrolem input from natural seeps as well as from heavy anti-n-opogenic activities. such as shipping, sewage outfalls and industrial effluents (Venkatesan et al., 1980a); but the sources for the Santa Monica Basin are either sedimented tar that had been washed off the local beaches or anthropogenic inputs. The $\delta^{34}S$ value for the Santa Monica Basin sediment trap particulate sample (+7.3 ‰) is similar to that for the nearby Redondo seep, which could be a dominant source of petroleum input into this area. The triterpanes in the Redondo seep consist predominantly of the $17\alpha(H),21\beta(H)$ hopane series containing the two major analogs $C_{28}H_{52}$. The mass spectrum of the C_{28} triterpane has been correlated with that of $17\alpha(H),18\alpha(H),21\beta(H)$-28,30 bisnorhopane. This compound is abundant in the Monterey Shale and in offshore seeps (Coal Oil Point) at Santa Barbara, and is either absent or present in only trace amounts in most other crude oils (Seifert et at., 1978) and has therefore been suggested to be a potentially characteristic molecular marker for petroleum from the southern California area (Simoneit and Kaplan, 1979). The presence of bisnorhopane in the trap particulate and the sediments thus indicates that seeps in the southern California Outer Continental Shelf may be the source of petroleum contamination in the Santa Monica and San Pedro area. However, the δ^{34}S values could be a potential indicator in differentiating between seeps, especially in the trap particulates. The ability to distinguish the source seep by δ^{34}S will beenhanced by the absence of anthropogenic input which dilutes the petroleum contribution from the seeps (Crisp et al., 1979).

[Table 5-2] Listed in Table 5-2 are the ranges of δ^{34}S values for southern California seeps and beach tars. Different chemically-separated fractions (i.e., total, methanol fraction, and asphaltenes) have relatively the same δ^{34}S composition for the Coal Oil Point samples. The methanol fraction has generally the same sulfur concentration as the total crude oil, but the asphaltene fraction is significantly enriched in sulfur. Of the 47 recent beach tars listed in Table 2, only two have 6^{34}S values significantly different from the seep sources. Six ancient tars scraped from archaeological specimens from both the offshore islands and coastal sites are also listed in Table ~~2~~ 5. The San Nicolas and Catalina Island samples appear to come from Coal Oil Point, substantiating the transport system suggested by Hartman (1978). The coastal material appears to be derived from another seep (possibly an onshore seep). “

The sulfur content and $\delta^{34}S$ value of some typical oils imported into” Los Angeles Harbor from various countries have been determined (UCLA, unpublished data). $\delta^{34}S$ of these oils range from -0.2 to +10.5‰. Only oils from Venezuela, Indonesia and Algeria have $\delta^{34}S$ values greater than >0‰. In “summary, it is interesting to note that the trap particulates from Santa Monica Basin have $\delta^{34}S$ values more positive (+7.3‰) than all but the Venezuela crude oil imported into Los Angeles Harbor. Although contribution from the Redondo seepage maybe important, anthropogenic contamination has been demonstrated to be predominant in the samples. studied. A mixture of sulfur from this source-and sulfur (+15‰) from’” Coal Oil Point could therefore lead to the intermediate isotope ratio measured in the trap particulate.

CONCLUSIONS

1. The sulfur isotope ratio of extractable organic sulfur in marine sediment appears to be altered by the contribution of petrogenic material. Sulfur compounds are concentrated in the refractory (polar and asphaltene) fraction of oils and exhibit little isotopic fractionation during transport and weathering. The isotopic ratio of petrogenic sulfur is often significantly different from that added to the sediment by bacterial reduction of seawater sulfate. The difference between Coal Oil Point seepage (+15‰)

and bacterial sulfur (-20 ‰) is over 30 ‰. Therefore, petrogenic material can be characterized and its presence in marine sediments measured.

2. The interpretation of sulfur isotopic distribution is consistent with the distributions of hydrocarbons analyzed in the sediments and aid in delineating the sources of pollution. Sediments known to be clean by organic geochemical measurements show $\delta^{34}S$ values < - 16‰. Extractable sulfur in petroleum-contaminated sediments has been found to have $\delta^{34}S$ values intermediate between those of uncontaminated sediment and the value of the sulfur in the crude oil source.

3. Sediment traps may collect material that do not contain a bacterial contribution to extractable organic sulfur and hence measured $\delta^{34}S$ values should be similar to those of the source(s) of deposition.

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REFERENCES

Bailey, S.A. and Smith, J.W. (1972). Improved method for the preparation of sulfur dioxide from barium sulfate for isotope ratio studies. Anal. Chem. 44; 1542-1543.

Clark. R.C. and Blumer, M. (1967). Distribution of paraffins in marine organisms and sediments. Limnol. Oceanogr. 12; 79-87.

Crisp, P.T'., Brenner, S., Venkatesan, M.I., Ruth, E. and Kaplan, I.R. (1979}. Organic chemical characterization of sediment-trap particulates from San Nicolas, Santa Barbara, Santa Monica and San Pedro Basins, California. Geochim. Cosmochim. Acts 43; 1791-1801.

Dastillung, M. and Albrecht, P. (1976).' Molecular test for oil pollution in surface sediments. Mar. Pollut. Bull. 7; 13-15.

Eglinton, G. and Hamilton, R.J. (1963). The distribution of alkanes, pp. 187-217, in: Chemical Plant Taxonomy (T. Swain, ed.), Academic Press, N.Y.

Farrington, J.W., Frew, N.M., Gischwend, P.M. and Tripp, B.W. (1977). Hydrocarbons in cores of northwestern Atlantic coastal and continental margin sediments. Estuarine Coastal Mar. Sci. 5; 793-808.

Goldhaber, M.B. and Kaplan, I.R. (1974). The Sulfur Cycle. In: The Sea, Vol. 5--Marine Chemistry, (Goldberg, E. D., cd.), John Wiley and Sons, Inc.; pp. 569-655 .

Grizzle, P.L., Coleman, H.J., Sweeney, R.E. and Kaplan, I.R. (1979). Correlation of crude oil source with nitrogen, sulfur and carbon stable isotope ratios. Symp. Preprints, ACS/CSJ, Div. of Petroleum Chem. (1979), Honolulu, Apr. 1-6; pp. 39-57.

Hartman, B.A. (1978). The use of carbon and sulfur isotopic ratios and total sulfur content for identifying the origin of beach tars in Santa Monica Bay, California. Ph.D. Thesis, University of Southern California.

Kaplan, I.R., Emery, K.O., Rittenberg, S.C. (1963). The distribution and abundance of sulphur in Recent marine sediments off Southern California. Geochim. Cosmochim. Acts 27; 297-331.

Kaplan, I.R., Smith, J.W. and Ruth E. (1970). Carbon and sulfur concentration and isotopic composition in Apollo 11 lunar samples. Proc. Apollo 11 Lun. Sci. Conf., (Geochim. Cosmochim. Acts Suppl. 2); 1317-1329.

Kaplan, I.R., Reed, W.E., Sandstrom, M. and Venkatesan, M.I. (1977). Characterization of organic matter in sediments from Gulf of Alaska, Bering and Beaufort Seas. Annual Report to U.S. Dept. of Commerce, NOAA, Contract No. 03-6-022-352. R.U. No. 480; pp. 16.

*

Kollatukudy, P.E. and Walton, T.J. (1972). The biochemistry of plant cuticular lipids. In: Progress in the Chemistry of Fats and Lipids, Vol. 13, pt. 3, (R-T. Holman, ed.), Pergamon; pp. 121-175.

Mankiewicz, P.J. (1980). Hydrocarbon composition of sediments, water, and fauna in selected areas of the Gulf of Mexico and Southern California marine environments, Ph.D. Thesis, University of California at Los Angeles.

Nissenbaum, A. and Kaplan, I.R. (1972). Chemical and isotopic evidence for the in situ origin of marine humic substances. Limnol. Oceanogr. 17; 570-582.

Reed, W.E., Kaplan, I.R., Sandstrom, M., and Mankiewicz P. (1977) Petroleum and anthropogenic influence on the composition of sediments from the Southern California Bight. Proc. 1977 Oil Spill Conference, New Orleans; Louisiana, API, EPA and USCG; pp. 183-188.

Seifert, W.K., Moldowan, J.M., Smith. G.W. and Whitehead, E.V. (1978). First proof of C_{28}-pentacyclic triterpane in petroleum. Nature 271; 436-437.

Shokes, R. and Mankiewicz, P. (1978). Geochemical Baseline Study TEXOMA offshore brine disposal sites. Annual Report Strategic Petroleum Reserve Office, DOE Contract No. EL-77-C-01-8788 to SAI, Inc.

Simoneit, B.R.T. and Kaplan, I.R. (1980). Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern California Bight. Mar. Environ. Res 3; 113-128.

Simoneit, B.R.T., Mazurek, M.A., Stuermer, D.H., Toth, D., Kalil, E., and Kaplan, I.R. (1978). Organic geochemistry of Recent sediments from Walvis Bay, Southwest Africa. In: Distribution and Fate of Biogenic and Petroleum-Derived Substances in Marine Sediments. Annual Report to DOE/BLM, Contract No. EY-76-S-03-0034; pp. 8.

Spears, G.C. and Whitehead, E.V. (1969). Crude Petroleum. In: Organic Geochemisty, (Eglinton, G. and Murphy, M.T.J., eds.), Springer-Verlag, New York; pp. 638-675.

Sweeney, R.E. and Kaplan, I.R. (1978). Characterization of oils and seeps by stable isotope ratios. Proceedings Energy/Environment California, 1978, SPIB; pp. 281-293.

Venkatesan, M.I., Brenner, S., Ruth, E., Bonilla, J. and Kaplan, I.R. (1980a). Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochim. Cosmochim. Acta, 44; 789-802.

Venkatesan, M.I., Sandstrom, M., Brenner, S., Ruth, E., Bonilla, J., Kaplan, I.R. and Reed, W.E. (1980b). Organic geochemistry of surficial sediments from Eastern Bering Sea. In: The Bering Sea Shelf; Oceanography and Resources, (Hood, D.W., ed.), Chapter 25; (in press).

FIGURE CAPTIONS

5-)

FIGURE 1: Index map of southern California Bight. The locations of the Redondo and Coal Oil Point seeps are shown along with the sites of tar and sediment collections.

Seep	x
Sediment	○
Trap	⊕
Beach Tar Locations	▲
Ancient Tar	●

5-)

FIGURE 2: Representative gas chromatograms of hexane fractions of lipids from sediments in eastern Bering Sea (EBBS), Alaska and San Pedro Basin (Southern California Bight). Numbers 15-33 refer to carbon-chain length of n-alkanes; Pr: pristane; UCM: unresolved complex mixture; I.S.: Internal standard (Hexamethylbenzene).

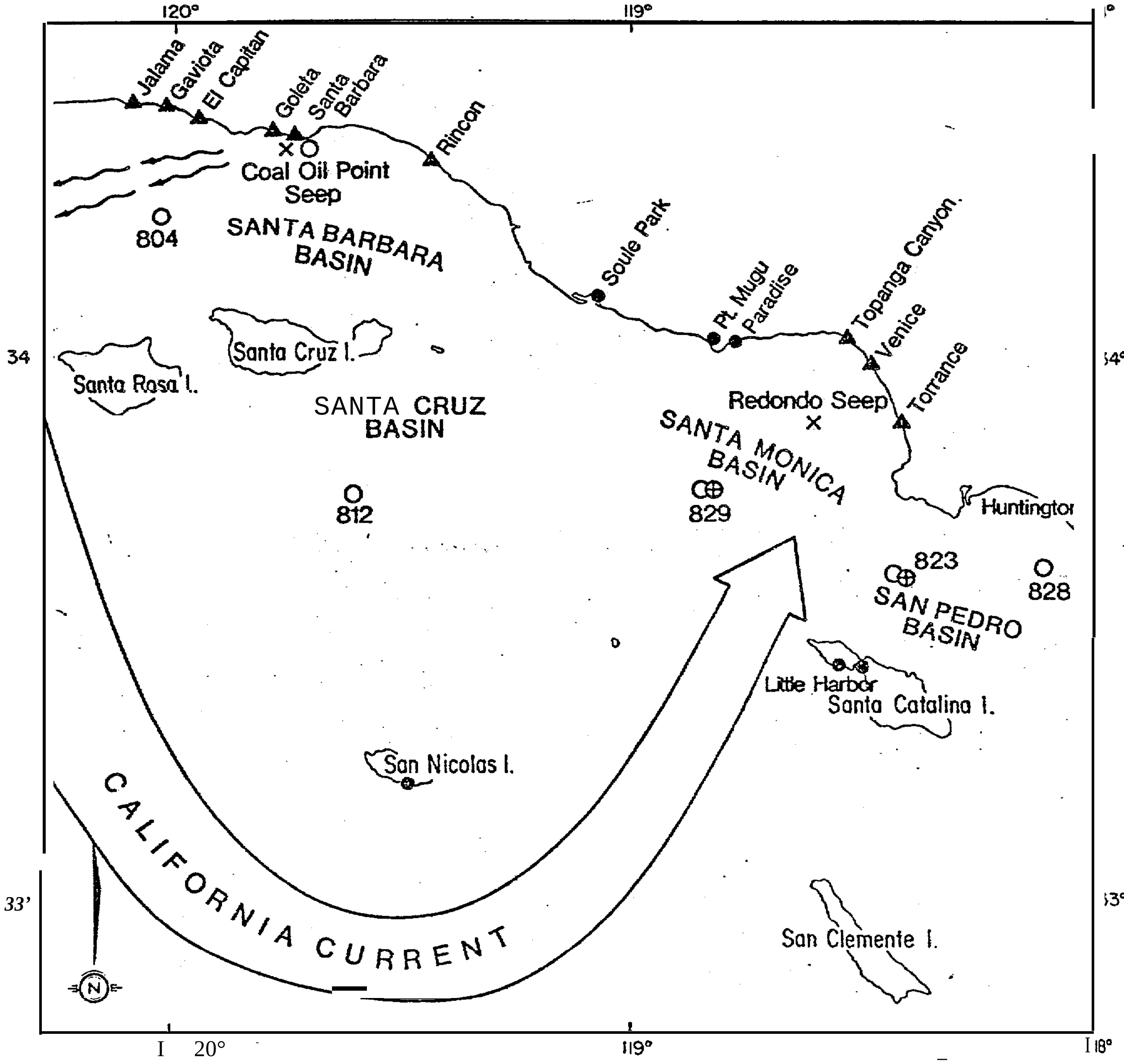
120°
119°
Jalama
Gaviota
El Capitan
Goleta
Santa Barbara
Rincon
Coal Oil Point Seep
804
SANTA BARBARA BASIN
Soule Park
Pt. Mugu
Paradise
Topanga Canyon.
Venice
Torrance
34
34°
Santa Rosa I.
Santa Cruz I.
SANTA CRUZ BASIN
Redondo Seep
SANTA MONICA BASIN
812
829
Huntington
823
828
SAN PEDRO BASIN
Little Harbor
Santa Catalina I.
San Nicolas I.
CALIFORNIA CURRENT
33'
33°
San Clemente I.
N
120°
119°
118°

Fig. 5-1

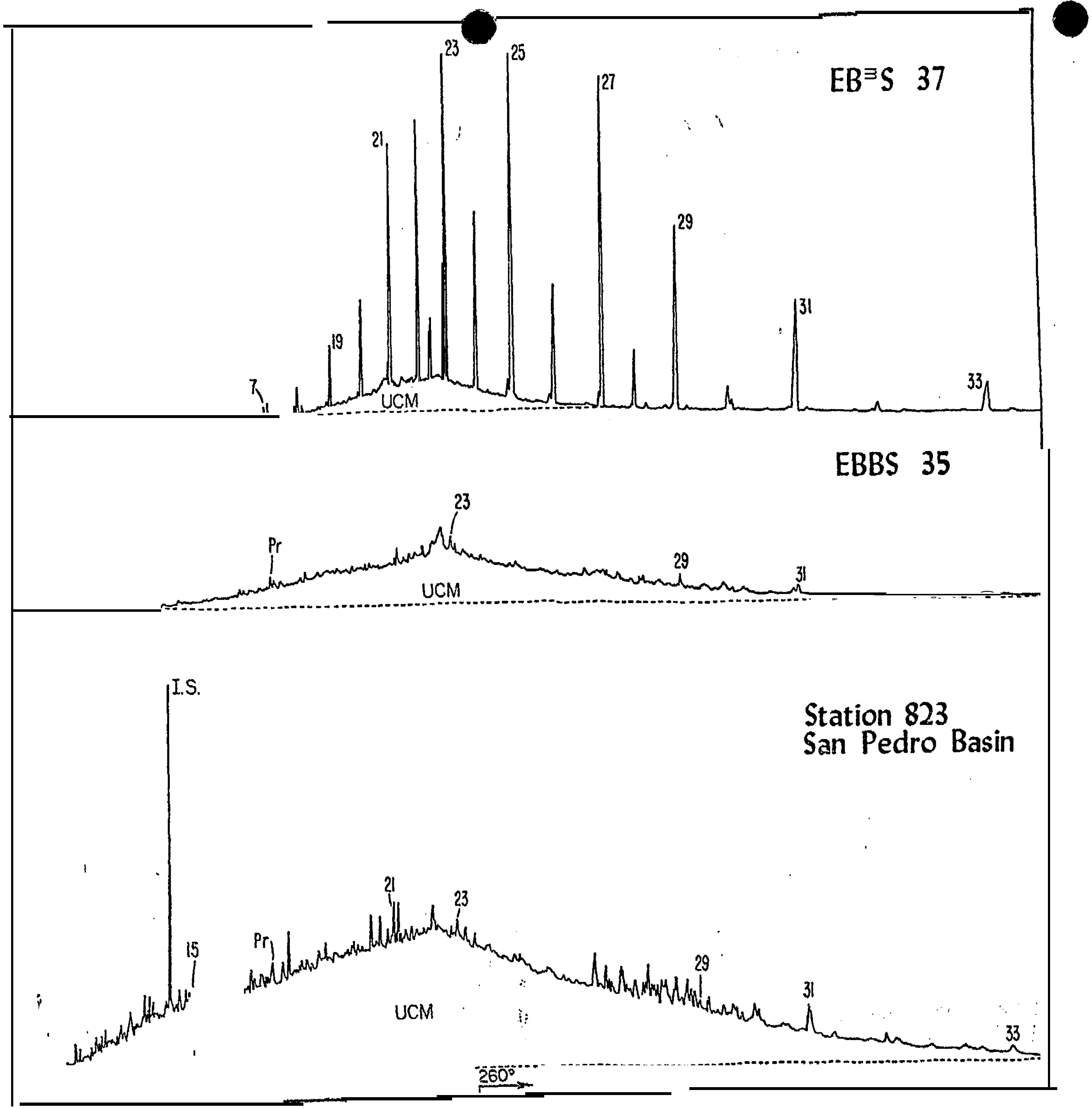
EB≡S 37
7
19
21
23
25
27
29
31
33
UCM
EBBS 35
Pr
23
29
31
UCM
Station 823
San Pedro Basin
I.S.
15
Pr
21
23
29
31
33
UCM
260°

Fig. 5-2

TABLE 1: Content and $\delta^{34}S$ of Sulfur in the Extractable Organic Matter from Recent Sediments and Sediment Traps

Location	Sulfur (%)	$\delta^{34}S$ (‰)	Comments.
Walvis Bay[1]			
Core 38	0.8	-21.2	Reducing sediment, no petroleum contamination
Box Core 2	0.5	-21.1	
Gulf of Alaska[2]			
GASS composite	0.4	-17.3	Oxidizing sediment, no petroleum contamination
Eastern Bering Sea[3]			
EBBS - composite	0.2	-17.9	Oxidizing sediment, no petroleum contamination
EBBS - 35	0.5	-7.1	Petroleum contamination
Gulf of Mexico[4]			
Big Hill	--	-15.7	(Increasing ↓ petroleum contamination)
West Hackberry I	--	-12.7	
West Hackberry II	--	-6.1	
Southern California Bight[5]			Petroleum contamination
Coal Oil Point	1.6	+13.5	500 meters from seep
Santa Barbara Basin			
(0-131 cm)	1.1	+5.6	Composite sections of core with the break (131 cm) representing 1000 years
(131-400 cm)	″	+2.1	
(Surface)	---	+2.3	BLM station 804
San Pedro Basin	0.7	-2.5	BLM Station 823
San Pedro Basin	1.1	-6.8	BLM Station 823
Offshore Huntington Bch.	--	+2.2	BLM Station 828
Santa Cruz Basin	--	-3.3	BLM Station 812
Sediment Traps[6]			
Santa Monica Basin	--	+7.3	BLM Station 829
San Pedro Basin	--	+3.0	BLM Station 823

For station locations, see references: [1] Simoneit *et al.*, 1978; [2] Kaplan *et al.*, 1977; [3] Venkatesan et al., 1980b; [4] Shokes and Mankiewicz, 1978; [5] Figure 1, this paper; [6] Crisp et al., 1979.

5-

TABLE 2: Summary of sulfur content and isotope ratio for seep and beach tars collected in the Southern California Borderland.

Location	NO. of Samples	Sulfur Content (%)	$\delta^{34}S$ (‰)	References and Comments
Natural Seeps				
Coal Oil Point				
Total	5	4.6-5.2	+14.1-+15.1	Sweeney & Kaplan (1978)
Methanol Eluate	3	4.4-4.5	+12.2-+14.0	
Asphaltenes	13	7.5-8.3	+13.7-+15.0	Hartman (1978)
Redondo Seep				
Asphaltenes	4	4.5-6.7	+ 7.9-+12.3	Hartman (1978)
Manhattan Seep				
Asphaltenes	1	5.0	+7.7	Hartman (1978)
Recent Beach Tars (Asphaltenes)				
Jalama to Venice Beach	9		+13.2-+14.7	Sweeney & Kaplan (1978).
Topanga Canyon	2		+13.0-+14.8	Hartman (1978)
Venice Beach	20		*(+1.9) +6.8-+15.9	Hartman (1978)
Torrance Beach	16		*(+4.9) +9.7 -+16.4	Hartman (1978)
Ancient Tars (Total Sample)				
San Nicolas Island		3.6	+15.7	Age unknown
Catalina Island, west side		2.4	+14.4	≈2,000 years old (Kaufman, Pers. Com.)
Little Harbor		3.9	+12.9	
Paradise Cove		2.2	+10.8	
Point Mugu (Simomo)		0.3	+ 7.2	≈1,000 years old. (Kaufman, Pers. Com.)
Ventura Co. (Soule Park)		1.2	+ 6.5	

* Anomalous Results

IV. PAPERS PUBLISHED DURING 1980-1981

1. Stable isotope composition of dissolved sulfate and hydrogen sulfide in the Black Sea. Mar. Chem. 9; 145-152 (1980), R.E. Sweeney and I.R. Kaplan.
2. Diagenetic sulfate reduction in marine sediments. Marine chemistry 9; 165-174 (1980), R.E. Sweeney and I.R. Kaplan.
3. Tracing flocculent industrial and domestic sewage transport on San Pedro Shelf, Southern California, by nitrogen and sulphur isotope ratios. Mar. Env. Res. 3; 215-224 (1980), R.E. Sweeney and I.R. Kaplan.
4. Characterization of domestic and industrial sewage in Southern California coastal sediments using nitrogen, carbon, sulphur and uranium tracers. Mar. Environ. Res. 3; 225-243 (1980), R.E. Sweeney, E. Kalil and I.R. Kaplan.
5. Extractable organic matter in urban stormwater runoff. I. Transport dynamics and mass emission rates. Env. Sci. Tech. 15; 310-315 (1981), R.P. Eganhouse and I.R. Kaplan.
6. Extractable organic matter in urban stormwater runoff. II. Molecular characterization. Env. Sci. Tech. 15; 315-326 (1981), R.P. Eganhouse, B.R.T. Simoneit and I.R. Kaplan.
7. Low ^{15}N/^{14}N in hydrothermal vent animals: Ecological implications. Nature 289; 484-485 (1981), Greg H. Rau.
8. Hydrothermal vent clam and Tube worm ^{13}C/^{12}C: Further evidence of non-photosynthesynthetic food sources. Science 213; 338-340 (1981), Greg H. Rau.

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STABLE ISOTOPE COMPOSITION OF DISSOLVED SULFATE AND HYDROGEN SULFIDE IN THE BLACK SEA*

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ABSTRACT

Sweeney, R. E. and Kaplan, I. R., 1980. Stable isotope composition of dissolved sulfate and hydrogen sulfide in the Black Sea. Mar. Chem., 9: 145-152

The stable isotope ratio of sulfur ($^{34}S/^{32}S$) in dissolved sulfate and hydrogen sulfide was measured for 20 water samples from two deep hydrocasts from the south-central Black Sea. The isotope ratio of total reduced sulfur was also measured for surface sediment collected below each hydrocast. The range in the $\delta^{34}S$ measurements for sulfate was +18.20 to +20.17% and for hydrogen sulfide -38.71 to -4.85‰. The distribution pattern for $\delta^{34}S$ in both sulfate and sulfide appears to be the result of in situ sulfate reduction.

INTRODUCTION

The Black Sea is a large marine basin in which permanent anoxic conditions have persisted in the deep water layer for the last 2000 years. The present oxic—anoxic boundary exists between 125 and 250 m below the surface. Sulfate reduction is considered the dominant microbiological process below this boundary. Measurements of the distribution of dissolved constituents in the Black Sea water column are summarized or referred to in Caspers (1957), Skopintsev (1962), Skopintsev et al. (1967) and Brewer and Spencer (1974). The chemical gradients developed with depth are, in general, considered similar throughout the basin. Only two major studies are known to have been made of stable isotope distributions in the Black Sea water column. Vinogradov et al. (1962) measured the $^{34}S/^{32}S$ isotope distribution for dissolved sulfate and hydrogen sulfide, and Deuser (1970) measured the $^{13}C/^{12}C$ isotope distribution for dissolved carbon dioxide. The former study consisted of 12 measurements of sulfate (from two hydrocasts) and 19 measurements of sulfide (from four hydrocasts).

In the present investigation 20 water samples were collected *from* two

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adjacent hydrocast stations in the south-central Black Sea (Woods Hole "Chain" Cruise 120/1, April, 19'75). The concentration and isotopic composition were measured for dissolved sulfate and hydrogen sulfide to determine whether stable isotope gradients exist with depth and, if so, how the isotope distribution correlates with concentrations,

EXPERIMENTAL

Dissolved hydrogen sulfide was precipitated as CdS by the addition of 10 ml of 5% cadmium acetate solution to each 1-1 water sample, immediately after collection. Upon return to the laboratory, 800-900 ml of precipitate-free water was decanted. The CdS suspension was acidified and the hydrogen sulfide produced was flushed into a 5% $AgNO_3$ solution, forming Ag_2S which was analyzed gravimetrically. The dry silver sulfide was reacted with cuprous oxide at 850°C to form SO_2 for isotope analysis (Sweeney, 19'72). Three 10-ml aliquots were taken from the "decanted" water for sulfate analysis; the sulfur content was determined gravimetrically after precipitation as $BaSO_4$. The barium sulfate was directly decomposed at high temperature, forming SO_2 for $\delta^{34}S$ analysis (Baily and Smith, 1972).

The hydrogen sulfide samples were measured relative to sample 1135 (taken at 1400 m), and subsequently transformed to the Canyon Diablo Meteorite "6" scale. The sulfate samples were measured relative to sea water sulfate and, likewise, corrected to the meteorite standard scale. Reduced sulfur species were oxidized to sulfate by aqua-regia treatment. The sulfate was then precipitated as $BaSO_4$ and prepared for mass spectrometer analysis as above.

RESULTS

Sample site locations for this study (1135 and 1136) and for the study by Vinogradov et al. (1962) are shown in Fig.1. Results of measurements on

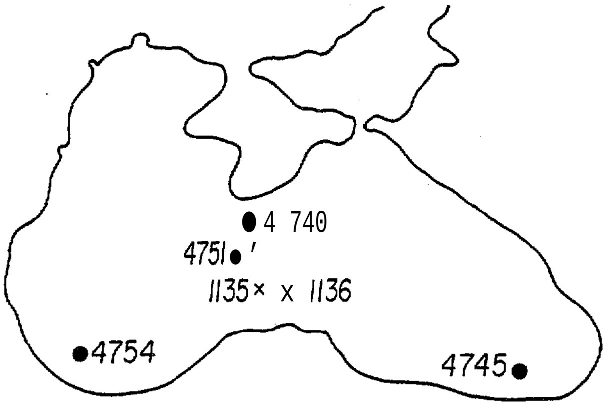

Fig. 1. Locations of stations 1135 and 1136 in the Black Sea (crosses). Also included are stations (dots) from Vinogradov et al. (1962).

water and sediment samples are shown in Tables I and H, respectively. Triplicate measurements of sulfate concentration *were* made for each sample. The average range for the replicates was 0.15 m*M*. An increase in sulfate concentration from 16.2 m*M* at 100 m to 18 m*M* at 1000 m corresponds directly to the increase in chlorinity shown by Skopintsev et al. (1967) and Kremling (1974), for equivalent depths. A direct non-linear correlation between δ^{34} S and sulfate concentration is shown in Fig.2. The δ^{34} S values for deep water sulfate are approximately 1.5-2 ‰ more positive than that in the surface water.

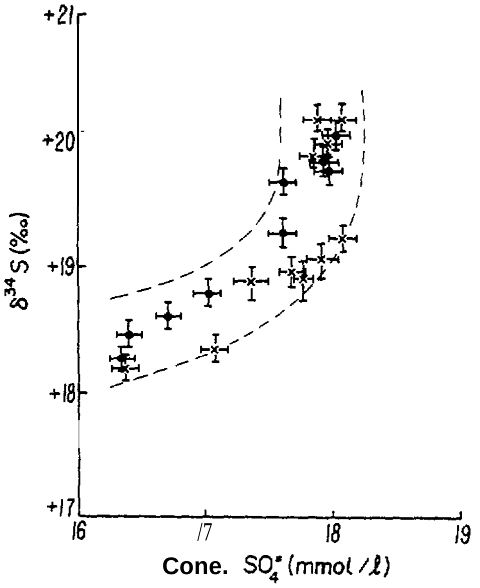

Fig. 2. Correlation between δ^{34} S and concentration of sulfate in Black Sea water column. Experimental point-s are for station 1135 (dots) and station 1136 (crosses).

The concentration of hydrogen sulfide at each depth corresponds to previous measurements reported in the literature (Brewer and Spencer, 1974). The δ^{34}S values of the 14 samples measured were within 2.2‰ of each other. Isotope depth profiles are given in Fig.3, and are compared with the measurements of Vinogradov et al. (1962), the δ^{34}S values measured in the present study being significantly more negative than values from those studies. A decrease in δ^{34}S of dissolved sulfide occurs between the surface and 750 m for both hydrocasts. This is in accord with the measurements of Vinogradov et al. (1962). However, a corresponding increase in δ^{34} S near the sediment surface is not apparent in the hydrocasts 1135 and 1136. The δ^{34} S of total sulfur in the sediment is 11—14 ‰ more positive than hydrogen sulfide in the hydrocasts.

TABLE **I**

Measurements of the concentrations and isotopic composition of sulfide and sulfate in Black Sea water column*

Station	**Depth** (m)	Sulfide		Sulfate	
		(μM)	$\delta^{34}S$(‰)	(mM)	$\delta^{34}S$(‰)
1135	125			**16.17**	**+18.25**
	145			**16.40**	**+18.47**
	190	15	‘38.71	**16.71**	**+18.61**
	235	25	-39.15	17.03	**+18.79**
	260	40	-39.51		
	500	126	‘40.62	17.61	**+19.27**
	750	186	-40.59	17.63	**+19.69**
	1000	290	-40.12	17.94	**+19.81**
	1400	296	‘40.62	18.03	+20.03
	2050	349	-40.29	17.97	**+19.76**
1136	100			16.36	**+18.20**
	165			17.07	**+18.35**
	180	6		**17.38**	**+18.83**
	200	9		17.86	**+18.72**
	300	**12**	‘38.71	17.’72	**+18.91**
	500	115	-39.89	17.92	**+18.82**
	750	148	-40.85	18.08	**+19.20**
	1000	242	-39.33	18.08	**+20.17**
	1800	353	‘39.12	17.89	**+20.17**
	2000	256	‘39.62	**17.97**	**+19.97**

*California coastal seawater 28.8 mM, +19.7dVm.

TABLE **II**

The δ^{34} S values of dissolved hydrogen **sulfide** in the water column and reduced mineral sulfur in the related surface sediment

Station	Hz S **hydrocast** $\delta^{34}S$(‰)[a]	Reduced sulfur sediment $\delta^{34}S$(‰)[b]	$\Delta(\delta^{34} S_{H_2S} - \delta^{34}S$ **sediment**$)$[c]
1135	‘38.7 to ‘40.6	-27.4	-11,3 to -13.2
1136	-38.7 to ‘40.9	–27.0	-11.7 to -13.3
4751†	-30.9 to ‘35.2	-19.3	‘11.6 to ‘15.9
4740†	-23.7 to **−31.3**	-32.7	+9.0 **to** +1.4
4745†	–30.7 to -35.4	-33.0	+2.3 to -2.4
4754†	**−31.4** to **−36.1**	-26.3	**−4.8 to −0.8**

[a] The range of δ^{34} S of dissolved hydrogen sulfide in **hydrocasts** from several stations.

[b] δ^{34} S of total reduced **sulfur** in the surface sediment below each **hydrocast.**

[c] The isotopic difference, A, between dissolved hydrogen sulfide in the deep water and reduced sulfur in the sediment.

† **After Vinogradov** et **al.** (1962).

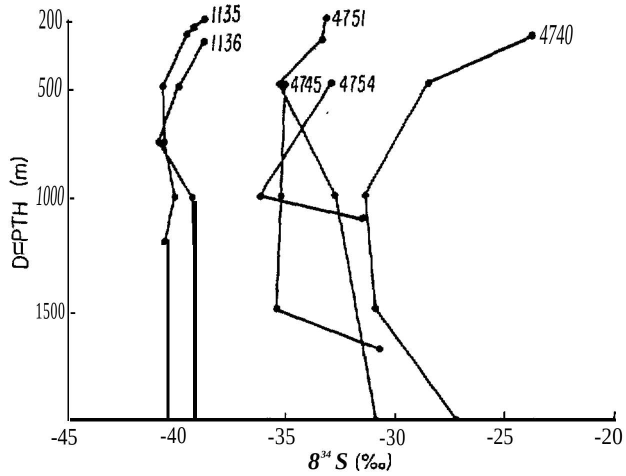

Fig.3. Distribution of δ^{34} S for dissolved sulfide in the Black Sea. Measurements at stations 1135 and 1136 are from this study, others are from Vinogradov et al. (1962).

DISCUSSION

Cline and Kaplan (1975) and Kroopnick and Craig (1976) were able to substantiate in situ denitrification and oxygen consumption in the ocean by the use of chemical and stable isotope data. For both studies the zone of reaction was located within the water column and did not directly intersect the sediment surface. The depletion depth interval and the in situ removal were exemplified by lesser intermediate concentrations than predicted for mixing between the extreme water masses. A different situation exists for dissolved sulfate in the Black Sea. The sediment itself is the likely zone of most active sulfate reduction and therefore will contain the lowest relative concentration of sulfate. Here, the distinction between a mixing curve and a mixing—reaction curve is more difficult to distinguish.

Although dissolved sulfate and chloride both increase with depth in the Black Sea (Table I; Skopintsev, 1957), the SO_4/Cl ratio continuously decreases below 1000 m (Skopintsev, 1957; Kremling, 1974). It is therefore apparent that dissolved sulfate is not a conservative component in the deep water and has been removed relative to dissolved chloride. This depletion could occur as a result of in situ reduction to hydrogen sulfide in the water column or as a consequence of diffusive mixing with relatively low-sulfate "bottom" water, produced by sulfate reduction in the sediment.

Figure 2 shows that the positive correlation between δ^{34} S and the concentration of sulfate is apparently not near-linear, as would be produced by conservative mixing between "bottom" water and "surface" water. Figure 4 shows the correlation between concentration of total sulfur (sulfate plus hydrogen sulfide) and the mean δ^{34} S of each sample. The correlation is

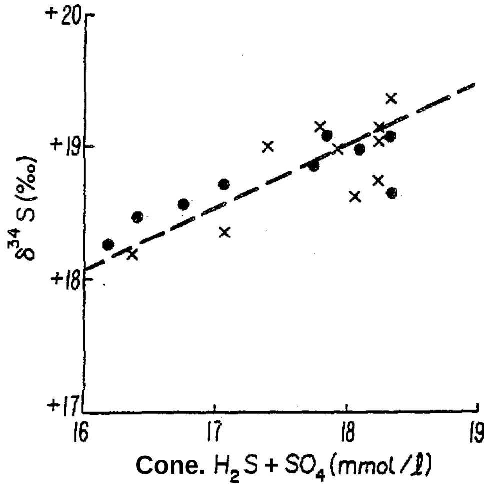

Fig.4. Correlation between δ^{34} S (mean for each sample) and total dissolved sulfur (sulfate + hydrogen sulfide). Experimental points are for station 1135 (dots) and station 1136 (crosses).

consistent with a mixing relation, where total sulfur is a conservative component.

Since the isotopic distribution of total dissolved sulfur is controlled by mixing, then the more positive δ^{34} S values for deep water column sulfate must be due to enrichment by in situ sulfate reduction. From Fig.4, it could be estimated that the δ^{34} S for sulfate in the deep water would initially be about +19.0‰, compared to the measured value (after sulfate reduction) of ~+19.8‰. This δ^{34}S value (+19.0 ‰) for saline water entering the Black Sea is less than the average δ^{34} S value of ~+20 ‰ for modern sea water. Vinogradov et al. (1962) state that the deep water in the Black Sea should be isotonically lighter than sea water due to previous mixing with stream waters impoverished in ^{34}S.

Dissolved hydrogen sulfide in the surface 750-1000 m of the Black Sea water column has slightly more positive δ^{34} S values than hydrogen sulfide at greater depth. This could be due to a kinetic isotope fractionation during the oxidation of hydrogen sulfide migrating from depth, as suggested by Vinogradov et al. (1962), or due to different kinetic isotope effects in sulfate reduction near the top and bottom of the water column. Jannasch et al. (1974) have observed that sulfate-reducing bacteria are abundant below the "intermediate $O_2 - H_2S$ layer" which is generally between 125 and 300 m (Skopintsev, 1962), thus supporting our interpretation that sulfide is generated within the water column. Isotopic fractionation resulting from biogenic sulfate reduction may conceivably control the δ^{34} S of dissolved sulfide throughout the water column and in the sediment (Kaplan and Rittenberg, 1964).

Goldhaber and Kaplan (1974) have shown that δ^{34} S of reduced sulfur in marine sediments is an indicator of the rate of sulfate reduction which may be controlled by the availability of easily degradable organic matter. A relatively higher rate of sulfate reduction near the "intermediate O_2—H_2S layer" would produce hydrogen sulfide with a more positive δ^{34} S than hydrogen sulfide produced in deeper water. The large range in δ^{34} S values measured both vertically and horizontally in the Black Sea demonstrates that the fractionation factor for sulfate reduction is not uniform. Vinogradov et al. (1962) have noted that the more positive δ^{34} S values in hydrogen sulfide correlate with areas of more rapid sulfate reduction. In Table 11 the δ^{34} S of reduced sulfur in the sediment is shown to be quite different from the δ^{34} S for hydrogen sulfide in hydrocasts 1135 and 1136. This difference (11–14‰) is too large to be explained by isotopic enrichment of the pore water sulfate. For comparison, the δ^{34} S values of two of the four hydrocasts listed in Vinogradov et al. (1962) are also more negative than the reduced sulfur in the underlying sediment. The more positive δ^{34} S values of reduced sulfur in the sediment are consistent with a more rapid rate of sulfate reduction occurring in the sediment than the water column. The δ^{34} S values of hydrogen sulfide in the water column approach the most negative values measured for sulfur in the marine environment (Goldhaber and Kaplan, 1974).

CONCLUSIONS

Continuous concentration and isotope gradients exist for dissolved sulfate in the Black Sea water column. The gradients are due to convective mixing of marine and fresh water and isotope fractionation during in situ sulfate reduction. Although the dissolved sulfide constitutes ~2% at most of the total dissolved sulfur in the water column, its δ^{34} S value is such as to significantly alter the mean δ^{34} S of the total sulfur. Variation in the δ^{34} S values of dissolved hydrogen sulfide in the water column may be controlled by the rate of sulfate reduction.

ACKNOWLEDGEMENTS

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REFERENCES

Baily, S. A. and Smith, J. W., 1972. Improved method for the preparation of sulfur dioxide from barium sulfate for isotope ratio studies. Anal. Chem., 44: 1542–1543.

Brewer, P. G. and Spencer, D. W., 1974. Distribution of some trace elements in the Black Sea and their flux between dissolved and particulate phases. Am. Assoc. Pet. Geol. Mere., 20: 137–143.

Caspers, H., 1957. Black Sea and Sea of Azov. Geol. Sot. Am. Mere., 67:801-889.

Cline, J. P. and Kaplan, I. R., 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern Tropical North Pacific Ocean. Mar. Chem., 3: 271–299.

Deuser, W. G., 1970. Carbon-13 in Black Sea waters and implications for the origin of hydrogen sulfide. Science, 168: 1575—1577.

Goldhaber, M. B. and Kaplan, I. R., 197'4. The sulfur cycle. In: E. D. Goldberg (Editor), The Sea. John Wiley, New York, NY, Vol. 5. Ch. 17, Pp. 569-655.

Jannasch, H. W., Truper, H. G. and Tuttle, J. H., 1974. Microbial sulfur cycle in the Black Sea. Am. Assoc. Pet. Geol. Mere., 20:419--425.

Kaplan, I. R. and Rittenberg, S. C., 1964. Microbiological fractionation of sulfur isotopes. J. Gen. Microbiol., 34: 195–212.

Kremling, K., 1974. Relation between chlorinity and conductiometric salinity in Black Sea water. Am. Assoc. Pet. Geol. Mere., 20: 151–154.

Kroopnick, P. and Craig, H., 1976. Oxygen isotope fractionation in dissolved oxygen in the deep sea. Earth Planet. Sci. Lett., 23: 375–388.

Skopintsev, B. A., 1957. Investigation of the oxidation-reduction potential in the water of the Black Sea. Gidrokhim. Mater., 27: 21—38.

Skopintsev, B. A., 1962. Recent work on the hydrochemistry of the Black Sea. Deep-Sea Res., 9:349-357.

Skopintsev, B. A., Timofeyeva, S. N., Danilenko, H. F. and Sokalova, M. V., 1967. Organic carbon, nitrogen, phosphorus and their mineralization products in Black Sea water. Oceanology, 7: 353—355.

Sweeney, R. E., 1972. Pyntization during diagenesis of marine sediment. Ph.D. dissertation, University of California, Los Angeles, CA, 198 PP.

Vinogradov, A. P., Grinenko, V. A. and Ustinov, U. S., 1962. Isotopic composition of sulfur compounds in the Black Sea. Geochemistry, 10: 973—997.

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DIAGENETIC SULFATE REDUCTION IN MARINE SEDIMENTS*

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ABSTRACT

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The importance of interstitial pore water as a vehicle for transport of dissolved ions between sediment at depth and the overlying ocean reservoir maybe overestimated. The major cause of this overestimation is the assumption that the rate of ionic diffusion through the sediment is of a similar magnitude to the rate of reaction occurring within the sediment column. Examples are given to indicate that the above assumption may not be correct, at least for diagenetic sulfate reduction. Closed-system modeling, although approximate, is shown to be consistent, both qualitatively and isotonically, with measured changes that are observed for several sedimentary environments.

INTRODUCTION

The oxidation of particulate organic matter by bacterial sulfate reduction, is one of the dominant diagenetic reactions that occurs in recent marine sediments. Kaplan et al. (1963) show that, in general, the amount of sulfur added to the sediment through transport as mineral or organic debris is not significant. Therefore, the amount of reduced sulfur present in the sediment can be used to determine the extent of in situ reaction. The relatively large amount of reduced sulfur (iron sulfide and elemental sulfur) measured in surface samples has led to the conclusion (Kaplan et al., 1963; Hartman and Nielson, 1969) ‘that rapid sulfate reduction occurs in the few centimeters of the sediment nearest the surface. The corresponding depletion of dissolved sulfate in this zone is almost completely eliminated by the advective mixing of the water column. With increasing depth in the sediment, the water becomes more stagnant and perturbation is essentially limited to that due to burrowing organisms and compaction.

The amount of reduced sulfur contributed to the sediment by sulfate reduction during burial is limited by the amount of sulfate in the trapped pore water, plus the amount that diffuses into the sediment from seawater due to a decreasing sulfate concentration gradient with depth. Sweeney

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(1972) attempted to quantitatively relate the decrease in dissolved sulfate in the pore water during burial to the amount of reduced sulfur added to the solid sediment. For this, it was necessary to separate the sulfur compounds formed at the surface (syngenetic) from those formed at depth in the sediment (diagenetic). It was shown that the amount of syngenetic sulfur formed in the sediment was related to the amount of organic carbon deposited (Berner, 1970), and that the latter may vary with time. From the analyses of several sediment cores (including data from the literature) it was concluded that the diagenetic addition of sulfur was sufficiently masked by the heterogeneous distribution of syngenetic sulfur to disallow its quantitative estimation by mass-balance calculations, this concept being summarized by Goldhaber and Kaplan (1974). It was suggested, however, that because the isotopic composition of diagenetic sulfur was different from syngenetic sulfur (Kaplan et al., 1963), isotopic mass-balance calculations may be used to determine the contribution of diagenetic sulfur in given sediment sections.

The amount and isotopic composition of diagenetic sulfur have been calculated by Sweeney (1972) from the amount of dissolved sulfate remaining in the pore water using a closed-system model. This model assumes that the original concentration and isotopic composition of dissolved sulfate in the pore water is similar to that in the overlying seawater and that excess sulfate added by ionic diffusion is-negligible. The calculated results for core profiles from Catalina Basin, Cariaco Trench and San Pedro Martir Basin (Gulf of California) and sites 26 and 2’7 (cores from Deep Sea Drilling Project) corresponded sufficiently to the measured data that it was concluded that the addition of sulfur by ionic diffusion to the sediment during burial was small with respect to the amount reduced.

Continuing along the same line, Goldhaber (1974) made “core-profile” measurements of the sediment from five Gulf of California basins. For Pescadero Basin (core 50G), it was observed that the reduced sulfur content consistently increased and the organic carbon content decreased with depth in the sediment. It was concluded that both were the consequence of diagenetic sulfate reduction. Calculations determined that the amount of sulfur added to the sediment was over five times that calculated by the closed-system model. It seemed reasonable to suggest that this excess sulfur must have been brought into the system by ionic diffusion of dissolved sulfate. The effective ionic diffusion coefficient of dissolved sulfate necessary to explain the excess sulfur in core 50G should also produce a 2—3 times excess sulfur in the sediment from San Pedro Martir Basin. This excess was not observed by Sweeney (1972).

This is the second. of a two-part discussion (see Goldhaber and Kaplan, 1980), contrasting the closed-system interpretation of pore-water chemistry with the diffusion-dominated open system. Sulfur isotope data are presented to demonstrate that a closed-system model can also be used to explain the distribution of sulfur in marine sediments. Sample locations and experimental methods are given in Sweeney (1972) and Goldhaber and Kaplan (1980).

RESULTS

Sediment containing syngenetic sulfur

With burial and isolation of the interstitial water, the residual sulfate becomes relatively enriched in ^{34}S at depth due to the preferential reduction of ^{32}S during production of sulfide (Kaplan et al., 1963). Therefore, as reduction of sulfate continues after burial, the δ^{34}S of the sulfate remaining increases, following a Rayleigh distillation curve (Sweeney, 1972). However, an increase in δ^{34}S of sulfide formed by in situ reduction is generally not reflected in the pyrite-sulfur fraction of the sediment. This is due to the fact that the amount of pyrite formed at the surface is large relative to the amount of sulfur added after burial. In the Santa Barbara Basin (Kaplan et al., 1963) and the Catalina Basin, the δ^{34}S of the pyrite fraction becomes more negative with depth (Sweeney, 1972). This trend cannot be produced by isotope fractionation occurring during burial. It appears that the δ^{34}S values of syngenetic pyrite vary unpredictably with depth in the sediment column. That is, the average fractionation during reduction of sulfate was not constant with respect to time. By contrast, the δ^{34}S of reduced sulfur in the sediment from the San Pedro Martir Basin (Gulf of California) increases continuously with depth (Table I). This increase in δ^{34}S could either be due to continued sulfate reduction during burial from a depleting sulfate reservoir, or may reflect the δ^{34}S of reduced sulfur mineralized in that layer when it was at the sediment surface.

To derive an estimate of the δ^{34}S of the reduced sulfur incorporated near the sediment surface, the amount and δ^{34}S of sulfide added during burial is subtracted from the values measured in the sediment. This is accomplished using the following equations

$$\delta_A = (\delta_0 C_0 - \delta_1 C_1 - \delta_2 C_2)/(C_0 - C_1 - C_2) \qquad (1)$$

$$S_A = [0.0032P/(1.024\ (100 - P))]\ [C_o - C_1 - C_2] \qquad (2)$$

$$\delta_S = (S_M \delta'_M - S_A\ \delta_A)/(S_M - S_A\ ) \qquad (3)$$

where: C_0 = concentration sulfate in seawater (mmol l^{-1}); C_1 = concentration of sulfate in pore water (mmol l^{-1}); C_2 = concentration of hydrogen sulfide in pore water (mmol l^{-1}); S_A = amount of reduced sulfide added to sediment during burial (Y.); S_M = amount of reduced sulfur measured in sediment (%); P = water content of sediment (9%); δ_S = δ^{34}S value calculated for syngenetically formed reduced sulfur (96); δ_0; δ_1; δ_2; δ_A and δ_M correspond to the isotopic values of the species described above; 1.024 is the average density of pore water and 0.0032 is the conversion factor of sulfur from molarity to mass.

TABLE I

San Pedro Martir Basin, Gulf of California: (a) concentration and $\delta^{34}S$ of pore-water sulfate and hydrogen sulfide; (b) content and $\delta^{34}S$ of reduced sulfur measured in the sediment and the calculated $\delta^{34}S$ for the syngenetically-formed reduced sulfur. A water content of 50% was used in the calculations

(a) Pore water Depth (cm)	Sulfate		Hydrogen sulfide	
	Concentration (mmol l^{-1})	$\delta^{34}S$ (‰)	Concentration (mmol l^{-1})	$\delta^{34}S$ (‰)
4–14	23.1	+28.2	0.4	-9
15–25	19.9	+31.1	0.6	-11.7
86–95	3.9	+47.2	3.3	+17.3
118–128	2,9	+24.6	2.6	+23.2
190-200	0.6	+19.3	0.7	+25.3
344–354	0.6	+18.6	0.3	+23.7
501–511	1.2		0.0	—

(b) Sediment Depth (cm)	Measured		Diagenetic addition		Calculated syngenetic S
	Sulfur (%)	$\delta^{34}S$ (‰)	Sulfur (%)	$\delta^{34}S$ (‰)	$\delta^{34}S$ (‰)
4–14	0.620	-20.6	0,017	-14	–20.7
15-25	0.837	-21.9	0.026	-6	-22.4
86–95	0.632	-15.1	0.067	+16	–18.8
118–128	0.286	-8.2	0.073	+19	-17.5
190-200	0.564	–16.1	0.086	+20	–22.6
344–354	0.269	-9.1	0.087	+20	-23.0
501–511	0.323	-6.0	0.086	+20*	-15.4

*Estimate.

Using $C_0 = 28.9$ mmol l^{-1} and $\delta_0 = +20$, the calculated $\delta^{34}S$ values of the syngenetically mineralized sulfur (Table I) fall in a more narrow range (–15.4 to -23.0‰) than that measured for the sediment (-6.0 to -21.9‰). This calculated range of $\delta^{34}S$ values of the pyrite formed at the sediment surface is consistent with values obtained from other near-shore marine basins (Goldhaber and Kaplan, 1974). It may be concluded, therefore, that the measured increase in $\delta^{34}S$ of reduced sulfur with depth in San Pedro Martir Basin results from sulfate reduction during burial of sulfur under closed-system conditions.

Calculations for cores from the Carmen (core 38G) and Pescadero (core 50G) Basins in the Gulf of California are shown in Table II. In general, the

TABLE II

Content and $\delta^{34}S$ of reduced sulfur in cores 38G and 50G and calculated $\delta^{34}S$ for syngenetic pyrite. Acid volatile and pyrite sulfur are summed (data are from Goldhaber, 1974, except the $\delta^{34}S$ values in parentheses)

Core no.	Depth (cm)	Total sediment sulfur dry wt. (%)	$\delta^{34}S$ (‰)	Calculated syngenetic sulfur $\delta^{34}S$ (‰)	Core no.	Depth (cm)	Total sediment sulfur dry wt. (%)	$\delta^{34}S$ (‰)	Calculated syngenetic sulfur $\delta^{34}S$ (‰)
50G	16-20	0.30	‘23.6	‘24.0	38G	43 -46.5	0.39	-18.2	-18.0
	20-30	0.22	‘23.2	‘24.3		50-55	0.28	(21.5)	‘22.0
	30-40	0.31	‘23.2	‘24.3		65--70	0.41	–17.3	-18.0
	50-60	0.39	‘22.7	‘24.2		90--100	0.38	(14.2)	‘23.0
	70-80	0.54	‘24.0	‘25.9		110–120	0.33	-10.9	-22.0
	90-100	0.48	’22.0	‘24.2		165–170	0.53	(-7.5)	-21.0
	100-110	0.71	-17.0	-19.0					
	120-130	0.64	–16.1	-18.5					
	130-140	0.73	‘15.6	‘17.6					
	140-150	0.66	‘14.6	–16.7					
	170--180	0.67	–13.8	-17.7					
	190–200	0.70	‘13.6	‘17.2					

isotope change with depth can be accounted for by closed-system diagenetic sulfate reduction. It should be noted, however, that because of the non-constancy of the isotopic ratio of pyrite formed at the sediment surface, the above calculations are not equally applicable to all sediments.

Sediment deficient in syngenetic sulfur

Sediment samples have been obtained from two cores taken on Leg 4 of the Deep Sea Drilling Project in the SW. Atlantic Ocean (Presley and Kaplan, 1970). The sample sites 26 and 27 are located east of the continental slope of Venezuela.

The concentrations and $\delta^{34}S$ values for pore-water sulfate are shown in Table III, along with the calculated values for the sulfate reduced during burial at each depth. Table III also lists the measured contents and $\delta^{34}S$ values calculated for diagenetic addition using eqs. 1 and 2. The calculated and measured quantities of sulfur are within 0.006% of eachother and the $\delta^{34}S$ values are separated by only 2 ‰ or less.

The most probable causes of error in the calculation of534S for reduced sulfur in the sediment are the measurements of the concentration of pore-water sulfate and the assumed concentration of sulfate in seawater. In Table 111, the range in the calculated $\delta^{34}S$ values are shown, assuming the measured value of pore-water sulfate concentration to be accurate to within ±1 mmol l^{-1}. Only the measurement of $\delta^{34}S$ for sample 26/100 (+2.0‰) falls outside of the corresponding calculated range (–1.2 to +1.3 ‰).

TABLE III

List of the contents and δ^{34}S values of sulfur (measured and calculated) for sediment cores, sites 26 and 27, Deep Sea Drilling Project (Presley and Kaplan, 1970)

(a) Pore water

Site/ depth (m)	Measured sulfate		Calculated sulfate reduced		Water content (%)
	Conc. (mmol l^{-1})	δ^{34}S (‰)	Conc. (mmol l^{-1})	δ^{34}S (‰)	
26/100	*13.3*	+43.4	*15.6*	+0.0	*32*
478	*5.3*	*+43.0*	*23.6*	+14.8	*26*
27/237	*12.1*	+40.9	*16.8*	*+ 4.9*	*31*
249	11.7	+44.7	*17.2*	+ *3.1*	*28*

(b) Sediment

Site/ depth (m)	Measured reduced sulfur		Calculated diagenetic addition		Range[a]
	Sulfur (%)	δ^{34}S (‰)	Sulfur (%)	δ^{34}S (‰)	
26/100	0.020	+2.0	0.023	+0.0	‘1.2–1.3
478	0.025	+13.4	0.026	+14.8	+13.4—+15.0
27/237	0.015	+3.8	0.023	+4.9	+3.5—+5.8
249	0.015	+3.7	0.021	+3.1	+1.9—+4.1

[a] Precision of calculation : values for the concentration of sulfate in pore water equals ±1 mmol l^{-1} from the measured value.

Mass balance of sulfur isotopes in size fractions of sediment

The first iron sulfide phase formed from solution is not pyrite, but metastable iron sulfide (amorphous mackinawite, $FeS_{0.9}$, or greigite, Fe_3S_4). Since the crystal structures of these phases are different from pyrite, overgrowth of pre-existing pyrite grains may not occur during early diagenesis (Sweeney and Kaplan, 1973). Diagenetically-formed iron sulfides may initially be concentrated in the finest size fraction of the sediment.

Sweeney (1972) has shown that only minor differences (l–2 ‰) exist for the δ^{34}S values of pyrite in the various size fractions of surface sediment or sediment sections from cores where sulfate depletion does not occur. Where sulfate reduction has occurred during burial, the $< 44\mu$ fraction of the sediment has a consistently more positive δ^{34}S value. If the more positive δ^{34}S values for sulfide in the $< 44\mu$ fraction are due to diagenetic addition of isotonically heavy sulfur, then the δ^{34}S value of the syngenetic component can be calculated as previously. Table IV-lists the calculated δ^{34}S values for pyrite formed at the sediment surface ($< 44\mu$) for a set of samples taken from a core in the Santa Catalina Basin. Before correction, the mean difference between the $< 44\mu$ fraction and the average $> 44\mu$ fraction is +6.4 ‰. After correction, the difference is only −0.7 ‰.

TABLE IV

Santa Catalina Basin: the δ^{34}S values of pyrite sulfur in the fine and coarse size fractions of the sediment. Also shown is the calculated δ^{34}S of the sulfur in the fine size fraction of the sediment after the effect of diagenetic sulfate reduction is eliminated (data from Sweeney, 1972)

Depth (cm)	δ^{34}S of pyrite sulfur *in* sediment (‰)		
	Average > 44/l	Measured < 44/l	Calculated sediment surface < 44μ
160-167	-44.5	‘35.6	-45.1
248–256	-42.5	-35.4	-41.9
314–322	-42.1	–38. 5	‘42.6
356–361	-40.9	‘35.6	-43.3
415–423	-42.5	‘35.2	-43.3

Similar measurements were made for a sediment sample from the Cariaco Trench (JOIDES, Leg 15, Hole 147 b), where, at the sediment depth analyzed, no sulfate remained in the interstitial water (Sayles et al., 1973). The measured δ^{34}S values of pyrite from different size fractions (104, 104—74, 74–44 and < 44μ) of samples 2-6 (54-64) are shown in Table V. The δ^{34}S value of the < 44μ fraction is over 3‰ more positive than the others. Calculations of the initial δ^{34}S value of this fraction, assuming complete reduction of sulfate from the interstitial water and 5070 water content in the sediment, yields a δ^{34}S value of −32.7‰, which is more consistent with the834S values (-30.0°/00 and -31.20/..) for the larger size fractions.

TABLE V

δ^{34}S *of* pyrite in different size fractions of **Cariaco** Trench sediment samples 2—6 (54—64), **and** the calculated δ^{34}S value of surface-formed pyrite in <44μ fraction

104 μ		104–74 μ		74–44 μ		<44μ measured		<44μ calculated (surface)
S(%)	δ^{34}S(‰)	S(‰)	δ^{34}S(‰)	S(%)	834S(‰)	S(%)	δ^{34}S(‰)	δ^{34}(‰)
0.34	-30.0	0.43	-30.0	0.17	‘31.2	0.78	‘26.9	‘32.7

DISCUSSION

Sulfate migration by ionic diffusion during burial does not seem to bean important factor in controlling the isotopic or chemical mass balance of sulfur species in sediment from JOIDES sites 26 and 27, where both sedimentation and rate of sulfate reduction during burial are relatively slow.

Marine basins located on the continental shelf, where the rate of sedimentation is greater, have a large amount of syngenetic pyrite present in the sediment. Direct sulfur measurements cannot be used to determine the diagenetic sulfate—sulfide mass balance. A method was employed here to calculate the isotopic composition of the syngenetically-formed iron sulfide by correcting for the change in the $^{34}S/^{32}S$ ratio due to closed-system diagenetic sulfate reduction. The calculated $\delta^{34}S$ values of initially-formed sulfur in these organic-rich sediments appear to be internally consistent. It can be argued that excess sulfur addition to the sediment by sulfate diffusion is quantitatively small, and does not produce a large discrepancy between the measured and calculated results.

Theoretical calculations can be made concerning the flux of sulfate into the sediment. However, it is necessary to know the rate of reduction during burial and the effective ion diffusion coefficient. Sholkovitz (1973) has compared the sedimentation rate in the Santa Barbara Basin (0.4 cm y^{-1}) and vertical water displacement by compaction with suggested ionic diffusion coefficients. Based on concentration gradients of Mg^{2+} and dissolved silica, he concludes that the rate of deposition is sufficiently rapid that the sediment is closed with respect to sulfate addition. Other calculations, (Berner, 1964; Jorgensen, 1979; Goldhaber and Kaplan, 1980), suggest that ionic diffusion into sediments is of relatively' great importance. Although the extent of sulfate diffusion cannot be precisely estimated by the methods employed here, its influence on the isotopic ratio of the pyrite formed in the sediment is apparently not large (probably within the range ±2‰).

The corresponding decrease in organic carbon and increase in reduced sulfur content with depth in Pescadero Basin sediment (core 50G) has been " used by Goldhaber and Kaplan (1980) to estimate the effective ion-diffusion coefficient of dissolved sulfate in marine sediments, assuming constant sedimentation conditions. If non-steady-state incorporation of reduced sulfur and organic carbon occurs during deposition, the derived values would be in error. For example, Fig. 1 is a plot of (a) reduced sulfur and (b) organic carbon content versus depth for core 50G and core 7G (from the adjacent Farallon Basin). The depth scale for core 7G is twice that of core 50G to more closely represent equivalent time rec orals (the sedimentation rate in the former is about 100 cm/1000 y and the latter, 45 cm/1000 y; van Andel, 1964). In core 7G, sulfate depletion does not occur above 3 meters' depth. Corresponding changes in both sulfur and organic carbon are observed for both cores. The chronological coincidence of these changes is suggestive of a sedimentation control, evidenced by an increase of reduced sulfur in the absence of sulfate depletion from the sediment core 7G.

It is believed that non-steady-state deposition of organic carbon is largely controlled by changing climatic conditions in recent geologic history. Stevenson and Cheng (1972) have shown that, for the Argentine Basin, the distribution of organic carbon and nitrogen in the sediment fluctuates with

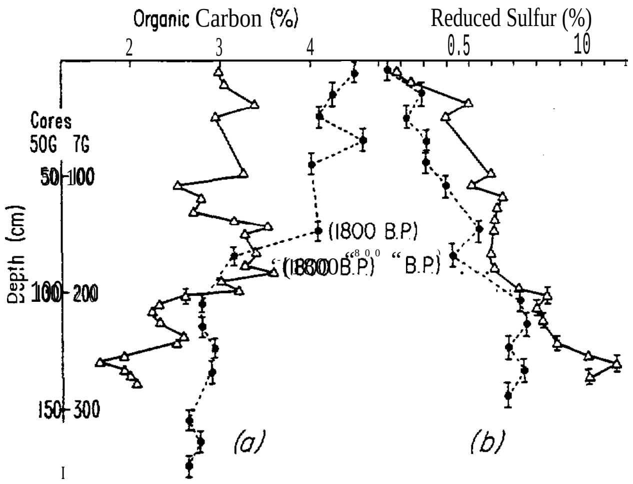

Fig.1. Plot of (a) the organic carbon and (b) the sulfur contents vs. depth in sediment for core 50G (Pescadero Basin; points indicated by ●) and core 7G (**Farallon** Basin; points indicated by △).

depth and corresponds to glacial and interglacial stages. Diagenetic reactions in shallow reducing basins are probably not a major control on organic carbon distribution in marine sediments. The degree to which diagenetic sulfur is added to marine sediments is determined by the degree of sulfate depletion in the pore water.

There is no conflict with theoretical diffusion arguments which incorporate small effective ionic diffusion coefficients for sediments. Goldhaber and Kaplan (1980) have shown that the importance of diffusion is greatest in "rapidly-accumulating, near-shore, organic-rich environments". However, in these environments, the relative importance of syngenetically-produced sulfide also seems to mask the effect of diagenetic addition. We believe these arguments create a dilemma for determining the precise mechanism for the addition of excess sulfur in an unlithified sediment column.

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REFERENCES

Berner, R. A., 1964. An idealized model of dissolved sulfate distribution in recent sediments. Geochim. Cosmochim. Acts, 28: 1497—1503.

Berner, R. A., 19’70. Sedimentary pyrite formation. Am. J. Sci., 268: 1–23.

Emery, K. O. and Rittenberg, S. C., 1952. Early diagenesis of California basin sediments in relation to the origin of oil. Bull. Arm Assoc. Pet. Geol., 36: 735—806.

Goldhaber, M. B., 1974. Equilibrium of dynamic aspects of the marine geochemistry of sulfur. Ph.D. Thesis, Univ. California, Los Angeles, CA, 399 pp.

Goldhaber, M. B. and Kaplan, I. R., 1974. The sulfur cycle. In: E. D. Goldberg (Editor), The Sea, Marine Chemistry. Wiley, New York, NY, VOL 5, pp. 569-655.

Goldhaber, M. B. and Kaplan, I. R., 1980. Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California. Mar. Chem., 9: 97–146.

Hartman, W. M. and Nielson, K. H., 1969. δ^{34}S werte in rezenten meeressedimenten und i hre heutung am Biespiel eininger sedimentprofile aus der westlichen *ostee.* Sender. GeoL, Rund., Z58: 621–655.

Jorgenson, B. B., 1979. A theoretical model of the stable sulfur isotope distribution in marine sediment-s Geochim. Cosmochim. Acts, 31: 363—374.

Kaplan, I. R., Emery, K O. and Rittenberg, S. C., 1963. The distribution and isotopic abundances of sulfur in recent marine sediment off Southern California. Geochim. Cosmochim. Acts, 27: 297–331.

Presley, B. J. and Kaplan, I. R., 1970. Interstitial water chemistry: Deep Sea Drilling Project, Leg 4. Initial Reports of the Deep Sea Drilling Project. U.S. Govt. Printing Office, Washington, DC, Vol. 4, pp. 415–430.

Sayles, F., Manheim, F. and Waterman, L., 1973. Interstitial water studies on small core samples, Leg 15. Initial Reporta of the Deep Sea Drilling Project, U.S. Govt. Printing Office, Washington, DC, Vol. 10, pp. 783–804.

Sholkovitz, E., 1973. Interstitial water chemistry of the Santa Barbara Basin sediment. Geochim. Cosmochim. Acts, 37:2043.

Stevenson, F. J. and Cheng, C. N., 1972. Organic geochemistry of the Argentine baain sediments: Carbon-nitrogen relationship and Quaternary correlations. Geochim. Cosmochim. Acts, 36:653.

Sweeney, R. E., 1972. Pyritization during early diagenesis of marine sediments. Ph.D. Thesis, Univ. California, Los Angeles, CA, 194 pp.

Sweeney, R. E. and Kaplan, I. R., 1973. Pyrite framboid formation: laboratory synthesis and marine sediments. Econ. GeoL, 68: 618—634.

Van Andel, T. H., 1964. Recent marine sediments of the Gulf of California. In: T. H. van Andel and G. G. Shor Jr. (Editors), Marine Geology of the Gulf of California. Am. Assoc. Pet. Geol. Mere., 3: 216–310.

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TRACING FLOCCULENT INDUSTRIAL AND DOMESTIC SEWAGE TRANSPORT ON SAN PEDRO SHELF, SOUTHERN CALIFORNIA, BY NITROGEN AND SULPHUR ISOTOPE RATIOS*

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ABSTRACT

Domestic and industrial sewage is discharged at a depth of 60 m near Whites Point on the San Pedro Shelf, Southern California borderland. A density-stratified thermocline, above the outfall at a depth of 20 to 30 m, is thought to prevent most effluent particles from reaching shallower depths and recreational facilities. in this investigation, measurement of the natural abundance of nitrogen isotopes (${}^{15}N/{}^{14}N$) is used to determine the level of sewage contribution to flocculent suspended material persisting at water depths of 7, 13 and 20 m. Organic nitrogen at 20 m depth was shown to be predominantly of sewage origin and at 7 m, predominantly of marine origin. Organic nitrogen at 13 m depth and within 3 km of the outfall pipes is predominantly sewage in origin.

Stable isotope composition of sulphur (${}^{32}S/{}^{34}S$) in the flocculent material indicates that the effluent particles contain metabolic sulphur, incorporated from dissolved seawater, as well as bacterially produced mineral sulphide.

INTRODUCTION

Submarine discharge of sewage and waste water is conducted by the Los Angeles County Sanitation District (LACSD) at Whites Point, on the shelf near San Pedro, California. The effluent is dispersed in a general northwesterly direction by the prevalent bottom current. However, the thermocline is often disrupted and sewage is turbulently transported to the surface. The contents of volatile solids (SCCWRP, 1973), organic carbon (Myers, 1974) and nitrogen (Sweeney *et al.*, 1980) have been

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used to trace sewage dispersal below the thermocline. This is possible because sewage particulates are high in organic matter (-60%) relative to the normal marine detritus (-2 %). Quantitative estimates of the amount of sewage contributed to the sediment have varied, due to the difficulty in determining the amount of sewage organic matter biologically degraded during sedimentation (Hendricks & Young, 197’4; Morel *et ai.*, 1975; Sweeney *et al.*, 1980). Stable isotope ratio measurements of carbon (Myers, 1974) and nitrogen (Sweeney *et al.*, 1980) have been shown to be sensitive indicators of the amount of sewage-derived organic matter incorporated into bottom sediments.

The LACSD has recently been concerned by the presence of flocculent material on the shallow rocky points of the area. This material, if sewage in origin, could have a detrimental effect on the growth of brown algae or filter-feeding benthic fauna. Sixteen samples of flocculent material have been collected across the shelf for $^{15}N/^{14}N$ measurement. Analyses of the contents of calcium carbonate, organic carbon, nitrogen and sulphur and $^{34}S/^{32}S$ ratio were made for comparison. The flocculent material was collected immediately above the ocean bottom by Scuba divers from LACSD using ‘slurp guns’. Data presented (Sweeney *et al.*, 1980) for surface sediment at 30, 60, 160 and 300 m depths are included for reference.

EXPERIMENTAL

Organic carbon and calcium carbonate were analysed by LECO combustion. Nitrogen, as ammonia, was released by closed tube combustion of organic matter with sulphuric acid followed by distillation into acid solution (Bremner & Edwards, 1965). The quantity of nitrogen was subsequently determined volumetrically after reaction with sodium hypobromide by vacuum line techniques (Cline & Kaplan, 1975). Sulphur compounds were oxidised to sulphate by Parr bomb combustion (*Technical Manual No. 130,* Anon., 1964) and the quantity measured gravimetrically after precipitation as barium sulphate. Gaseous SO_2 was obtained for isotope analysis by high temperature direct combustion of barium sulphate (Bailey&Smith, 1972). The precision of the quantitative measurements was 0·005% and 0·01% for nitrogen and sulphur, respectively.

Sulphur and nitrogen ratios were determined usinga Nuclide 6“-600 RMS mass spectrometer. The ratios are presented in the normally accepted ‘δ’ notation relative to Cañon Diablo meteoritic sulphur and atmospheric nitrogen standards with precision of 0·1‰ and 0·2‰, respectively.

$$\delta = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} - 1\right] \times 1000$$

where R $= {}^{34}S/{}^{32}S$ for sulphur and $^{15}N/^{14}N$ for nitrogen.

TABLE 1
LOCATION, DEPTH AND COLLECTION DATE OF FLOCCULENT MATERIAL

Sample	*Location*	*Depth (m)*	*Date*
F1	Pales Verdes Pt	7	6/4/76
F2	Long Pt	13	6/16/76
F3	Bunker Pt	20	6/14/76
F4	Pales Verdes Pt	20	6/17/76
F5	Royal Palms Pt	20	6/1 6/76
F6	Bunker Pt	13	6/16{76
F7	Long Point	20	10/8/76
F8	Abalone Cove	7	10/8/76
F9	Royal Palms Pt	13	6/17/76
F10	Bunker Pt	7	9/1/76
F11	Pales Verdes Pt	7	1 {26/76
F12	Abalone Cove	7	9/1/76
F13	Pipe	30	11/1/76
F14	Royal Palms Pt	7	11/1/76
F15	Pales Verdes Pt	13	11/1/76
F16	Long Point	7	10/8/76
F17	Catalina Harbour	20	6/9/76
F18	Catalina Harbour	13	6/9/76

TABLE 2
CONTENT OF $CaCO_3$, ORGANIC CARBON, NITROGEN AND SULPHUR; δ^1‘N, $\delta^{34}S$ AND C/N RATIO FOR FLOCCULENT MATERIAL

Sample	*$CaCO_3$ (%)*	*Organic carbon (%)*	*Nitrogen (%)*	*Sulphur (%)*	*$\delta^{15}N$ (‰)*	*$\delta^{34}S$ (%J*	*C/N (w)*
F1	48	1·86	0·24	0·19	+7·4	+11·3	7·8
F2	33	2·50	0·29	0·29	+ 6-4	+ 10”0	8·6
F3	19	2-78	0·25	0·25	+ 4·6	−2·2	11·2
F4	33	3·78	0·36	0·34	+5·6	+ 3-3	10·4
F5	23	3·22	0·30	0·31	+ 4·6	−3·1	10·9
F6	21	2·35	0·20	0·17	+ 5·8	+0·2	11·1
F7	28	1·62	0·17	0·23	+5·3	+ 3·8	9·3
F8	24	2·40	0·27	0·37	+ 6·6	+ 4·9	9·I
F9	22	3·73	0·35	0·50	+ 5·2	−1·1	11·0
F10	44	1·42	0·20	0·29	+ 6·6	+5·2	7·1
F11	46	3·58	0·42	0·33	+ 7·0	+ 10·7	8·6
F12	37	1·70	0·20	0·37	+6·7	+2·3	8·5
F13	12	5·22	0·41	0·68	+3·0	-12.9	12·7
F14	39	0·79	0·15	0·36	+7·3	+ 7·4	5·3
F15	34	3·15	0·42	0·23	+ 6·6	+ 10·6	7·4
F16	36	1·52	0·18	0·22	+ 7·4	+5·1	8·2
F17	47	1.47	0·26	0·10	+ 8·2	+8·8	5·7
F18	41	1·56	0·19	—	+ 7·6	—	8·2
Effluent	3*	31·5†	2·36†	1·00†	+ 2·5†	−0·1†	13·3†

•Myers (1974).
† Sweeney *et al.* (1980).

RESULTS AND DISCUSSION

The collection sites, depths and dates of collection for flocculent material are given in Table 1. The measurements of calcium carbonate, organic carbon, nitrogen and sulphur contents are listed in Table 2, along with $\delta^{15}N, \delta^{34}S$ and C/N weight ratio. The locations of the flocculent sampling sites and the LACSD sediment sampling grid are shown in Fig. 1. Samples F-17 and F-18 were taken at control stations in Catalina Harbour and are not shown. These samples are considered to represent the normal marine detritus of the area.

Figure 2 shows a schematic distribution of (A) δ^1 ‘N (‰) and(B) nitrogen content (%) for sediment and flocculent material on the San Pedro Shelf. Shown enclosed are locations where $\delta^1 5_N < +6‰$ and $N(\%) > 0{\cdot}200$. These values are chosen to indicate the presence of sewage-derived organic matter based on a mixing relationship between sewage-derived nitrogen (δ^1 ‘N $\sim 2{\cdot}5‰$; N - 2x) and marine nitrogen ($\delta^1 5_N \sim 10‰$; N $\sim 0{\cdot}1\%$). Of the 44 sampling sites occupied, 29 sediments analysed can be considered sewagedominated by criterion (A) and 21 by criterion (B). Twenty of the sites enclosed in Fig. 2 are common for both parameters. For the flocculent material analysed, 7 of the 16 collected samples can be identified as sewage-dominated by criterion (A) and ten by criterion (B). All the flocculent material with $\delta^1 5_N$ values falling in the sewage-dominated range overlie sediment with similar δ^1 ‘N values. Five of the sites with high nitrogen contents. are not adjacent to the other sites shown enclosed in Fig. 2. The consistency in the spatial distribution of $\delta^1 5_N$ of sediment and flocculent material enforces the supposition that a leak of sewage particles to the shallow water environment occurs.

Table 3 gives a list of the calculated quantities of marine and sewage nitrogen for each flocculent sample measured. The basis of the calculation is that the δ^1 ‘N value of the sample is determined by the proportion of sewage (+ 2·5‰) and marine nitrogen (+10‰) present. For calculation, the $\delta^{15}N$ of the marine component was considered to be + 10‰, as it is the maximum value measured in the sediment. The $\delta^{15}N$ values of the nitrogen in the Catalina control stations are -i- 7·6 and + 8·2‰. If $\delta^{15}N_M = +10‰$ is used, then the marine nitrogen fractions (F_m) calculated for the control stations are 0·68 and 0·76, suggesting that Catalina Harbour is either slightly polluted or had some other terrigenous input at the time of collection. Seven of the sixteen flocculent samples from the San Pedro Shelf have calculated sewage contributions of greater than 50 % of the organic nitrogen ($F_m < 0{\cdot}50$, Table 3).

The C/N ratio of marine organic matter and sewage effluent

Figures 3(A) and (B) are plots of $\delta^{15}N$ versus the calcium carbonate and carbon/nitrogen. weight ratio, respectively. A linear distribution of data points exists for both plots. The least-square best-fit lines are:

$$CaCO_3(\%) = 7{\cdot}4\,\delta^{15}N - 13{\cdot}3,\; r = -0{\cdot}92$$

$$C/N = 16{\cdot}9 - 1{\cdot}3\,\delta^{15}N,\; r = -0{\cdot}91$$

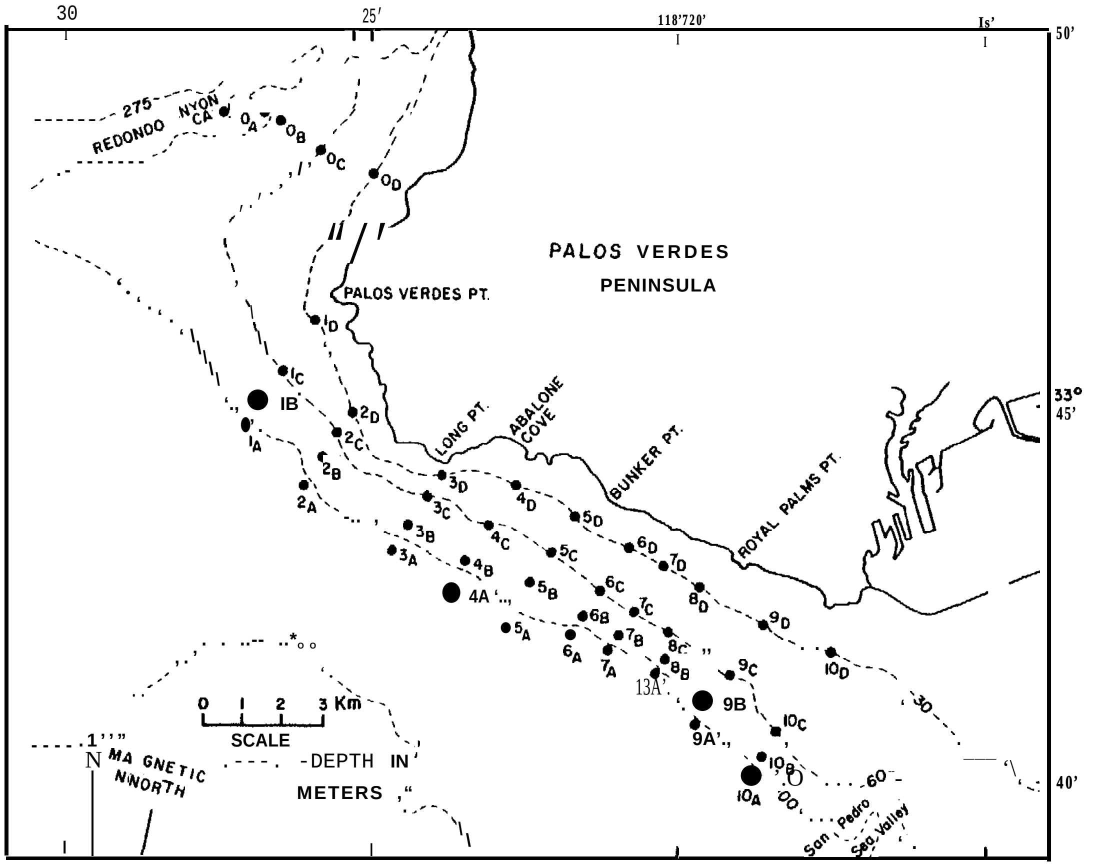

Fig. 1. Station Locations for flocculent sample sites on San Pedro shelf and the grid of sediment sample transects for LACSD collection.
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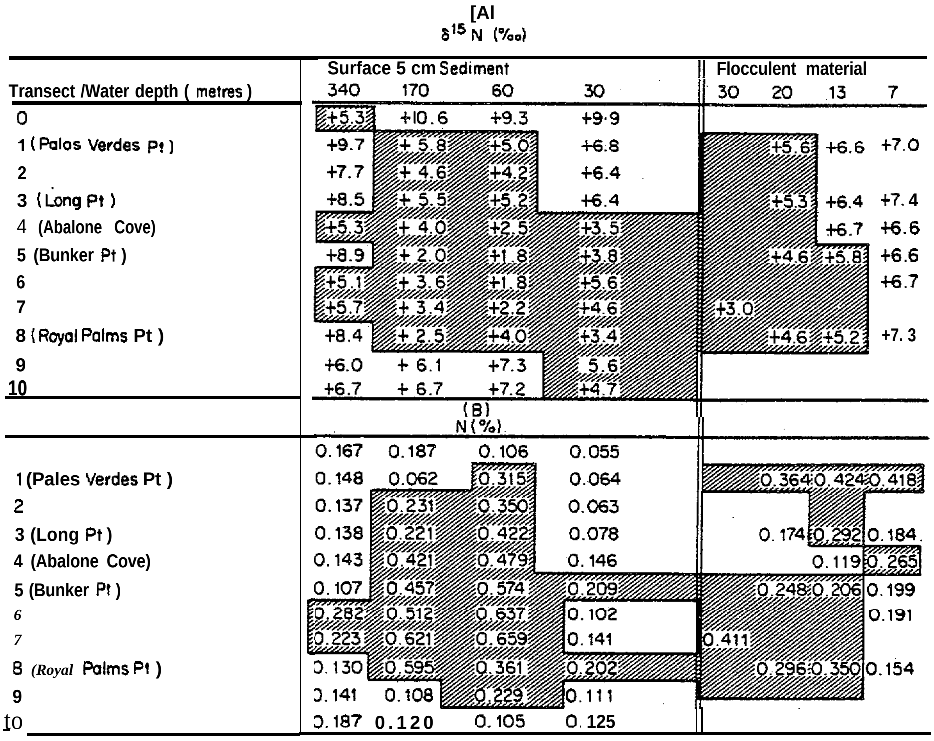

[A]
$\delta^{15}N$ (‰)

Transect /Water depth (metres)	Surface 5 cm Sediment 340	170	60	30	Flocculent material 30	20	13	7
0	+5.3	+10.6	+9.3	+9·9				
1 (Palos Verdes Pt)	+9.7	+ 5.8	+5.0	+6.8		+5.6	+6.6	+7.0
2	+7.7	+ 4.6	+4.2	+6.4				
3 (Long Pt)	+8.5	+ 5.5	+5.2	+6.4		+5.3	+6.4	+7.4
4 (Abalone Cove)	+5.3	+ 4.0	+2.5	+3.5			+6.7	+6.6
5 (Bunker Pt)	+8.9	+ 2.0	+1.8	+3.8		+4.6	+5.8	+6.6
6	+5.1	+ 3.6	+1.8	+5.6				+6.7
7	+5.7	+ 3.4	+2.2	+4.6	+3.0			
8 (Royal Palms Pt)	+8.4	+ 2.5	+4.0	+3.4		+4.6	+5.2	+7.3
9	+6.0	+ 6.1	+7.3	5.6				
10	+6.7	+ 6.7	+7.2	+4.7				

(B)
N (%)

Transect /Water depth (metres)	Surface 5 cm Sediment 340	170	60	30	Flocculent material 30	20	13	7
	0.167	0.187	0.106	0.055				
1 (Pales Verdes Pt)	0.148	0.062	0.315	0.064		0.364	0.424	0.418
2	0.137	0.231	0.350	0.063				
3 (Long Pt)	0.138	0.221	0.422	0.078		0.174	0.292	0.184
4 (Abalone Cove)	0.143	0.421	0.479	0.146			0.119	0.265
5 (Bunker Pt)	0.107	0.457	0.574	0.209		0.248	0.206	0.199
6	0.282	0.512	0.637	0.102				0.191
7	0.223	0.621	0.659	0.141	0.411			
8 (Royal Palms Pt)	0.130	0.595	0.361	0.202		0.296	0.350	0.154
9	0.141	0.108	0.229	0.111				
10	0.187	0.120	0.105	0.125				

Fig. 2. schematic distribution of δ^{1} ‘N values (‰) and nitrogen content (%) in sediment and flocculent material on the San Pedro shelf. Enclosed values represent material containing recognizable sewage input.

At each extremity of the distributions are the Catalina control stations and the sewage effluent. By extrapolation the calcium carbonate content and the C/N ratio of the marine debris are calculated to be 61 % and 5, respectively.

Since proteins, the main nitrogen compounds of living organisms, have a C/N ratio of about 3, animals which are rich in protein show low C/N ratios (Müller, 1977). The average C/N ratio of phytoplankton is considered to be 5·9, of zooplankton, 6·3 and of benthic animals and bacteria 4 to 5 (Bordovskiy, 1965). Particulate organic matter above the thermocline in the open ocean also has C/N ratios in this range (Helm-Hansen, 1969; Gordon, 1971). Deeper in the ocean, the C/N ratio of the particulate organic matter increases to 10 or greater (Müller, 1977). It is now generally accepted that the change of the C/N ratio with depth in the ocean is caused by proteins being utilised more readily than carbohydrates during degradation of organic matter (Gordon, 1971). Thus, C/N ratio of organic matter in marine sediment is between 8 and 12 (Trask, 1932; Rittenberg *et al.*, 1955; Bordovskiy, 1965). The C/N ratio for the 44 surface sediment samples across the San Pedro Shelf was found to be in the range 116 to 29·7 (Sweeney *et al.*, 1980).

TABLE 3
CALCULATED MARINE AND EFFLUENT CONTRIBUTIONS OF NITROGEN TO FLOCCULENT MATERIAL AT EACH STATION USING 6'5 NMW,C EQUAL TO •1-10‰

Sample	$\delta^{15}N$(‰)	f_m[a]	%N_M[b]	%N_E[c]
F1	+7·4	0·65	0·16	0·08
F2	+6·4	0·52	0·15	0·14
F3	+4·6	0·28	0·07	0·18
F4	+5·6	0·41	0·15	0·21
F5	+4·6	0·28	0·08	0·21
F6	+5·8	0·44	0·09	0·12
F7	+5·3	0·37	0·07	0·11
F8	+6”6	0·54	0·14	0·13
F9	+5·2	0·41	0·14	0-21
F10	+6·6	0·55	0·11	0·09
F11	+7·0	0·60	0·25	0·17
F12	+6·7	0·56	0·11	0·09
F13	+3”0	0·07	0·03	0·38
F14	+7·3	0·64	0·10	005
F15	+6·6	0·55	0·23	0·19
F16	+7·4	0·65	0·12	0·06
F17	+8·2	0·76	0·20	0·06
F18	+7·6	0·68	0·13	0·06

[a] F_m = fraction nitrogen from marine source (δ^{1}'N - 2·5)/(10 - 2·5).
[b] %N_M = marine component (. %N).
[c] %N - %N_M = effluent component (%N - %N_M).

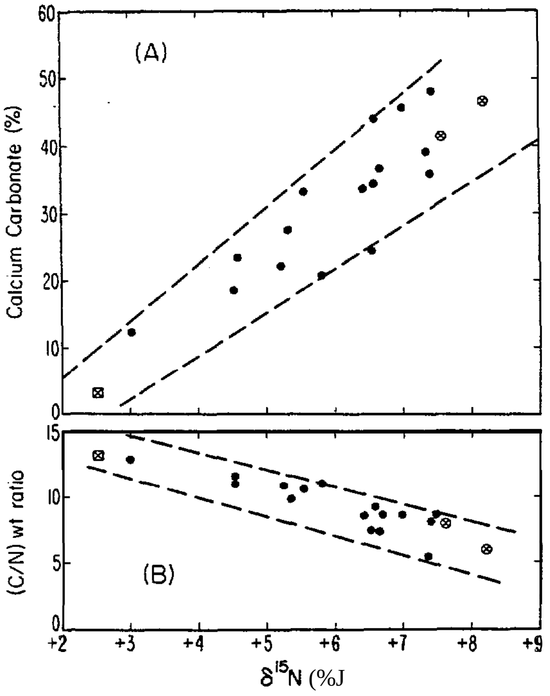

Fig. 3. Plot of δ^{15}N(‰) versus calcium carbonate content (%) and C/N weight ratio for flocculent material. . San Pedro Shelf samples. ⊗ Catalina Harbour control station. ⊠ Sewage effluent.

The low C/N ratio extrapolated for the marine organic matter present in the flocculent samples is indicative of high protein content. The C/N ratio extrapolated for the sewage component of the flocculent material (Fig. 3(B)) is similar to that of the discharged effluent, or about 13. The protein content of the effluent is apparently low and even after 30x degradation has occurred during sedimentation (Myers, 1974), the C/N ratio is little altered. This indicates that the C/N ratio of effluent is alone not a useful parameter for estimating bacteria] degradation of sewage after discharge into the ocean.

Significance of sulphur isotope composition of flocculent material

Figure 4 is a plot of $\delta^{15}N$ versus $\delta^{34}S$ for the flocculent samples. A direct positive correlation exists. Values for the Catalina control station lie at one extreme of the distribution shown in Fig. 3, whereas sewage effluent falls outside the mixing relationship. Also plotted in Fig. 4 are the values of $\delta^{15}N$ and $\delta^{34}S$ for surface sediment from stations along transect 7. At stations 7B and 7C, near the discharge pipe, the $\delta^{15}N$ value of surface sediment shows high sewage contamination. The value of $\delta^{34}S$ for these samples is about -10‰ and is considered to represent addition of equal amounts of sewage sulphur (0‰) and biogenic sulphur (- 20‰) produced by sulphate-reducing bacteria metabolizing sewage material deposited in the sediment (Sweeney *et al.*, 1980). The sulphur in sediments less contaminated by sewage, i.e. 7A and 7D, becomes progressively more enriched in the marine bacterial component, as indicated by the arrow in Fig. 4.

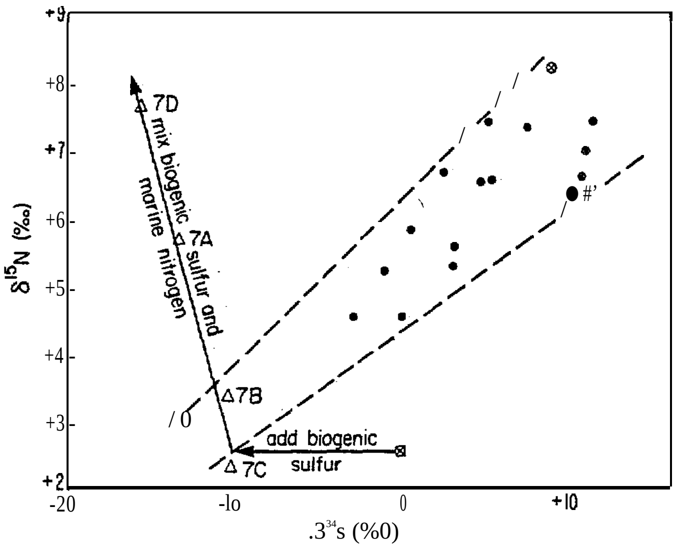

Fig. 4. Plot of $\delta^{15}N$(‰) for flocculent material near the discharge pipes. ● San Pedro shelf flocculent material. @Catalina Harbour control station. ☒ Sewage effluent. △ Sediment samples along transect 7.

The marine end-member sulphur, in the flocculent material, extrapolated from Fig. 4, has a $\delta^{34}S$ value of ≥ 10‰. This value is different from the bacterial marine sulphide component for the sediments. Sulphide produced from bacterial reduction of seawater sulphate is not the source of the sulphur for this end-member, but rather seawater sulphate assimilation is the process involved in protein synthesis—a process accompanied by little isotopic fractionation. Seawater sulphate has a $\delta^{34}S$ of about + 19·5‰ and measurements of $\delta^{34}S$ for various marine organisms are very close to this value (Kaplan *et al.*, 1963). The sulphur content of the marine component can be calculated by a similar method employed for determining the nitrogen contents shown in Table 3. The average S/N ratio for the marine component is about 1. The high amounts of nitrogen and sulphur in marine organic matter and the very positive $\delta^{34}S$ values of the sulphur demonstrate the proteinaceous nature of this material.

The extrapolated $\delta^{34}S$ value of the effluent sulphur end-member in the flocculent material is about 10‰ more negative than the particulate sulphur discharged ($\sim$0‰) onto the shelf. Four of the samples have $\delta^{34}S$ values which are negative (–1”1; –2”2; –3”1; – 12·9‰). These samples ‘must contain bacterially-produced mineral sulphide. This sulphide could have been incorporated during the sample collection, by including some bottom sediment material, or could have been produced by bacterial sulphate reduction during storage. However, if neither of the above contaminations occurred, then the $\delta^{34}S$ value of the effluent sulphur end-member indicates that the particulate effluent material must have been exposed to a reducing marine environment before collection. Sedimentation of the particulate near the discharge pipe (see 7B; 7C in Fig. 4), followed by resuspension and transportation above the thermocline, would fulfill this requirement. This matter needs further study before it is resolved.

SUMMARY

Sewage particles discharged at 60 m depth, below a stratitied thermocline on the San Pedro Shelf, may eventually be transported to shallower depths. The amount of sewage nitrogen present in flocculent material collected at various depths and localities is both a function of depth and of distance from the outfall pipes. For about two-fifths of the flocculent samples collected, the nitrogen was predominantly from a sewage source. The C/N ratio of the effluent is about 13 and that for marine debris, about 5. Therefore, for equivalent locations, the sewage contribution for organic carbon will be about three times greater than for nitrogen.

The marine component of the flocculent material has an apparent high protein content. The C/N ratio is similar to those of living organisms and surface water particulate organic matter in the open ocean. The S/N ratio of particulate marine organic matter is about 1 and the $\delta^{34}S$ value of the sulphur, $\sim +15$‰.

The presence of some bacterially-produced sulphur in the sewage component of the flocculent material is indicated by the negative values of. $\delta^{34}S$ for some of the samples. One possible interpretation is that the sewage particles are first deposited in the sediments near the discharge pipe and subsequently resuspended before transport above the thermocline.

ACKNOWLEDGEMENTS

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REFERENCES

ANON. (I 964). *Technical Manual No. 130,* Pair Instrument Company.

BAILEY, S. A. & SMITH, J. W. (1972). Improved method for the preparation of sulfur dioxide from barium sulfate for isotope ratio studies, *Anal. Chem., 44, 1542.*

BORDOVSKIY, O. K. (1965). Transformation of organic matter in bottom sediments and its early diagenesis, *Mar. Geol., 3, 83.*

BREMNER, J. M. & EDWARDS, A. P. *(1965).* Determination and isotope ratio analysis of different forms of nitrogen in soils: 1. Apparatus and procedure for distillation and determination of ammonium, *Soil* Sri. *Soc. Am. Proc., 29, 502.*

CLINE, J. & KAPLAN, I. R. (1975). Isotope fractionation of dissolved nitrate during denitrification in the Eastern Tropical North Pacific Ocean, *Marine Chem., 3,271.*

GORDON, JR, D.C. (1971). Distribution of particulate organic carbon and nitrogen at an oceanic station in the central Pacific, Deep *Sea Res.,* 18, 1127.

HENDRICKS, T. J. &YOUNG, D. R. (1974). *Modeling the fates of metals in ocean discharge waste waters.* TM208—Southern California Coastal Water Research Project, El Segundo. California.

HOLM-HANSEN, O. (1969). Determination of microbial biomass in ocean profiles, *Limn. Oceanog., 14, 740-7.*

KAPLAN, I. R., EMERY, K. O.& RITTENBERG, S. C. (1963), The distribution and isotopic abundance *of* sulfur in recent sediments off Southern California, *Geochim. Cosmochim. Acta, 27, 297-331.*

MOREL, F., WESTALL, J. C., O'MELIA, C. R. & MORGAN, J. J. (1975). Fate of trace metals in Los Angeles County wastewater discharge, *Environ.* Sci. & *Tech., 9, 756.*

MÜLLER, P. J. (1977) ., C/N ratios in Pacific deep-sea sediments. Effects of inorganic ammonium and organic nitrogen compounds sorbed by clays, *Geochem. Cosmochim. Acts, 41, 765-76.*

MYERS, E. P. *(1974). The concentration and isotopic composition of carbon in marine sediments affected by sewage discharge.* PhD Dissertation, Calif. Inst. Technology, Pasadena, California.

RITTENBERG, S. C., EMERY, K. O. & ORR, W. L. (1955). Regeneration of nutrients in sediments of marine basins, *Deep Sea Res., 3,23.*

SCCWRP (1 973). *The ecology of the Southern California Bight: Implications for water quality management. TR 104,* Southern California Coastal Water Research Project, El Segundo, California.

SWEENEY, R. E., KALIL, E. K. & KAPLAN, I. R. (1980). Characterization of domestic and industrial sewage in Southern California coastal marine sediments using nitrogen, carbon, sulfur and uranium tracers, *Marine Environ. Res., 3, 225-43.*

TRASK, P. D. (1932). *Origin and environment of source sediments of petroleum,* p. 327. Houston, Texas, Gulf of Publ. Co.

Marine Environmental Research 3 (1980) 225-243

CHARACTERISATION OF DOMESTIC AND INDUSTRIAL SEWAGE IN SOUTHERN CALIFORNIA COASTAL SEDIMENTS USING NITROGEN, CARBON, SULPHUR AND URANIUM TRACERS*

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ABSTRACT

A degradation-mixing model has been developed to aid in the interpretation of geochemical processes occurring in sewage-contaminated marine sediment near San Pedro, California. The nitrogen isotope ratio ($^{15}N/^{14}N$) is shown to bean effective tracer of sewage discharge on the San Pedro Shelf. Isotopic fractionation of $^{15}N/^{14}N$ during release of amino compounds or ammonia (as a consequence of bacterial degradation of organic detritus) appears to be negligible. The nitrogen isotope ratio, therefore, may be considered a conservative component for tracing the source of organic matter deposited in marine sediment.

Uranium enrichment from seawater is shown not to occur in the highly reducing sewage-contaminated sediments. The content of uranium in the effluent particulates (18 ppm) is large compared with the content in the uncontaminated sediment (3 to 5 ppm). This allows the content of uranium to also be used as a tool for tracing the deposition of sewage particles in marine sediment. Uranium and nitrogen are shown to be incorporated in the organic fraction of sewage effluent and are released during bacterial degradation of the organic matter. Cadmium and sulphur are shown not to be mobilised during sewage deposition and degradation. The stable isotope ratio of sulphur ($^{34}S/^{32}S$) is used to demonstrate that sulphur enrichment occurs in the sediment by in situ *reduction of seawater sulphate. The data summarised by Morel* et al. *(1975) are presented and discussed in accordance with the above model.*

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INTRODUCTION

Submarine discharge of sewage and wastewater is conducted by the Los Angeles County Sanitation District near Whites Point, on the shelf near San Pedro, California. This sewage outfall has been held responsible for the general deterioration of the scenic Pales Verdes coast because of the daily discharge of three-hundred-and-fifty (350) million gallons of primary treated effluent per day (SCCWRP, 1973). The outfall is located at a depth of 60m and below a density stratified thermocline and the effluent is dispersed in a general northwest direction by the prevalent bottom current. However, the thermocline is often disrupted and the sewage boils to the surface.

The area has been studied to determine the dispersion of particulate sewage material and its effect on the marine environment (SCCWRP, 1973). Investigations of trace element mobilisation (Galloway, 1972; Hendricks &Young, 1974) and the fate of sewage organic matter (Myers, 1974) have also been conducted in the area. A grid of collection stations has been established by the Los Angeles County Sanitation District to monitor sewage dispersal across the shelf. Station locations and the distribution of organic carbon in the sediment are shown in Fig. 1.

The first objective of this study was to test whether the measurement of nitrogen isotope ratios ($^{15}N/^{14}N$) can be used to determine the presence of effluent organic matter in the shelf sediment. The isotopic ratio of nitrogen in the sediments depends on the relative contribution of effluent and normal marine nitrogen. The isotope ratio of the effluent material can be measured directly on material collected from the digestor. The isotopic ratio of nitrogen in normal marine debris, composed of organic matter either synthesised in the euphotic zone of the ocean or brought in by river runoff, can be measured in relatively uncontaminated sediment more distant from the discharge site. It has already been shown that $\delta^{15}N$ of nitrogen in marine sediments can be used to trace terrestrially formed nitrogen in the marine environment (Sweeney *et al.*, 1978; Peters *et al.*, 1978).

The second objective of this study is to construct a model which can be used to determine the mobilisation of elements as a consequence of sedimentation and bacterial decay. Conflicting conclusions have been reached concerning the fate of trace elements in sewage discharged into the marine environment. Hendricks & Young (1974) interpreted the relatively low metal concentrations in the sediments adjacent to outfall pipes to indicate that trace elements are 'mobilised' during the deposition of sewage material. Morel *et al.* (1975) suggest that Zn, Hg, Cu, Cd and Pb are present in the sewage as very insoluble sulphides and are not mobilised in the vicinity of the outfall. Both interpretations were reached using the same sediment trace element data measured by Galloway (1972).

The different interpretations for the geochemical processes controlling the trace element distribution in sewage-contaminated sediments stem from the fact that the degree of dilution of sewage particulates by normal marine sediment, impoverished

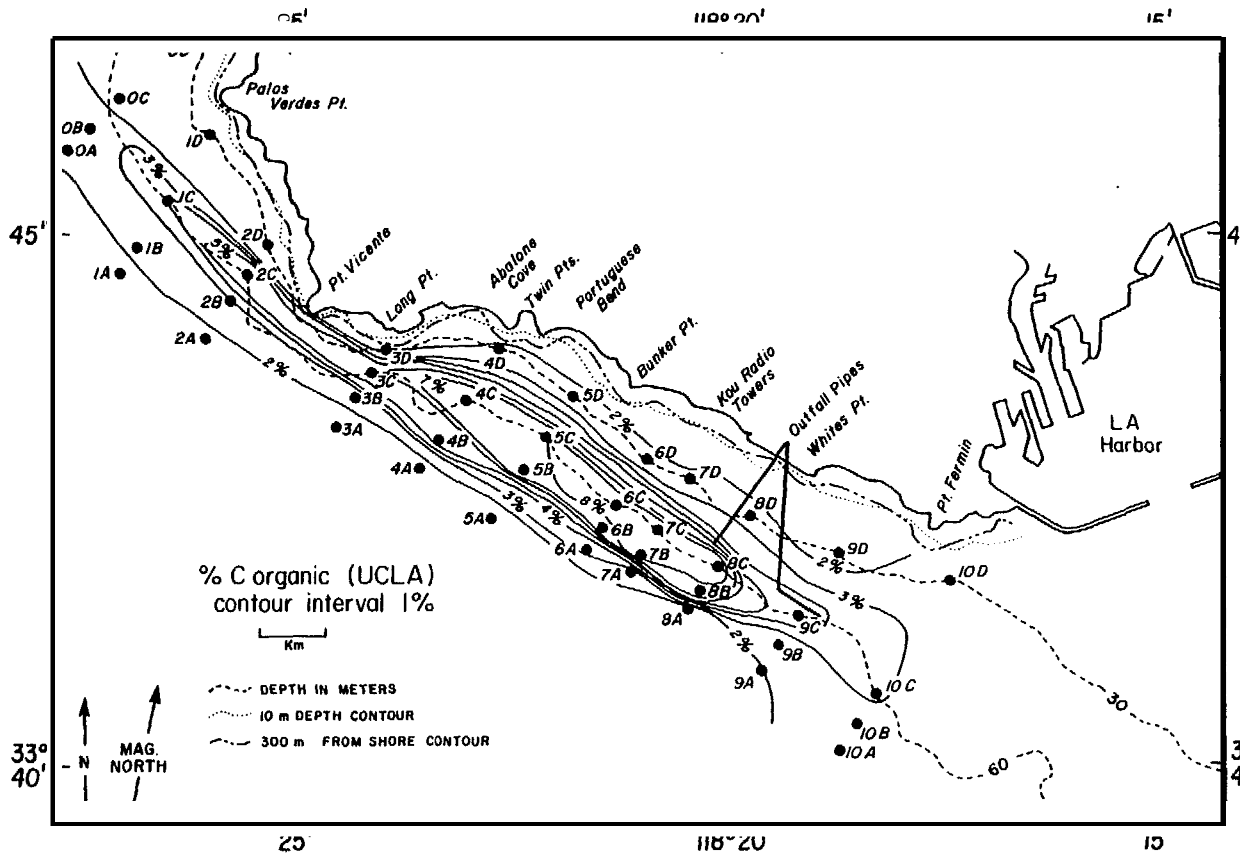

Fig. 1. Location of sample stations on San Pedro Shelf. Distribution of organic carbon in the surface sediment is shown by 1% organic carbon contours. Data was measured at UCLA.

in trace elements, is difficult to determine. Myers (I 974) shows that the maximum organic content in shelf sediment adjacent to the outfall (13%) is less than half that of the particulate effluent (34%). If little sewage material is decomposed prior to settling on the sediment surface, then the sewage particles in the sediment must be diluted by marine detritus containing low organic carbon. This situation, as discussed by Morel *et al.* (1975), would explain the distribution of most trace elements in the sediment. Hendricks & Young (-1974) calculated that the sediment depositing near the outfall is almost completely sewage derived. To obtain the low (13%) organic carbon content measured in the sediment, they suggest that over 50 % of the organic matter in the sewage must have been decomposed prior to burial.

In this study, the measured correlations between organic carbon, sulphur, nitrogen and uranium for the San Pedro Shelf sediment are used to construct a model which demonstrates the relationship between these elements as a function of bacterial degradation of sewage and the addition of marine debris. This model is used to explain the distribution of metals in the San Pedro Shelf sediment measured by Galloway (1972) and the Cd-organic matter correlation shown by Mitchell & . Schafer (1975) to exist in the nearby Santa Monica Bay sediment (produced by effluent discharge from the Hyperion Sewage Treatment Plant).

METHODS

Surface sediment samples” were collected by a Shipek grab sampler from the *collection* stations shown in Fig. 1. All sediment samples were freeze-dried and sieved at 264p before analysis. Uranium was analysed by counting delayed neutrons using the UCLA nuclear reactor (Kalil, 1976). Organic carbon and sulphur contents were determined by separate combustion in a LECO induction furnace and subsequent analysis of the produced gas. The amount of carbon dioxide found by combustion was measured by absorption in KOH. The amount of sulphur dioxide formed was measured by titration with KIO_3 in a starch–KI solution. Total nitrogen extraction was accomplished by digestion with sulphuric acid at 400 °C in evacuated, sealed tubes. After heating, the tubes were opened and the ammonium was distilled into acid by the addition of sodium hydroxide following the method of Bremner & Edwards (1965). The concentrated ammonium sulphate solution was then reacted with sodium hypobromide in a vacuum line to release nitrogen which was measured volumetrically y by the method described by Cline & Kaplan (1975).

The isotope ratios were determined on a Nuclide 6“-600 Dual-Collector Mass Spectrometer relative to a standard gas. The results are presented in the commonly used’ δ’ notation with air-nitrogen and Cañon Diablo meteorite sulphur used as standards.

The precision of the isotope ratio measurements of nitrogen is ±0·2‰ and of carbon and sulphur, ±0· 1 ‰. The precision for the quantitative measurements of nitrogen is ± 0-002%; organic carbon, ±0·01% and uranium, ±0·01 ppm.

RESULTS

Nitrogen isotope distribution

An equation relating the content and isotopic composition of nitrogen for the mixing of effluent material into marine sediment can be developed by combining eqns (1) and (2):

$$N_T = XN_x + (1 - X)N_y \tag{1}$$

$$\delta_T N_T = \delta_x X N_x + \delta_y(1 - X)N_y \tag{2}$$

arriving at:

$$N_T = \frac{N_x N_y(\delta_x - \delta_y)}{N_x(\delta_x - \delta_T) + N_y(\delta_T - \delta_y)} \tag{3}$$

where: $N_x\delta_x$ = content and isotopic ratio of nitrogen in refractory effluent; $N_y\delta_y$ = content and isotopic ratio of nitrogen in normal marine sediment and $N_T\delta_T$ = content and isotopic ratio of nitrogen measured in the sediment.

TABLE 1

CONTENT OF ORGANIC CARBON, NITROGEN, SULPHUR AND URANIUM IN EFFLUENT PARTICULATE FROM THE WHITES POINT DIGESTOR. δ^{15}N AND δ^{34}S FOR NITROGEN AND SULPHUR IN THE PARTICULATES AND FOR THE DISSOLVED AMMONIA–NITROGEN AND HYDROGEN SULPHIDE–SULPHUR IN THE SEDIMENT PORE WATER AT STATION 7C

Effluent particulates

Organic carbon (%)	*Nitrogen* (%)	*Sulphur* (%)	*Uranium* (*ppm*)	$\delta^{15}N$ (%0)	$\delta^{34}S$ (%)
30·8	2·33	1·0	18·6	+3·0	−0·1
31·7	2·38	1·3	—	+2·0	−0·2
31·8	2·37	1·2	—	+2·4	0·0
31·7	2·36	1·3	—	+2·5	+0·1

Pore water, Station 7C

Depth (*cm*)	$\delta^{15}N$ (%0)	$\delta^{34}S$ (%0)
0-5	+2·6	-20.2
5-10	+3·1	—
10-15	+3·0	—

Tables 1 and 2 list the contents and isotopic ratio of nitrogen in the sewage effluent and in surface sediment samples, respectively. The mean δ^{15}N value of effluent nitrogen is +2.5%0 and the most positive δ^{15}N value measured in the sediment is + 10·6‰. The content of nitrogen in the effluent is 2·36% and the minimum content in the sediment, 0·062%. Figure 2 is a plot of δ^{15}N versus the nitrogen content for the surface samples listed in Table 2. The curve shown is

TABLE 2

CONTENTS OF ORGANIC CARBON, NITROGEN, URANIUM AND δ^{15}N FOR SURFACE SAMPLES COLLECTED ACROSS THE SAN PEDRO SHELF. SAMPLES COLLECTED IN 1972

Surface sample	$\%C_{org.}$	$\%N$	U (*ppm*)	$\delta^{15}N$ (‰)
0A1	2·64	0·167	—	+5·3
0B1	2·43	0·187	—	+10·6
0C1	1·58	0·106	—	+9·3
0D1	1·01	0·055	—	+9·9
1A1	1·97	0·148	(3·84)	+9·7
1B1	1·66	0·062	(3·63)	+5·8
1C1	4·04	0·315	(4·20)	—
1D1	0·90	—	(1·67)	—
2A1	1·79	0·137	(3·71)	+7·7
2B1	3·03	0·231	(3·11)	+4·6
2C1	5·44	0·350	(6·63)	+4·2
2D1	1·29	0·063	(3·34)	+6·6
3A1	1·67	0·138	3·41	+8·5
3B1	2·66	0·221	3·17	+5·5
3C1	5·62	0·422	5·64	+5·2
3D1	1·52	0·058	3·02	+6·4
4A1	1·71	0·143	(4·22)	+5·3
4A2	1·84	0·133	4·29	—
4B1	5·67	0·421	6·06	+4·0
4C1	7·34	0·479	3·79	+2·5
4D2	1·71	—	3·79	—
4D3	2·19		4·29	—
4D4	2·50	—	3·65	—
5A1	1·81	0·107	4·46	+8·9
5B1	7·57	0·457	4·32	+2·0
5C1	7·89	0·564	6·06	+1·8
5D1	2·71	—	3·17	—
6A1	3·28	0·282	5·24	+5·1
6B1	7·89	0·512	7·28	+3·6
6C1	8·53	0·637	5·91	+1·8
6C2	9·89	—	—	—
6C3	8·21	—	—	—
6C4	7·80	—	—	—
6D1	2·11	0·102	4·92	+5·6
7A1	2·85	0·223	3·82	+5·7
7B1	8·70	0·621	6·35	+3·3
7C1	8·76	0·659	6·45	+2·2
7D1	2·08	0·141	3·52	+7·7
8A1	1·38	0·091	(3·91)	+8·4
8B1	7·81	0·595	(5·85)	+2·5
8C1	8·84	—	—	—
8C2	8·60	—	8·27	—
8C3	9·47	—	—	—
8C4	9·93	—	—	—
8D1	2·66	0·202	6·28	+3·4

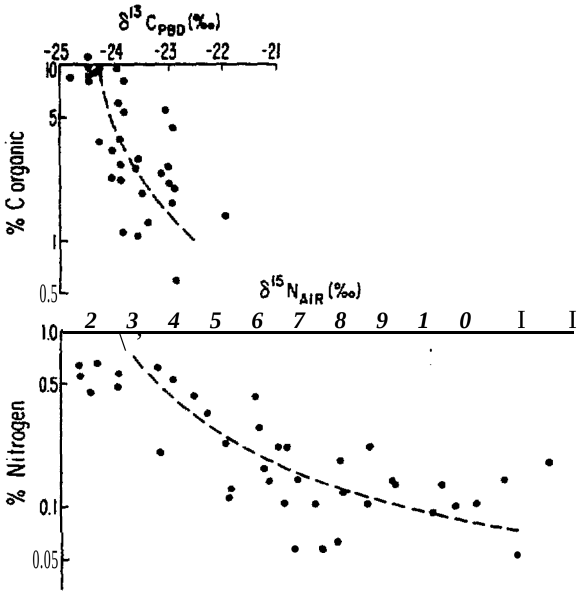

Fig. 2. Comparison between per cent organic carbon–$\delta^{13}C$ and per cent nitrogen–$\delta^{15}N$ for similar surface samples on the San Pedro Shelf. The carbon data are after Myers (1974) and the nitrogen data were measured at UCLA.

TABLE 3

CONTENTS OF ORGANIC CARBON, NITROGEN, URANIUM AND $\delta^{15}N$ FOR SEDIMENT SECTIONS OF CORES TAKEN AT STATIONS 6C AND 7C. CORE 6C WAS COLLECTED IN 1972 AND CORE 7C IN 1975

Core/Depth (cm)	*%$C_{org.}$*	*%N*	*U (ppm)*	*$\delta^{15}N$(‰)*
6C 0–2	9·69		7·01	
2–4	9·42	—	7·82	—
4–6	10·5		7·64	
6–8	9·34	—	7·63	—
8–10	6·87		8·67	
11	5·63	—	7·50	—
7C 0–1	8·79	0·635	7·07	+3·2
1–2	9·92	0·756	7·51	+3·8
2–3	11·4	0·699	8·87	+2·4
4–5	12·2	—	6·55	—
5–6	13·1	—	8·71	—
7–8	13·8		12·2	
8–9	11·0	—	23·5	—
10–11	—	0·757	7·83	+3·1
11–12		0·747	7·87	+2·5
15–16	8·05	0·500	9·29	+4·6
16–17	6·83	0·324	5·55	+4·0
17–18	2·16	0·138	4·54	+8·4
18–19	1·87	0·128	3·79	+7·2
19–20	2·47	—	4·08	—

determined from solving **eqn** (3) using $N_x = 2{\cdot}36\,\%$, $\delta_x = +2{\cdot}5‰$ (mean **values** of measurements of effluent nitrogen), N_y = 0.075% and δ_y = + 10‰ (values chosen to approximate the least sewage contaminated sediment). Shown also in Fig. 2 is a **plot** of δ^{13}C versus the organic carbon content for surface samples **collected** on the San Pedro **Shelf** (data from Myers, 1974). **A curve** of the form that **would** relate δ^{13}C and carbon content for sewage **effluent-enriched** sediment is also shown.

The distribution of data points for both nitrogen and carbon appears to coincide with the mixing curves derived from **eqn** (3). The range in δ^{1} ‘N is 9‰ compared with 2‰ for δ^{13}C. The δ^{1} ‘N values for sediment most contaminated with sewage effluent

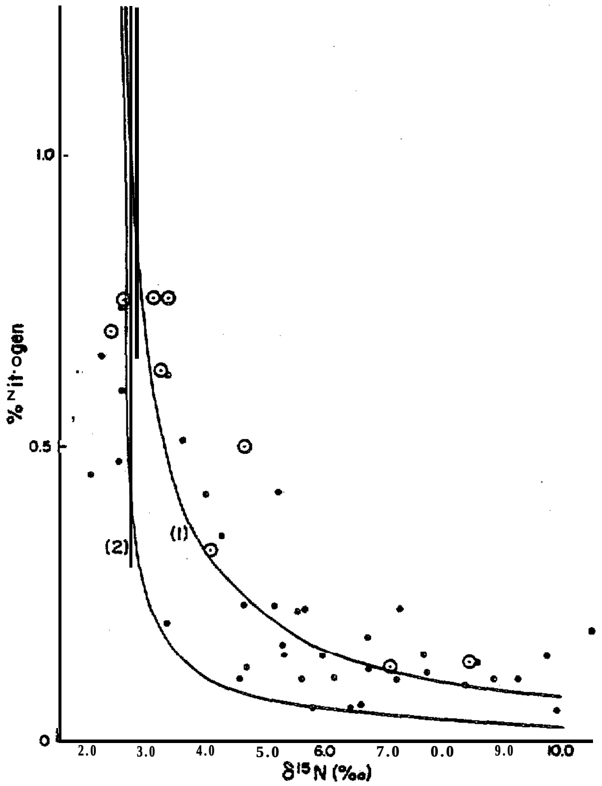

Fig. 3. Comparison between two *mixing* curves and the nitrogen data shown in Table 1. Surface samples: ● . Core 7C: ○.

End-members	*Curve (1)*	*Curve (2)*
% Nitrogen sewage	1·8	1·8
δ^{15}N sewage	+ 2·5‰	+ 2·5‰
% Nitrogen marine	0·075	0·025
δ^{15}N marine	+ 10‰	+ 10‰

(*i.e.* >0·5% nitrogen) range from + 1·8 to + 3·6‰ and are comparable with the δ^1 'N values for the effluent (+ 2-O to + 3·0‰) and for the pore water ammonia in the sediment (+2.6 to + 3· 1 ‰). This agreement indicates that little nitrogen isotope alteration has occurred during sedimentation and bacterial degradation. Myers (1974) noted a 1%0 decrease in the $\delta^1 3_C$ for the effluent material incorporated into the San Pedro Shelf sediment.

Table 3 lists the nitrogen content and δ^1 'N values for samples measured at various depths in cores taken at stations 6C and 7C. Figure 3 is a plot of $\delta^1 5_N$ versus nitrogen content for all sediment samples analysed. Curve(1) represents the mixing relationship for the previously mentioned end-members except that N_x has been changed to 1·8%, which represents the content of nitrogen in the refractory sewage, assuming that 25% of the initial content (2·4% N) is lost during deposition (Myers, 1974). There is no significant difference between the curve in Fig. 2 and curve(1) in Fig. 3. This is because the term $N_y(\delta_T - \delta_y)$ in eqn (3) is generally small compared with the term $N_x(\delta_x - \delta_T)$. Therefore, changes in N_x are mainly offset by its presence in both the numerator and the denominator. Curve(2) of Fig. 3 represents the mixing relationship using the same end-member values as curve (1) except $N_y = 0{\cdot}025\%$. Changing N_y significantly alters the value of the numerator but it only has a significant effect on the denominator when δ_T differs greatly from δ_y.

Due to the hyperbolic form of the mixing curve, the most sensitive end-members for altering the shape of the curve are δ_x and N_y. Non-constancy in both the δ^1 'N value of discharge effluent and the nitrogen content of normal marine debris are considered to be the main determinants for the scatter of data points for the δ^1 'N versus nitrogen content plots.

Bacterial degradation and mixing of effluent particles

Tables 2, 3 and 4 list the measured values of organic carbon, nitrogen, uranium and sulphur for the sediment samples analysed. Figure 4 shows the plot of nitrogen versus uranium content. The positive correlation suggests that the uranium and nitrogen are both enriched by sewage discharge in the sediment. In order to describe the process by which uranium is enriched in the sediment, a simplified quantitative model was developed to demonstrate the combined effects of degradation and mixing of the effluent particles with normal marine debris.

The basic assumption for the model is that a component behaves as if it is either completely associated with the organic fraction or is completely in the inorganic fraction of the effluent. An element is considered to be associated with the organic fraction if it is solubilised (or lost) in direct proportion to the amount of organic matter destroyed during bacterial degradation. If an element is contained in a refractory mineral then that element will not be lost during organic degradation. An element concentrated in the organic fraction which reprecipitates after release from the organic host will behave as an inorganic constituent.

TABLE 4
CONTENT AND $\delta^{34}S$ OF SULPHUR ON SAN PEDRO SHELF AND THE CALCULATED EFFLUENT (S_E) COMPONENT OF TOTAL SULPHUR CONTENT

Surface *samples*	s{%)	$\delta^{34}S$(‰)	s{ %)$_E$*
OD1	0·12	−5·6	008
2D1	0·24	−0·8	0·22
5D1	0·80	-12.9	0-28
6D1	0·44	-13.9	030
7D1	0·48	-15.8	010
8D1	0·77	− 16·7	0·13
9D1	034	-14.2	0·10
10D1	0·64	−16·1	0·13
0C1	0·14	−4·7	0·11
2C1	070	-6.3	0·39
5C1	1·30	-12.3	0·50
7C1	1·27	−10·6	0·60
9C1	0·78	-10.9	0-35
10C1	0·39	-10.9	0·18
7A1	046	− 13·4	0·15
7B1	1·10	-10.6	0·52
Core 7C/Depth (cm)			
4-5	1·30	−5·6	0·94
8-9	1·23	-5.9	0·87
15-16	1·16	−7·9	0·70
17–18	0·18	-15.7	0·04
18-19	0·20	−16·3	0·04
19-20	0·22	−17·0	0·04

$$^{*}S(\%)_E = S(\%)\frac{\delta^{34}S - \delta^{34}S_B}{[\delta^{34}S_E - \delta^{34}S_B]}$$

where: $\delta^{34}S_B$ = isotope ratio biogenic sulphur = - 20‰. $\delta^{34}S_E$ = isotope ratio effluent sulphur = −0·1‰.

The concentration of a component, X, in the inorganic fraction is initially:

$$X_I = \frac{X_{E_0}}{1 - 2C_0} \tag{4}$$

where: X_I = fraction of component X in inorganic fraction; X_{E_0} = fraction of component X in total effluent and CO = fraction of organic carbon in total effluent (which is assumed to be approximately half the organic matter content).

Following a loss of organic matter, the content of component Xcan be expressed by eqn (5):

$$X_{E_1} = \frac{“(1 - 2C_1)}{(1 - 2C_0)} X \tag{5}$$

where subscripts O and 1 represent component X, initially and after loss of organic matter.

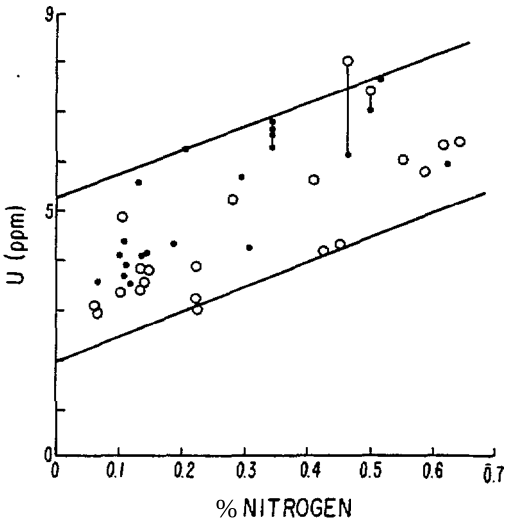

Fig. 4. Comparison between the uranium and nitrogen content in surface sediment samples. Tie lines connect data points for uranium measurements on different grab samples from the same station. The envelope of data points indicates a positive correlation between uranium and nitrogen. .: Measurements made on same grab sample. 0: Measurements made on different grab samples; same station.

Figure 5 illustrates the effects of mixing and degradation of organic carbon, both with and without loss of associated elements. The original particulate effluent is described by CO, X_{E_0} and the marine constituent by C_m, X_M. The line connecting Co, T_0 with C_m, X_M is the mixing curve (G) and assumes no reactions or degradation but only dilution of the sewage with marine debris.

Where there is degradation of organic matter and the associated component remains within the residue, the component is enriched relative to its initial concentration. This is represented by curve A which plots the increase of the content of a component as a function of the amount of organic matter destroyed during degradation (developed from eqn (5)). Mixing curves B and C correspond to the projected distribution in the sediment of an inorganic component of sewage where the refractory or residual fraction of the organic matter, r_f (content residual carbon/content effluent carbon), is 0·5 and 0.75, respectively.

When effluent organic matter is solubilised with loss of the associated component in the same ratio to carbon lost, the decrease will follow curve F. Curves D and E represent the mixing curves for r_f = 0·75 and 0·50, respectively, between the remaining component content in the effluent and its content in the normal marine sediment.

The above model can be applied to the results obtained by Mitchell & Schafer (1975) in their study of the cadmium distribution in Santa Monica Bay sediment, near the Hyperion discharge pipes. During a seven-month period in 1974, these

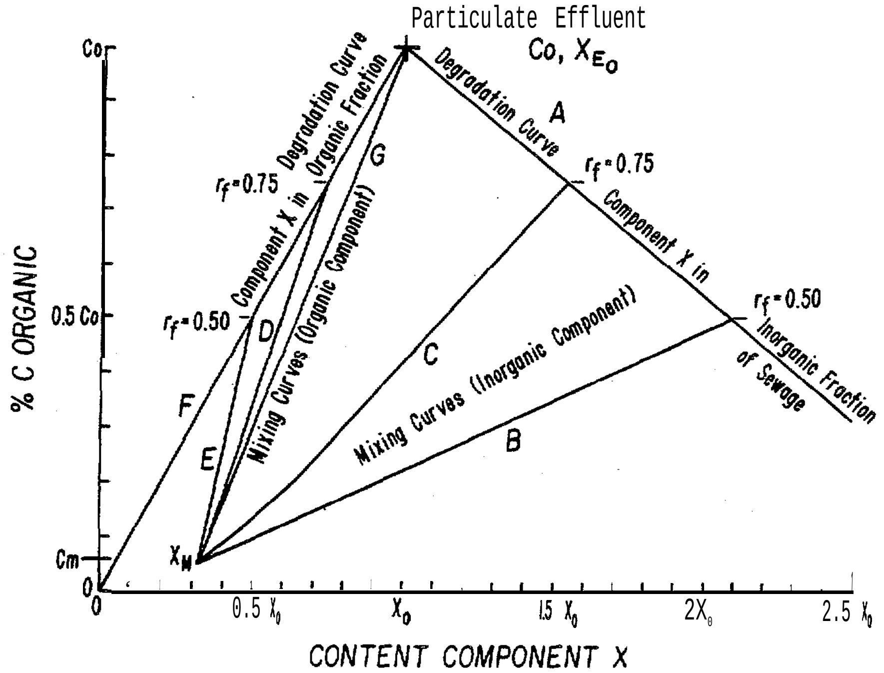

Fig. 5. Normalised content of component X in relation to organic carbon, C, after degradation and mixing with normal marine sediment—X_m; C_m. F = Degradation curve for organic component. A = Degradation curve for inorganic component. G = Mixing curve for unreacted effluent. E, D = Mixing curves for organic component after 50% and 25% of organic matter is lost by degradation, respectively. B, C = Mixing curves for inorganic component after 50x and 25 % of organic matter is lost by degradation, respectively.

authors collected numerous samples in the area of sewage discharge. Particulate matter in the lower water column was collected by sediment traps situated at various distances from the discharge pipes. Samples of surface sediment were collected at each location. Effluent particulate were collected from the digestor and trap and sediment samples were collected from a non-polluted control station in Catalina Canyon. Figure 6 is a reconstruction of their plot of the content of cadmium versus labile organic matter for all samples. They showed empirically that the weight per cent of total organic matter equals twice that of the organic carbon content. The distribution of data points for the trap samples lie intermediate between the data points for the effluent particulate and the control station at Catalina Canyon. This distribution is compatible with the mixing curve(G) in Fig. 5 and indicates that little bacterial degradation has occurred in the sediment traps before collection. The distribution of data points for the sediment samples conforms to a line which lies to the right of the values of the effluent particulate. This distribution pattern is bounded by mixing curves(B) and (C)in Fig. 5 and indicates that cadmium behaves

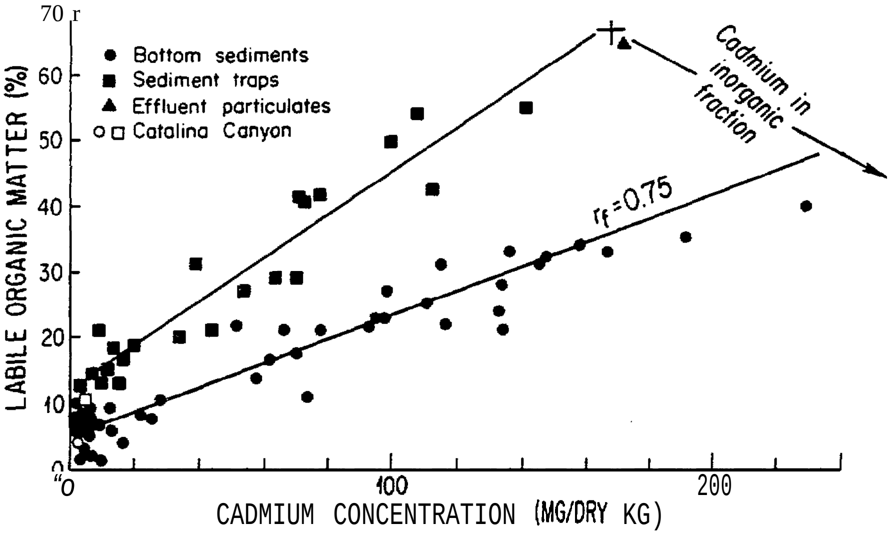

Fig. 6. Distribution of Cd and labile organic matter (2 x organic carbon) for **Hyperion** outfall area. Sediment trap data correspond to a simple mixing curve between **effluent** and normal marine detritus. Bottom sediment data correspond to a degradation-mixing curve.

as an inorganic constituent in Hyperion effluent. Note that certain sediment samples contain more cadmium than the effluent material.

Assuming that the distribution of data points from trap sediments correspond to mixing curve G in Fig. 5 and the distribution for the bottom sediment samples corresponds to mixing of an inorganic component after bacterial degradation, r_f can be calculated for the effluent material in this area. Using eqn (5) and the content of decomposable organic matter equal to twice the carbon content (Mitchell & Schafer, 1975), the curve relating the enrichment of cadmium in the particulate to the content of remaining organic matter can be determined. The intersection of this curve with the least-squares line for content of organic matter versus cadmium content for the bottom sediment samples will denote the remaining fraction of refractory organic sewage particulate. From Fig. 6 the ratio of the content of refractory organic matter to the original organic matter (r_f) is about 0·75.

Figure 7 shows the correlation between nitrogen and organic carbon from the samples measured in this study from the Whites Point area. The degradation curve for nitrogen in the organic fraction is indistinguishable from the mixing curve because the C/N of the effluent is about the same as the normal marine component. Figure 8 shows the correlation between organic carbon and uranium. As for nitrogen, the distribution of data points corresponds to a mixing curve for an organic component. If the effluent discharged at Whites Point undergoes bacterial degradation before incorporation into the sediment, some nitrogen and uranium must be solubilised and lost along with organic carbon.

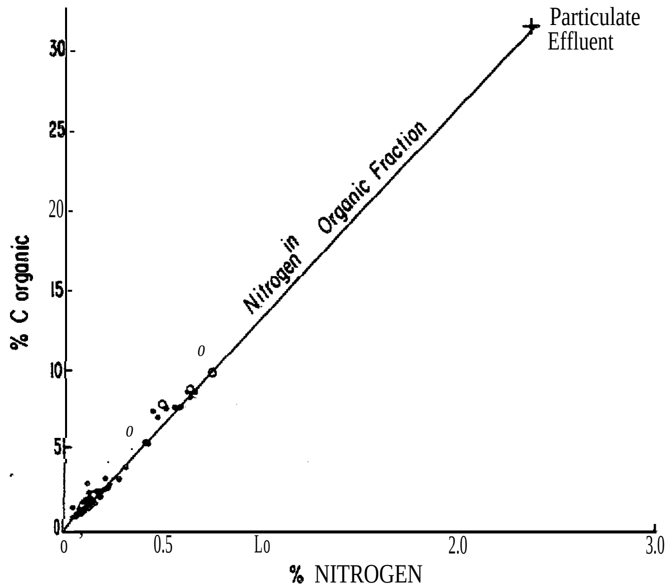

Fig. 7. Distribution of organic carbon and nitrogen on the San Pedro Shelf. Data correspond to a mixing curve for an organic component (nitrogen) with no preferential loss during degradation. ●: Surface samples. ○: Core 7C.

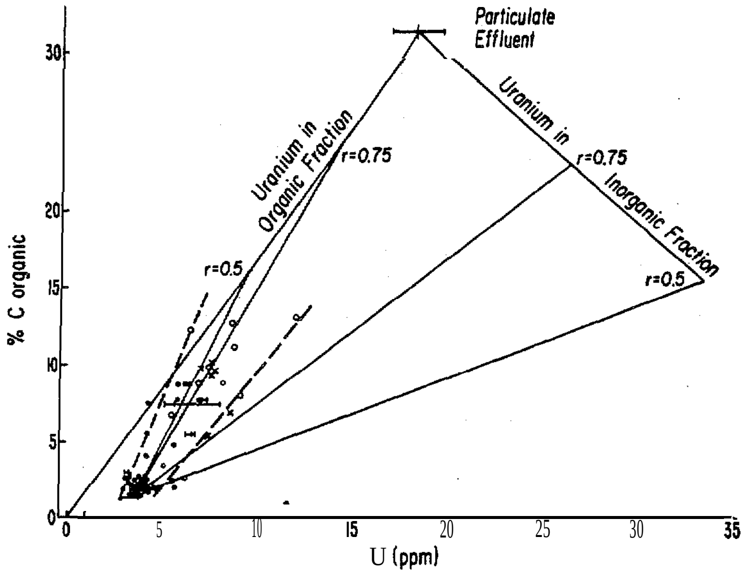

Fig. 8. Distribution of organic carbon and uranium on San Pedro Shelf. **Tie** lines connect data points for measurement of surface samples from the same station. Dashed Lines represent general envelope of data points. ●: Surface samples. ○: Core 7C. x : Core 6C.

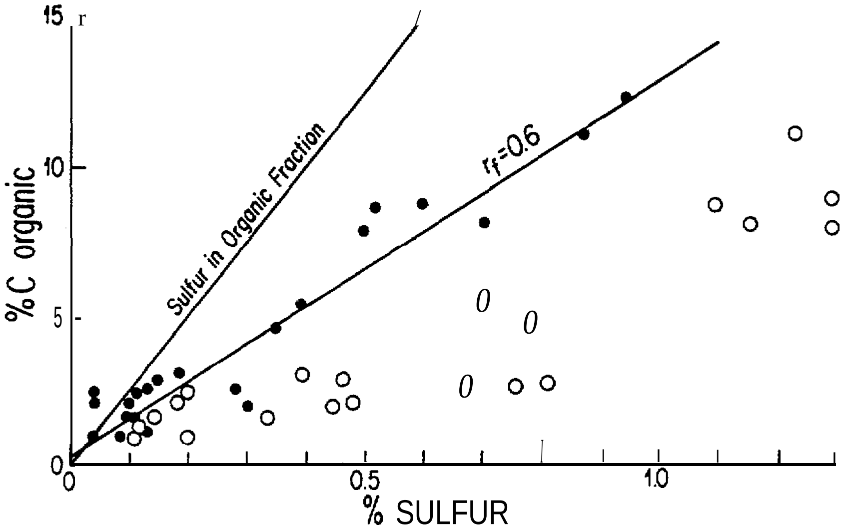

Fig. 9. Distribution of organic carbon and total reduced sulphur (○) and the calculated effluent sulphur (●) for sediment samples from the San Pedro Shelf. The line relating organic carbon and sulphur in the organic fraction is shown. The least-squares fit line for the organic carbon–effluent sulphur data yields a value of $r_f = 0{\cdot}6$.

It is known that *in situ* sulphur enrichment occurs in sewage-contaminated marine sediments due to the mineralisation of sulphide formed by bacterial sulphate reduction (Kalil, 1974). The measured sulphur in the sediment is therefore a combination of a detrital component added from sewage discharge and an authigenic component derived from seawater by bacterial activity. These two sources of sulphur, however, are isotonically different (Table 1). The $\delta^{34}S$ value of particulate sewage sulphur is $0{\cdot}1‰$ and the $\delta^{34}S$ value of the authigenically formed mineral sulphide in marine sediments is about $-20‰$ (Kaplan *et al.*, *1963)* which is the same as measured for dissolved hydrogen sulphide in the pore water. Assuming that the sulphur in the sediment is a combination of the above end-members, the detrital contribution from the sewage can be calculated for each sample. These values are listed in Table 4. Figure 9 shows a plot of organic carbon versus both total sulphur and the calculated effluent sulphur in the sediment. The least-squares fit line for the plot of organic carbon versus effluent sulphur yields an r_f value of 0·6, or similar to the value calculated for Hyperion discharged sewage in the Santa Monica Bay (Fig. 6).

DISCUSSION

For a component to be successfully used for determining the mixing relationship between two sources it must be conservative. Domestic organic effluent is not a conservative component in the marine environment, due to bacterial oxidation of organic carbon and the release of ammonia in both the water column (Richards, 1965) and in the sediment (Kaplan *et al.*, 1963). However, if a refractory fraction of the organic matter remains unreacted, then this residue may be used as a conservative component if it can be shown to have recognizable properties. Myers (1974) used organic carbon and $\delta^{13}C$ to differentiate between sewage effluent and normal marine carbon for the San Pedro Shelf sediments. The present study, based on nitrogen distribution and isotopic ratio (Peters *et al.*, 1978) indicates that nitrogen isotope measurements of bulk organic matter are superior to carbon isotope measurements for defining the relative contribution of each source (see Fig. 2). The isotopic difference between the end-members is observed to be 9‰ for nitrogen, compared with 2‰ for carbon. The $\delta^{15}N$ of the whole effluent is shown to be the same as the refractory fraction deposited and thus $\delta^{15}N$ can be considered a conservative component. This is not the case for carbon, as Myers (1974) notes a 1‰ shift in the $\delta^{13}C$ of sewage effluent deposited in marine sediments.

A model is presented which treats individual components as belonging either to the organic fraction or the inorganic fraction of sewage material. When applied to nitrogen, this model demonstrated that nitrogen exists entirely in the organic fraction and that losses, in nitrogen and organic carbon occur at a constant C/N ratio. Uranium also behaves as a component belonging to the organic fraction. It appears that all the uranium, above the normal marine background (-3 ppm) comes from sewage particulates. Although there is abundant H_2S (4 mM) in the surface sediments, there is no evidence that this is responsible for fixing any significant amounts of uranium from seawater (by reducing U^{+6} to insoluble U^{+4}).

Cadmium (Hyperion outfall area) and detrital sulphur (Whites Point outfall area) both appear to be inorganic components which are not lost together with organic carbon (Figs 6 and 9) and correlate with a residual organic fraction of 0·75 and 0·6, respectively. The amount of residual fraction determined in this study is in agreement with the experimental determinations of Myers (1974). A comparison between the organic carbon content of sediment traps and bottom sediment shown in Fig. 6 demonstrates conclusively that degradation of sewage organic matter does occur in the sediment. This is further substantiated by the large amount of authigenic sulphur (reflected in the isotope ratios) formed within the Pales Verdes Shelf sediment (Table 4). It therefore appears that the model presented by Morel *et al.* (1975), which suggests dilution of organic effluent particulate rather than decomposition, cannot be correct.

The relative concentrations of trace elements in sewage and outfall sediments are shown in Table 5 (Table 3 from Morel *et al.*, 1975). It is apparent from these data that Ag, Cr, Cu and Co have the same relative concentrations, normalised to Zn, in both the sewage and in the sediment, whereas Cd and Pb are enriched by about a factor of two in the sediment relative to the sewage. It has been shown (Fig. 6) that Cd behaves simply as an inorganic component in sediments surrounding the Hyperion outfall area and is not appreciably mobilised during organic

TABLE 5

THE PER CENT CONCENTRATION OF VARIOUS TRACE ELEMSNTS RELATIVE TO ZINC (AFTER MOREL *et d.*, 1975)

Metal	*Sewage* *Total* (*SCC WRP, 1973*)	*Particulate* (*Galloway, 1972*)	*Top 4 cm of sediment* *B-21*	*B-20*
Zn	100	100	100	100
Ag	0·83	0·78	0·89	0·93
Cr	36	41	41	41
Cu	23	27	28	29
Pb	10	14	19	20
Cd	1·2	1·6	2·7	3·1
Co	0·41	0·20	0-22	0·32

decomposition. Therefore, by contrast, the most probable reason why Zn, Ag, Cr, Cu and Co are not enriched like Cd is that they are mobilised with the labile organic material and lost in the same proportion as organic carbon. If this interpretation is correct, these elements, by analogy with U and N, are bound to organic compounds in the sewage and are partially released in a soluble form during initial metabolic or oxidative decay of organic matter.

CONCLUSIONS

In the San Predo Shelf area of Southern California, the nitrogen isotope ratio (^{1}5N/’4N) of organic matter in the particulate sewage effluent (+ 2·5‰) is significantly different from the organic matter in uncontaminated sediment of the same area (+ 10‰). The isotopic ratio of nitrogen does not change during partial degradation of the organic matter in the marine environment. Therefore, the distribution of δ^{1} ‘N values in the sediment beneath the sewage plume conforms to a simple mixing relationship from two point sources.

The fraction of organic matter in the particulate effluent that is refractory to bacterial degradation during deposition is about 0·6 to 0·75. The residual sewage debris is further diluted by normal marine elastic sediment. The ratio of the rates of sedimentation (normal marine solids/sewage particles), is approximately unity near the outfall and increases with distance from that point.

About 30 to 40% of the discharged nitrogen and uranium in the particulate is also lost during sedimentation. Zn, Ag, Cr, Cu and Co may also behave in this manner, whereas cadmium is retained entirely in the sediment and sulphur is further enriched by *in situ* reduction of seawater sulphate.

ACKNOWLEDGEMENTS

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NOTE ADDED IN PROOF

The trace element data listed in Table 5 were taken from results published during 1972–73. More recently, Schafer (1978) lists the discharge rates of the trace elements in the year 1977 to have been: Zn = 100; Ag = 95; Cr = 45; Cu = 30; Pb = 23and Cd = 3. The Zn–Ag–Cr–Cu values are comparable to those for 1972–73; however, the relative discharge rates for Pb and Cd are twice the 1972–73 values. This 1977 list of relative trace element distribution is equivalent to the distribution measured in the sediment by Galloway (1972) (see Table 5).

From the discussion in the text, and Fig. 6, it was concluded that Cd is not appreciably lost from particulates during sedimentation and degradation. The enrichment of Cd in the sediment, due to its inorganic behaviour, was contrasted with the other trace elements listed in Table 5. Using the 1977 data, it now appears that Cd and Pb are not enriched in the sediment relative to the other trace elements. For this reason, based on the new data, all the trace metals studied would be influenced in part by binding to degradable organic material. These new facts do not alter the validity of the models presented in the paper.

REFERENCES

BREMNER, J. M. & EDWARDS, A. P. (1965). Determination and isotopic ratio analysis of different forms of nitrogen m soils: 1. Apparatus and procedure for distillation and determination of ammonium. *Soil Sot. Amer. Proc., 29, 504-7.*

CLSNE, J. & KAPLAN, 1. R. (1975). Isotopic fractionation of dissolved nitrate during denitrification in the Eastern Tropical North Pacific Ocean. *Mar. C/rem.,* 3,271-99.

GALLOWAY, J. N. (1972). Man's *alteration of the natural geochemical cycle of selected trace metals.* PhD Dissertation, U.C. San Diego.

HENDRICKS, T. J. &YOUNG, D.R.(1974). *Modeling the fates of metals in ocean discharge waste waters.* TM 208—Southern California Coastal Water Research Project, Los Angeles, California.

KALIL, E. (1974). Rapid pore water analysis for sediments adjacent to reactor discharges. Environmental Surveillance Around Nuclear Installations-Symposium, International AEC, Vienna.

KALIL,E.(1976). *Distribution and geochemistry of uranium in Recent and Pleistocene marine sediments.* PhD Dissertation, UCLA.

KAPLAN, I. R., **EMERY,** K. O. &RI-BERG, S. C. (1963). The distribution and isotopic abundance of sulfur in Recent sediments off Southern California. *Geochim. Cosmochim. Acts, 37, 297-331.*

MITCHELL, F. K. & **SCHAFER,** H. A. (1975). *Effects of ocean sludge disposal.* SCCWRP Annual Report. Bascomb, W. (Ed.) 153-67.

MOREL, F., WESTALL, J. C., **O'MELIA,** C. R. & MORGAN, J. J. (1975). Fate of trace metalsin Los Angeles County wastewater discharge. *Environ. Sci. & Tech., 9, 756.*

MYERS, E. P. (1974). *The concentration and isotopic composition of carbon in marine sediments affected by sewage discharge.* PhD Dissertation, Cal Tech.

PETERS, K. E., **SWEENEY,** R. E. & KAPLAN, 1. R. (1978). Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr., 23(4), 598-604.*

RICHARDS, F. A. (1965). Anoxic basins and fjords. In: *Chemical oceanography 1 (Riley,* J. P.& Skirrow, G. (Eds)), 61146, London and New York, Academic Press.

SCCWRP (1973). *The ecology of the Southern California Bight: Implications for water quality management*. Southern California Coastal Water Research Project. (G. E. Hlauka, Manager.)

SCCWRP (1975). Annual Report (W. Bascom, Ed.).

SCHAFER, H. A. (1978). ***Characteristics of municipal wastewater discharges, 1977.*** SCCWRP Annual Report. Bascomb, W. (Ed.) 97-101.

SWEENEY, R. E., LIU, K. K. & KAPLAN, 1. R. (1978). Oceanic nitrogen isotopes and their use in determining the source of sedimentary nitrogen. In: ***Stable Isotope Chemistry. Proc. Intl. Symposium, New Zealand Dept. Sci. Ind. Res.***, Bull. 220.

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Extractable Organic Matter in Urban Stormwater Runoff. 1. Transport Dynamics and Mass Emission Rates†

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■ Los Angeles River waters were collected during the progress of a storm event in 1978 and analyzed for solvent-extractable organic substances. The extracts from both fiitered and unfiltered samples were fractionated into five compound groups of differing polarity. No statistical relations were found between gross storm parameters and the organics carried by the runoff waters; however, the various fractions showed high intercorrelations. The majority of the extractable are associated with particulate matter; their partitioning between particulate and dissolved phases is controlled primarily by volubility. Maas emission rate estimates indicate that the Los Angeles River contributes nearly 1% of the annual world petroleum hydrocarbon input to the ocean via urban runoff.

Introduction

Present-day estimates for the input of petroleum residues to the ocean via surface runoff are on the order of 1.9 X 10^6 metric tons yr^{-1} (*1*). Calculations of this sort are fraught with serious drawbacks stemming primarily from a lack of reliable data. Clearly, it is impractical to routinely monitor urban runoff and nonurban river discharges on a regional or even local scale. However, the accuracy of our estimates could be greatly improved if we were able to delineate the transport dynamics involved. Furthermore, when considering surface runoff, one should make a distinction between the chronic discharge typical of continuously flowing rivers and the episodic behavior of seasonal rivers and streams.

In the present study, the Los Angeles River, a seasonally active urban drainage system, was selected for two reasons. First, it is the single most important river in southern California, accounting for ~28% of the total yearly flow (2). Second, it drsina a large portion of the highly urbanized Los Angeles basin, se well as surrounding undeveloped areas. Thue, both anthropogenic and natural terrigenoua materials are likely to be significant constituents of any transported organic matter. The river empties into a coastal environment presently receiving input of organic materials from a multitude of sources (3). Therefore, detailed molecular and isotopic (4) characterization of river-borne organics may aid the ultimate differentiation of these sources to coastal marine sediments.

In undertaking this project, we had three objectives in mind: (1) to study the transport of extractable organics in relation to dynamic features of the storm itself, (2) to investigate those factors controlling the distribution of organic molecular types between particulate and dissolved phases, and (3) to formulate mass-emission estimates for various organic compound types, including petroleum hydrocarbons, issuing into southern California's coastal waters via surface runoff. Details of the molecular (5) and elemental/isotopic (6) characteristics of these stormwaters will be presented subsequently.

Study Area

The modern-day Los Angeles River largely comprises man-made channels stretching from the San Gabriel Mountains to San Pedro Harbor (Figure 1). Under storm conditions, the flow is regulated by a number of reservoirs within the drainage basin. Mountainous, hilly, and coastal plain topographies characterize the more than 2100-km^2 basin, and a major part of metropolitan Los Angeles is drained by the system. Because of the high coverage of city surfaces by impermeable materials, infiltration is low, and storms can generate large runoff flows (7).

The rain pattern for the storm studied here (Figure 1) indicates that very little precipitation occurred in the mountain areas where the population density is low. Instead, the highly industrialized east central and harbor (south central) sections of the city experienced the greatest rainfall accumulation. Although small by comparison with other storms that occurred during 1978-1979, this storm event was the second of the rainy season. Consequently, flushing of organic residues that accumulate during the dry seaeon may have been particularly effective.

Experimental Section

Sampling. On November 21, 1978, 11 duplicate samples of runoff were collected at various times during a storm near the mouth of the Los Angeles River (Figure 1). Water samples were obtained from the middle of the channel by submerging a vaned 4-L steel collection device just below the stormwater surface. Upon retrieval, the sampler was thoroughly shaken to induce homogenization, and equal volumes were poured alternately into two glass containers. This procedure was repeated until exactly 3 L had been added to each bottle. After returning to the laboratory, we added 200 mL of hexane to one of the two bottles collected at each sampling time. This was done to prevent evaporative losses and to initiate extraction. A 1OO-35O-ML subsample was removed from each of the other (second) bottles for total suspended solids (TSS) determination (8), and then 2 L more were filtered through solvent-cleaned, precombusted glass-fiber filters (Whatman GF/A). The filtrates were transferred to clean glass containers and preserved with 200 mL of hexane. Thus, filtered (2 L) and unfiltered (3 L) samples corresponding to each of 11 sampling intervals were obtained. The contents of the bottles were spiked with $HgCl_2$ to terminate biological activity and stored at 100 C until extractions could be performed. The remaining sample (-900-650 mL) was also poisoned with $HgCl_2$ and allowed to sit for 48 h, after which the supernatant was removed and the settled solids were stored frozen for elemental and isotopic analysis.

Analyses. Liquid/liquid extractions were performed successively on all samples with the 200-mL hexane preservative followed by three portions of $CHCl_3$ (300 mL/3 L samples). The combined extract for each sample was concentrated to a small volume by rotary evaporation under reduced pressure at 30–35 ‘C, and the concentrate was dried with anhydrous Na_2SO_4. The extract was then passed over activated copper

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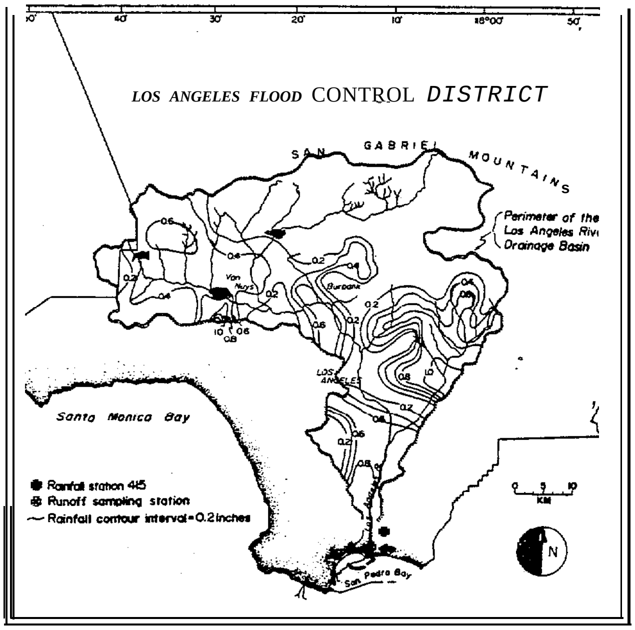


Figure 1. Map of the Los Angeles River drainage basin showing rainfall accumulation contours and runoff sampling station for the storm of November 21.1978.

to remove elemental sulfur, reduced to a known volume, and analyzed gravimetrically on a Mettler ME22 electrobalance for total extractable organics (TEO). A portion of each extract was removed for methylation of extractable fatty acids by a modification of the BF_3–MeOH technique (9). We were concerned that solvent-soluble triglycerides and nonmethyl esters of fatty acids might not be quantitatively transesterified by this procedure (*10*). Therefore, we compared the above method with a saponification/esterification procedure (*11*) using three of the samples. The fatty acid methyl ester (FAME) yields and molecular distributions were identical within experimental error for the two techniques.

Separation of the total extracts into five fractions was achieved by thin-layer chromatography using plates coated with 0.25 mm of silica gel G and developed in CH_2Cl_2. All plates were precleaned by running once in MeOH and twice in CH_2Cl_2 and removing the top 1 cm of silica gel after each elution. Five fractions were isolated: (1) total hydrocarbons (THC), $R_f \simeq 0.77$; (2) fatty acids (methyl esters) (FA), $R_f \simeq 0.63$; (3) ketones (KET), $R_f \simeq 0.50$; (4) polars (PLR), $0.48 > R_f \geq 0.02$; (5) nonelutable polar compounds (NEP), $R_f = 0$. The PLR fraction contains hydroxy F.AMEs, dicarboxylic acids, and a variety of polyfunctional moieties in addition to fatty *alcohols* and sterols (5). Total hydrocarbon, FA, KET, and PLR bends were eluted from the silica gel and analyzed for their content gravimetrically; the NEP fraction was estimated by mass balance. Three THC samples were further separated by thin-layer chromatography into aliphatic and aromatic fractions by pentane elution on silica gel G aliphatics, $R_f \simeq 0.95$; aromatics, $R_f \leq 0.92$. Only gravimetric results are presented here; gas-chromatographic and gas-chromatographic/mass-spectrometric identification of the fractions will appear elsewhere (5).

Results

The general flow characteristics and suspended solids distribution for the storm are presented in Figure 2. Streamflow data were determined by water stage recording stations located near the sample collection site (Figure 1). Figure 2 also contains cumulative rainfall data for station 415 on this day.

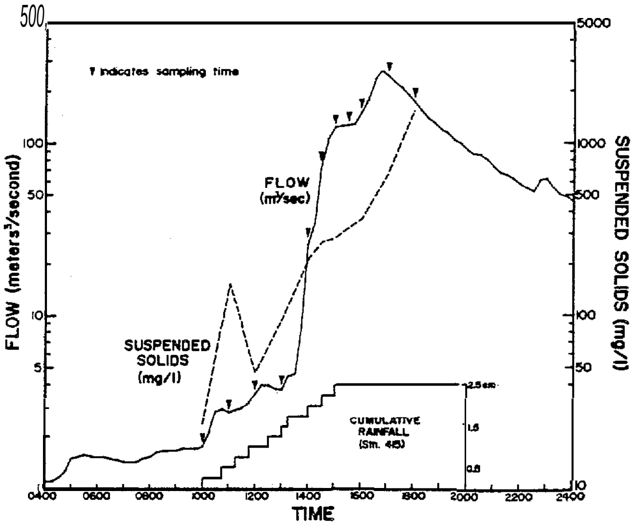


Figure 2. Flow, suspended solids, and rainfall variations during?& storm of November 21.1978.

The apparent lag between rainfall and streamflow is related to the discharge characteristics of the entire river system whose drainage basin is more than 65 km long in linear north/south distance. As indicated in Figure 2,” stormwaters were sampled from the beginning of the storm until just after peak flow had occurred. During this time, suspended solids levels generally increased.

The data for total extractable organics and the five fractions are summarized in Table I. Unfiltered samples showed a high variability for all measured parameters, In contrast, relatively constant levels were found for THC, FA, and KET fractions in filtered samples. Values for the “particulate? concentrations of various fractions were computed by subtracting data for filtered samples from that of the corresponding unfiltered samples. Mean values for the calculated “particulate” concentration of THC and ita “dissolved” (i.e., filtered) counterpart were 10.5 ± 6.4 and 0.39 ± 0.05 mg/L, respectively. MacKenzie and Hunter (*12*) found values in a Philadelphia storm sewer to be 2.7–5.1 mg/L (particulate) and 0.16-0.34 mg/L (dissolved); Zürcher et al. (*13*) noted similar levels in motorway runoff in Switzerland.

Figure 3 illustrates the data plotted against time for both filtered and unfiltered samples. Several features are readily apparent. First, in the unfiltered samples, all parameters show an increase in value at 1100 hours similar to the behavior of suspended solids (cf. Figure 2). Secondly, there is a marked increase from 1300 to 1500 hours. This change seems to correspond to the behavior of the flow during the same time. Statistical analysis, however, failed to yield a strong correlation between flow or suspended solids and any of the organic parameters (Table II). The apparent similarities in the concentration trends for TEO and the various subfractions are borne out by the high correlation coefficients obtained by linear regression analysis (Table II). Thirdly, comparison of the temporal variations for filtered and unfiltered samples of the same fraction indicates that only in the case of TEO and the PLR fraction is there a degree of resemblance ($r = 0.87$ and $r = 0.80$, respectively). The filtered THC data show an extremely small variation (coefficient of variation = 12.4%) considering the wide fluctuations evidenced in the unfiltered samples.

In agreement with the findings of others (*12–15*), most of the extractable and, in particular, the hydrocarbons are associated with the filterable particulate matter (Table HI). In the case of the hydrocarbons, the percentage in the “dissolved” phase relative to the total burden is consistently below 15%

Table 1. Summary of Gravimetric Data for Total Extractable Organics and Subfractions Recovered from Storm Runoff Samples [a]

sampling time, h	total extractable organics		total hydrocarbons		fatty acids		ketones		polars		nonelutable polar compds[b]	
	u	F	U	F	u	F	u	F	u	F	u	F
1000	2.55	1.55	0.99	0.420	0.194	0.064	0.133	0.066	0.967	0.154	0.266	0.846
1100	14.2	2.52	6.22	0.378	1.12	0.124	0.560	0.062	2.10	0.564	4.20	1.39
1200	6.25	1.85	2.54	0.360	0.449	0.095	0.163	0.045	0.958	0.469	2.14	0.880
1300	9.13	2.27	3.96	0.410	0.912	0.102	0.375	0.059	1.43	0.528	2.45	1.17
1400	18.1	2.00	10.5	0.490	1.41	0.109	0.700	0.068	2.22	0.930	3.27	0.400
1450	26.0	4.20	19.0	0.366	1.96	0.211	1.12	0.053	4.42	0.978	C	2.59
1500	30.8	4.22	18.2	0.388	4.27	0.137	1.49	0.143	4.69	1.56	2.15	2.00
1550	33.3	4.80	19.5	0.405	2.75	0.091	1.67	0.136	5.40	1.45	3.98	2.72
1600	25.7	3.53	10.4	0.357	2.37	0.127	1.58	0.042	4.43	1.15	6.92	1.85
1700	17.7	3.02	9.21	0.432	1.15	0.129	0.678	0.042	3.80	0.618	2.86	1.80
1800	27.7	2.64	15.9	0.302	1.72	0.093	0.858	0.049	5.61	0.893	3.61	1.30

[a] All data in mg/L. U = Unfiltered sample. F = Filtered sample. [b] Nonelutable polar compounds = TEL − {THC + FA + KET + PLR}. ‘ NEP < 0.

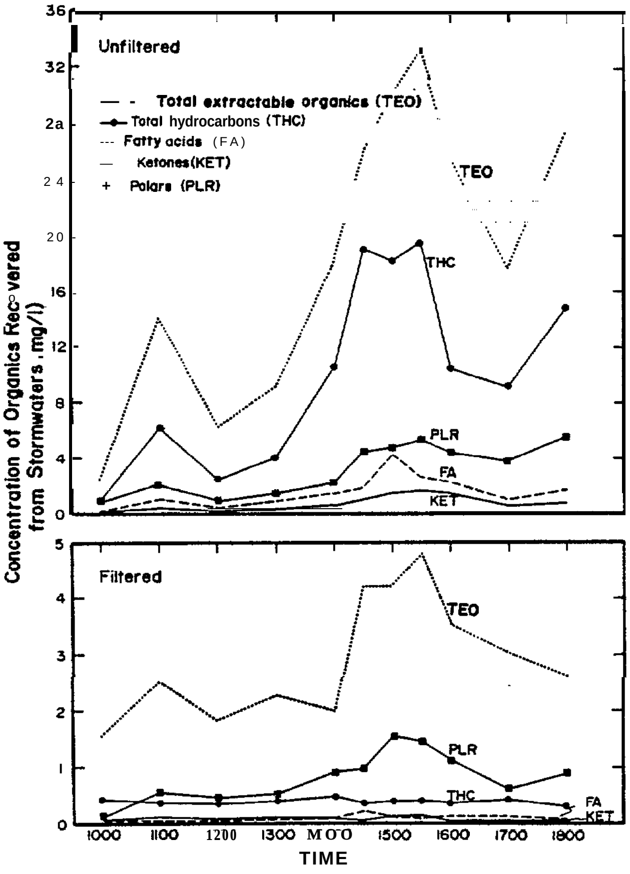


Figure 3. Changes in concentrations of organics during progress of the storm of November 21, 1978.

Table il. Correlation Coefficients from Linear Regression of Gross Storm Parameters, Total Extractable Organics, and Organic Subfractions (Unfiltered Samples)

	flow	TSS	TEO	THC	FA	KET	PLR
Flow	1	0.69	0.64	0.55	0.46	0.57	0.79
TSS		1	0.48	0.43	0.17	0.23	0.66
TEo			1	0.96	0.84	0.93	0.95
THC				1	0.79	0.84	0.91
FA					1	0.69	0.76
KET						1	0.85
PLR							1

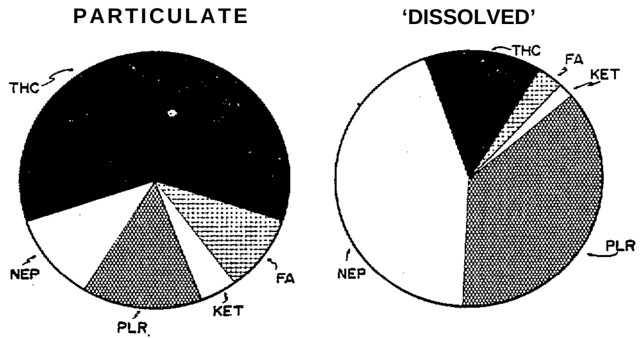
Table III. Percentage of Organic Components Passing through Whatman GF/A Filter

sampling time	TEO	THC	FA	KET	PLR
1000	60.8	42.4	33.0	49.8	15.9
1100	17.8	6.1	11.1	11.0	26.9
1200	29.6	14.2	21.2	27.6	49.0
1300	24.9	10.4	11.2	15.7	36.9
1400	11.1	4.7	7.7	9.7	41.9
1450	16.1	1.9	10.8	4.7	22.1
1500	13.7	2.1	3.2	9.6	33.2
1550	14.4	2.1	6.5	8.1	26.9
1600	13.8	3.4	5.4	2.6	26.0
1700	17.1	4.7	11.2	6.2	16.3
1800	9.5	1.9	5.4	5.7	15.9

except for the first, low-flow, sampling period. This low-flow response is seen for other parameters as well and probably reflects the reduced suspended solids levels maintained by the stormwaters under these hydraulic conditions.

To examine the partitioning of various organic fractions between particulate and dissolved phases, we calculated the average composition in each phase. These results are shown in Figure 4. The hydrocarbons clearly dominate the composition of the particulates followed by (in order of importance) PLR > NEP > FA > KET. Considering their hydrophobic nature, the hydrocarbons are in remarkable, although relatively decreased, abundance in the dissolved phase. Not surprisingly, the polar NEP fraction predominates in this phase. We also examined three THC fractions for partitioning of aliphatic and aromatic hydrocarbons. On the average, the aliphatic/aromatic ratio for the particulate was 11.5, whereas for the dissolved phase a mean ratio of 2.9 was obtained. This type of fractionation has been observed before (16-18) and is due to the greater polarity of aromatic hydrocarbons.

Having monitored the storm over the complete flow range, it seemed appropriate to make mass-emission calculations. Storm mass emissions were determined by applying measured



Fraction	% Total Extractable Organics Particulate	 'Dissolved'
Total hydrocarbons (THC)	59a ± 11.1	15,126.5
Fatty acids (FA)	10.0 ± 2.7	4.2 ± 1.0
Ketones (KET)	4.7 ± 1.3	2.5 ± 1.0
Polars (PLR)	14.2 ± 3.9	29.5s8.2
Non-elutable polar compounds (NEP)	11.3	48.?

Figure 4. Distributions of organic subfractions in particulate and dissolved phases of stormwater samples.

concentrations to the estimated discharge volumes according to the formula

$$\text{mass emission} = \sum_{i=1}^{n} C_i \int_{t_i}^{t_{i+1}} F(t)\,dt$$

where i = sample time interval, n = total number of samples, C_i = analytical concentration of parameters at time of sampling (mg/L), F(t)= stormflow (L/min), and t = time (min). The computed values for water, total suspended solids, and extractable organics (Table IV) apply only to that portion of the storm sampled. Annual mass emission rates were determined for the Los Angeles River by strict extrapolation of flow data from previous years (7).

The average concentration of aromatics is nearly the same as that found by MacKenzie and Hunter (13); however, the Los Angeles River appears to carry 3-4 times as much aliphatic hydrocarbons per unit volume. The projected annual mass emission rate of petroleum hydrocarbons for this drainage system amounts to 0.9% of the world estimate for urban runoff (*1*). Even though this figure appears to be high on a global basis, the river still only drains 2070 of Los Angeles county.

We were also interested in estimating the intensity of petroleum residue production/erosion in the Los Angeles River drainage basin and comparing it with other cities in the world. On the basis of population density maps derived from the 1970 U.S. census, we determined the population residing within the drainage basin and computed the annual per capita mass emission of hydrocarbons via urban runoff. The value so obtained was 875 g yr^{-1}. Unfortunately, no similar urban data could be found in the literature. Therefore, we made calculations based on current world and city population data. The global population is -4.321 X 10^9 and that of the world's 60 largest cities is 0.296 x 10^9. Assuming that the estimated value for worldwide emission of hydrocarbons via urban runoff of 0.3 X 10^6 metric tons yr^{-1} (*1*) can be attributed to this urban population, we find a per capita emission rate of 1014 g yr^{-1} person-l. Notwithstanding the many assumptions that go into these computed values, the Los Angeles River and world urban runoff values are in reasonable agreement. One can also calculate worldwide per capita emission rates for (nonurban) river runoff. According to the NAS study (*1*), 1.6 X 10^6 metric tons yr^{-1} of hydrocarbons enter the ocean via rivers. Using a nonurban world population of 4.025 X 10^9, we arrive at a per capita emission rate of 398 g yr^{-1} person–l for rivers. From these results we can conclude that (1) the first approximation estimate of the NAS study for emissions via urban runoff is supported by the present data, and (2) urban runoff contributes over 2.5 times as much petroleum to the oceans as nonurban rivers when compared on a per capita basis. This identifies the urban locale as a site of intense hydrocarbon usage and consequent deposition and erosion.

Table IV. Estimates for Storm Mass Emissions, Average Concentrations, and Annual Mass Emission Rates for Constituents in Los Angeles River Storm Runoff

	mass emission, metric tons/storm	av concn,[a] mg/L	projected L.A. River discharge,[b] metric tons/yr
water	2.6 X 10^6		2.1 x 10^8
total suspended solids	1858	715	1.5 x 10^5
total extractable organics	63	24.2	5010
total hydrocarbons	34.1	13.1	2712
aliphatics	30.0	11.5	2401
aromatics	4.1	1.6	311
fatty acids	5	1.9	393
ketones	3	1.1	228
polar compds	12	4.5	932
nonelutable polar compds	17	6.6	1366

[a] Calculated by dividing constituent mass emission by total volume of discharged water. [b] Estimated on the basis of average total flow for years 1960-1975 (7).

Finally, because the hydrocarbons are mainly derived from residual petroleum products on highways and pavement (5, 12, *13*), we calculated the annual mass emission rate relative to the total, as well as the developed portion, of the drainage basin surface area. Land-use data and aerial photography were used to estimate the fraction of land covered by impermeable surfaces. When normalized to the total basin surface area, the annual mass emission rate of hydrocarbons was 1.28 metric tons $km^{-2}\,yr^{-1}$; however, for the paved surface, it was 2.94 metric tons $km^{-2}\,yr^{-1}$.

Discussion

Relation of Storm and Organic Parameters. A primary objective of this study was to examine the relation between dynamic features of a storm and the extractable organics in the stormwaters. There is no "a priori" reason to assume that such simple relations exist. And yet, our present ability to estimate large-scale hydrocarbon emissions to the environment depends entirely on assumptions of this type. Attempts by others (*15*) to correlate storm and hydrocarbon parameters have been unsuccessful because of the inherent complexity of the storm event. For example, the timing of the storm, the nature and availability of the organic source material, and the intensity and duration of the rainfall all influence the transport behavior of stormwaters.

As shown in Table II, the measured organic parameters, with the exception of the PLR fraction, did not correlate with storm flow. This is not surprising as it is unlikely that either the supply of extractable organic compounds or the efficiency of their removal by scouring is uniform throughout the storm. The lack of correlation between suspended solids levels and extractable organic content in stormwaters indicates that, while the majority of the extractable are carried on particulate, their abundance is not directly related to the level of suspended solids, It is well known that hydrophobic organics favor association with particulate matter (19). There is, however. some controversy as to the nature of this association. Some researchers (20) believe that adsorption onto clay minerals is an important mechanism for removal of hydrocarbons from solution (and their ultimate deposition in sediments). But there is some question as to the role played by solvent-insoluble organic matter in hydrocarbon sorption. Meyers and Quinn (20) found that humic materials actually interfered with the uptake of hydrocarbons in sediments. In contrast, Pierce et al. (*19*) found that removal of humic substances reduced the absorption capacity of sediments for DDT. Button (1976) was unable to detect any uptake of dodecane from saturated solutions by either smectite or estuarine sediment (21), indicating that concentrations at or below saturation are insufficient to promote removal by adsorption. In studying the adsorption of anthracene, Herbes (22) observed the capacity of yeast cells to be an order of magnitude greater than that of clay minerals. Even more recently (23) there is evidence that the sorption capacity of a sediment is directly related to ita organic content. In systems more representative of stormwaters, that is, turbulent hydrocarbon-rich aqueous mixtures, Zürcher et al. (*13*) found that agglomeration, not adsorption, dominates the particle-hydrocarbon association. We attempted to evaluate our data in light of the foregoing information.

To test the hypothesis that organic content controls sorption capacity, we measured the amount of organic carbon in the particulate following extraction. Linear regression of total extractable organics vs. solvent-insoluble carbon yielded a correlation coefficient of 0.83. If the correlation is not spurious, these data seem to indicate that solvent-insoluble organics may participate in the sorption and stormwater transport of extractable organics.

A more satisfying result might have been achieved by sizing the particulate prior to analysis. Recent work by Thompson and Eglinton (24) indicates that the distribution of organic compounds among different sediment particle size ranges results in compositional and concentrational fractionation. Certainly, more detailed sedimentological and geochemical work is needed if the transport dynamics are to be fully elucidated.

The high correlations found among the various organic isolates offers some added hope for global input estimates based solely on TEO measurements (*1*). Data from Zürcher et al. (*13*) yielded a correlation between CCl_4 extractable and total hydrocarbons ($r = 0.98$, $m = 0.70$). We obtained similar results ($r = 0.96$, $m = 0.63$), indicating that, in the case of urban runoff, total hydrocarbons may represent a near-constant and sizeable fraction of the total extractable. This implies a homogeneous source and/or efficient randomization by stormwater mixing.

We also found greater concentrations of total hydrocarbons and, in particular, aliphatic hydrocarbons, than others have found in urban runoff (12, 13). This maybe attributed to the highly efficient removal of hydrocarbons during this storm. Because it was only the second to occur following the 1978 dry season, appreciable quantities of petroleum products were probably available on the pavement for scouring. In this context, the data for Switzerland and Philadelphia pertain more accurately to locations receiving year-round precipitation. Alternatively, the differences may represent real geographic variations in petroleum product type and usage.

Partitioning of Organic Compounds, Most of the extractable are associated with filterable particulate matter. The question is this: What determines organic composition in the dissolved phase? As referred to here, the dissolved phase includes all materials passing through a Whatman GF/A glass-fiber filter. Because the median retention size of this filter is -0.9 μm (25), a fraction of the colloidal particles smaller than this diameter are found in the filtrate. In terms of mass, these colloids probably represent only a small portion of the total dispersed (particulate) phase (26). However, it is well to remember that the "dissolved" phase includes some colloidal material.

The partitioning of organic compounds between particulate and "dissolved" phases depends on a variety of factors. These include the following: molecular volubility, composition of the particulate organic phase, tendency to form stable colloids, and position of the system relative to equilibrium. The present results (Figure *4)* illustrate the importance of volubility to partitioning. *Among* solvent-extractable organics, hydrocarbons and the NEP represent end members on the sale of molecular polarity. Thus, the dramatic difference in their phase distributions is not unexpected. Similarly, the FA, KET, and PLR fractions also show enrichments in the dissolved phase relative to total hydrocarbons.

The remarkable constancy of the content and composition (5) of total dissolved hydrocarbons suggests that the same degree of saturation may have been attained. Because equilibrium is not assured, it is difficult ***to assess*** the influence that particulate organic composition has on partitioning. Nevertheless, we attempted to correlate the percentage of each organic subfraction in the particulate phase with that found in the dissolved phase. No correlations were found. This indicates that particulate organic composition has had little or no obvious influence on the composition of the dissolved phase.

Mass-Emission Calculations. Because of the timing of this storm, the mass-emission estimates (Table IV) probably represent upper-limit values for storm conditions. However, roughly 30'% of the annual total flow for the Los Angeles River occurs during dry, not stormy, weather (2). Values for oil and grease concentrations (2) at these times are higher than doring storm conditions. Presumably this trend would apply to hydrocarbons as well. As a result, the present estimates are probably somewhat low overall on an annual basis. Extrapolating these figures to the entire southern California drainage system, one obtains a figure of 9.69 X 10^3 metric tons of THC $yr.^{-1}$ This value is most likely an overestimate because much of southern California's surface runoff is not from urban environments. Ultimately, these figures must be compared with the other major source of anthropogenic and natural terrigenous hydrocarbons (i.e., wastewaters). Aside from their possible compositional differences, wastewater and runoff-derived organics are delivered to the ocean in quite different ways. Wastewater discharge is continuous, whereas chronic runoff during dry weather is superimposed by intermittent, if not dramatic, storm flows.

Conclusions

Although the dynamics of stormwater runoff is poorly understood, especially in relation to its carrying capacity of organic materials, some conclusions can, nevertheless, be drawn from the present data.

(1) Whereas the majority of the extractable organics in stormwaters are carried by suspended solids, the abundance of these organics is not directly correlated with levels of suspended solids. Instead, transported solvent-soluble organics appear to be more closely related to the stormwater content of residual, that is, solvent-insoluble carbon compounds.

(2) The amount and the composition of dissolved organic extractable are controlled primarily by the solubilities of the compound types themselves, not by their abundance in the particulate phase.

(3) Per capita mass emission rates of petroleum hydrocarbons calculated for the Los Angeles River are in reasonable accord with corresponding worldwide values for urban runoff. Despite their relatively smaller drainage areas, cities con-

tribute significantly greater quantities of these materials to the ocean on a per capita basis than do nonurban rivers. This probably reflects the higher usage and surface deposition of petroleum in the urban locale.

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Literature Cited

(1) National Academy of Sciences "Petroleum in the Marine Environment"; Washington, D. C., 1975.
(2) "The Ecology of the Southern California Bight: Implications for Water Quality Management"; Southern California Coastal Water Research Project; Technical Report 104, March 1973.
(3) Reed, W. E.; Kaplan, I. R.; Sandstrom, M.; Mankiewicz, P. *API Publ.* 1977,4284, 183-8.
(4) Peters, K. E.; Sweeney, R. E.; Kaplan, I. R. *Limnol. Oceanogr.* 1978,23, 598.
(5) Eganhouse, R. P.; Simoneit, B. R. T.;Kapkm, I. R. *Environ. Sci. Technol.*, following paper in this issue.
(6) Eganhouse, R. P.; Lu, S.-T.; Kaplan, I. R. "Elemental and Isotopic Composition of Particulates Carried in Los Angeles Stormwaters", unpublished.
(7) Los Angeles County Flood Control District "Hydrologic Report 197475'1174, October 1, 1976.
(8) "Standard Methods for the Examination of Water and Wastewater", 13th ed, American Public Health Association: New York, 1971; p 537.
(9) Metcalfe, L. D.; Schmitz, A. A. *Anal. Chem.* 1961,33,363.
(10) Morrison, W. R.; Smith, L. M. *J. Lipid Res.* 1964,5,600.
(11) Farrington. J. W.: Henricks. S. M.: Anderson. R. *Geochim. Cosmochim.* Acts 1977,41, 289.' '
(12) MacKenzie, M. J.; Hunter, J. V. *Environ. Sci. Technol.* 1979, 13, 179.
(13) Zürcher, F.; Thuer, M.; Davis, J. A. "Importance of Particulate Matter on the Load of Hydrocarbons of Motorway Runoff and Secondary Effluents"; in *Proceedings of the International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons,* Ontario, Canada, May 1978.
(14) Van Vleet, E. S.; Quinn, J. G. *Environ. Sci. Technol.* 1977,11, 1086.
(15) Hunter, J. V.; Sabatino, T.; Gomperts, R.; Mackenzie, M. J. *J. Water Pollut. Control Fed.* 1979,51, 2129.
(16) Boylan, D. B.; Tripp, B. W. *Nature* (London) 1971,230,44.
(17) Zürcher, l?.; Thüer, M. *Environ. Sci. Technol.* 1978,12,838.
(18) Winters, K.; Parker, P. L. *API Publ.* 1977,4284,579-81.
(19) Pierce, R. H.; Olney, C. E.; Felbeck, G. T. *Geochim. Cosmochim. Acts* 1974,38, 1061.
(20) Meyers, P. A.; Quinn, J. G. *Nature* (London) 1973,244,23.
(21) Button, D. K. *Geochim. Cosmochim. Acts* 1976,40,435.
(22) Herbes, S. E. *Water Res.* 1977, 11, 493.
(23) Karickhoff, S. W.; Brown, D. S.; and Scott, T. A. *Water Res.* 1979,13, 24i.
(24) Thompson, S.; Eglinton, G- *Geochim. Cosmochim. Acts* 1978, 42 199.
(25) 'Sheidon. R. W. *Limnol. Oceanogr.* 1972.17.494.
(26) Stokes, V. K.; Harvey, A.C. *Proc. Jt. Conf. Prev. Control Oil Spills,* 19731973,457-65.

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Extractable Organic Matter in Urban Stormwater Runoff. 2. Molecular Characterization[†]

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■ A comprehensive molecular characterization of solvent-extractable and bound organic constituents of Los Angeles stormwater runoff has been conducted. The four classes of compounds inspected were hydrocarbons, fatty acids, ketones, and polar compounds. On the basis of molecular distributions and abundances, the extractable constituents appear to be largely anthropogenic. This is attributed to the dominance of petroleum residues on street surfaces and to their removal during the storm. The bound fraction comprises mainly microbial and higher plant debris derived from the original structural matrices of the source material or present in association with humic/fulvic acids and mineral phases.

Introduction

Urban storm drainage is one means by which natural terrigenous and anthropogenic organic matter is transported from land to the ocean. Whereas some efforts have been made to characterize stormwater-borne hydrocarbons (*1–3*), no details have yet been reported for other molecular species which may constitute up to 40% of the solvent-extractable organics (4). The identification and quantitative assessment of runoff-transported organic matter in nearshore marine sediments has not been possible owing to a lack of data. Consequently, it is unclear whether a threat is posed to local marine life by these inputs. Although the ability to completely control pollution caused by urban runoff is out of reach, a comparison of its chemical properties with controllable inputs such as municipal/industrial waste disposal and chemical dumping is not only important but attainable. This study, performed in Southern California, attempts to provide new information toward this end.

A comprehensive analysis was undertaken on solvent-extractable and bound organic compounds isolated from waters of the Los Angeles River during a storm sequence in the fall of 1978. Our objectives were to characterize the major components, examine specific molecular distributional features, assess the approximate anthropogenic contribution to the overall input, and search for marker compounds to be used in source identification.

Experimental Section

Samples of Los Angeles River storm runoff were collected at 11 intervals during a storm event on November 21, 1978 (4). Before extraction, the samples were spiked with two recovery standards: triisopropylbenzene (TIB) and *n*-nonadecanoic acid (NDA). Three basic sample types were prepared: (1)

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unfiltered samples, extracted directly without physical or chemical pretreatment, (2) filtered samples, i.e., runoff samples filtered through Whatman GF/A glass-fiber filters after which the filtrates were extracted, and (3) particulate, isolated by gravitational settling. Details of the sampling, the extraction, and the chromatographic separation of organic compounds into various classes are described in the preceding report (4).

Briefly, the $CHCl_3$-extractable organics from filtered and unfiltered samples were separated into four fractions for molecular analysis: (1) total hydrocarbons (THC), (2) fatty acids (FA), (3) ketones (KET), and (4) polar compounds (PLR). The particulate were extracted exhaustively with $CHCl_3$ to remove extractable organics and then saponified (5) to isolate the bound constituents. After methylation of the fatty acids with BF_3–MeOH, the bound organics were separated into four fractions as previously described (4). Bound fractions are hereafter identified by the prefix "B" before the fraction acronym. For example, BTHC refers to bound total hydrocarbons, whereas ETHC refers to (solvent) extractable total hydrocarbons.

All fractions were examined by high-resolution glass capillary gas chromatography using Carlo Erba FTV 2150 and 2350 instruments equipped with split injectors of the Grob design (6) and flame ionization detectors. Capillary columns (15 m) wall-coated with either OV-101 or SE-54 (0.25-mm id.) were used for diagnostic and quantitative purposes, while a 30-m SE-54 column of the same specifications was used for gas-chromatographic/mass-spectrometric analysis. Total hydrocarbon, FA, and KET fractions were analyzed by splitless injection (6), temperature programming the column 40-260 iso ‘C at 4 °C/min. The PLR fraction was silylated by using BSA (*N*,*O*-bis(trimethylsilyl) acetamide) before injection (7). Analyses of the PLR fraction were performed in two ways: (1) direct injection of the sample in excess BSA at 150 ‘C with temperature programming to 260_{iso} ‘C at 4 °C/min and (2) transfer to 9:1 hexane/ethyl acetate under dry N_2 followed by injection at 90 “C with temperature programming as before. The former method was used for examination of the sterols, and the latter for intermediate molecular weight species.

Tentative compound identifications are based on gas-chromatographic retention times and/or by analyses on a Finnigan Model 4000 quadruple mass spectrometer interfaced with a Finnigan Model 9610 gas chromatography. Spectrometric data were processed with a Finnigan INCOS Model 2300 data system.

Quantitative results for THC and FA fractions were achieved by comparing samples with external standards. These standards contained compounds distributed over the molecular-weight range of interest and were run the same day as the samples. Repetitive extractions showed that the isola-

Table L General Characteristics of Total Hydrocarbon Fractions in Storm Runoff Samples

sampling time	THC,[a] mg/L	Σ*n*-alkanes, μg/L	UCM,[b] maxima	max *n*-alkane	mean OEP[c]	(Σ*n*-alkanes > *n*-C_{24})/THC[d]	Pr/*n*-C_{17}	Pr/Ph
			Unfiltered Samples					
1000	2.0	68	1750/2800	C_{17}	1.0	0.1	1.6	2.1
1100	6.2	110	2750/ 1700	C_{29}	1.7	0.7	1.3	2.6
1200	5.1	200	1750/2800	C_{17}	1.4	0.3	1.4	2.2
1300	4.0	110	280011750	C,*	1.2	0.5	1.4	2.2
1400	10	220	2600/ 1900	C_{29}	1.4	0.9	1.3	1.7
1450	19	620	2650/ 1550	C_{15}	1.3	0.5	1.2	3.9
1500	18	360	2600	C_{18}	1.2	0.5	0.8	1.5
1550	20	360	2800	C_{17}	1.2	0.5	0.7	1.5
1600	10	220	2550	C_{17}	1.2	0.6	0.7	1.4
1700	9.2	210	2550	C_{29}	1.4	0.7	0.8	1.6
1800	16	240	2700	C_{29}	1.4	0.7	0.6	1.4
			Filtered Samples					
1000	0.42	18	180012850	C_{18}	1.0	1.5	1.7	2.1
1100	0.38	12	275017750	C_{23}	1.0	1.3	1.2	1.8
1200	0.36	20	1750/2750	C,*	1.0	0.8.	1.0	1.6
1300	0.41	10	2800/1750	C_{18}	0.9	0.5	1.7	2.0
1400	0.50	9.2	2800	C_{23}	1.0	0.7	1.3	1.7
1450	0.37	23	23001 1650	C_{18}	1.2	1.0	1.0	2.7
1500	0.39	12	2600	C_{18}	1.0	0.8	0.8	1.6
1550	0.40	6.4	2800	C_{18}	1.0	0.3	0.8	1.4
1600	0.36	5.3	2550	C_{17}	1.1	0.5	0.6	1.5
1700	0.43	4.0	2500	C_{17}	1.1	0.4	0.7	1.5
1800	0.30	2.3	2600	C23	1.0	0.4	0.6	1.2
			Particulate[e]					
1000	0.08	0.29	2250	C_{23}	1.4	0.1	1.8	1.2
1200	0.06	0.03	*f*	C_{23}	1.0	<0.1	0.8	1.2
1450	0.26	9.9	2300	C23	1.2	1.6	0.5	1.8
1500	0.28	2.7	2350	C_{23}	1.3	0.4	0.4	1.3
1700	0.68	8.4	2600	C_{29}	1.4	1.2	0.9	1.3

[a] Total hydrocarbons. measured gravimetrically. [b] Maxima of the unresolved complex maxima given in Kovats indexes; if bimodal, numerator refers to index of the dominant mode. [c] Mean OEP is average of all running OEP values (8). [d] Values are given as percentages. [e] "Bound" hydrocarbons in particulates (BTHC). [f] No data obtained because of insufficient samples.

tion scheme used here was effective in removing 95+% of the extractable organic material. Because we were interested primarily in qualitative features, no attempt was made to correct values for either extraction or recovery efficiencies, the latter of which were found to be 96% for NDA and 68% for TIB.

Results

Hydrocarbons. Table I summarizes general characteristics of the hydrocarbons in unfiltered and filtered samples and for bound hydrocarbons *in* particulate. All samples exhibited a broad envelope of unresolved components ranging approximately from n-C$_{13}$ to n-C$_{36}$+. Resolved components surmounting this envelope constituted, on the average, less than 17% of the total integrated area. The hydrocarbon distributions are characteristically of two types (Figure 1). Unfiltered and filtered samples collected up to, and including, 1450 hours (Figure 1A) had bimodally distributed, unresolved complex mixtures (UCM) with maxima occurring at n-C$_{17-19}$ and n-C$_{26-28}$. After 1450 hours, a unimodal UCM with a maximum in the range of n-C$_{23-28}$ was observed (Figure 1B). Bound hydrocarbons, examined at several sampling times (e.g., Figure 1C) had highly symmetrical, unimodal UCM'S with maxima at n-C$_{22-26}$.

When normal alkane distributions of unfiltered samples are plotted against time during progress of the storm, several features emerge (Figure 2). First, the levels of the total normal hydrocarbons (Σn-alkanes) are highly variable and correspond roughly to fluctuations in the total hydrocarbon burden (cf. Table I). These variations do not show strong correlations with gross storm parameters such as flow or suspended solids (*4*). Second. the normal alkanes in the range of n-C$_{13-24}$ maximize at n-C$_{17-18}$ and demonstrate a smooth distribution as evidenced by values of odd-even predominance, OEP (8), near unity. Finally, excluding samples taken at 1000 and 1200 hours, n-alkanes greater than n-C$_{24}$ show strong odd-even predominance (OEP >1) and maximize at n-C$_{29}$. The distribution of normal hydrocarbons in filtered samples is similar to that in unfiltered samples; however, the mean OEP values are consistently lower (Table I). Also, with the exception of

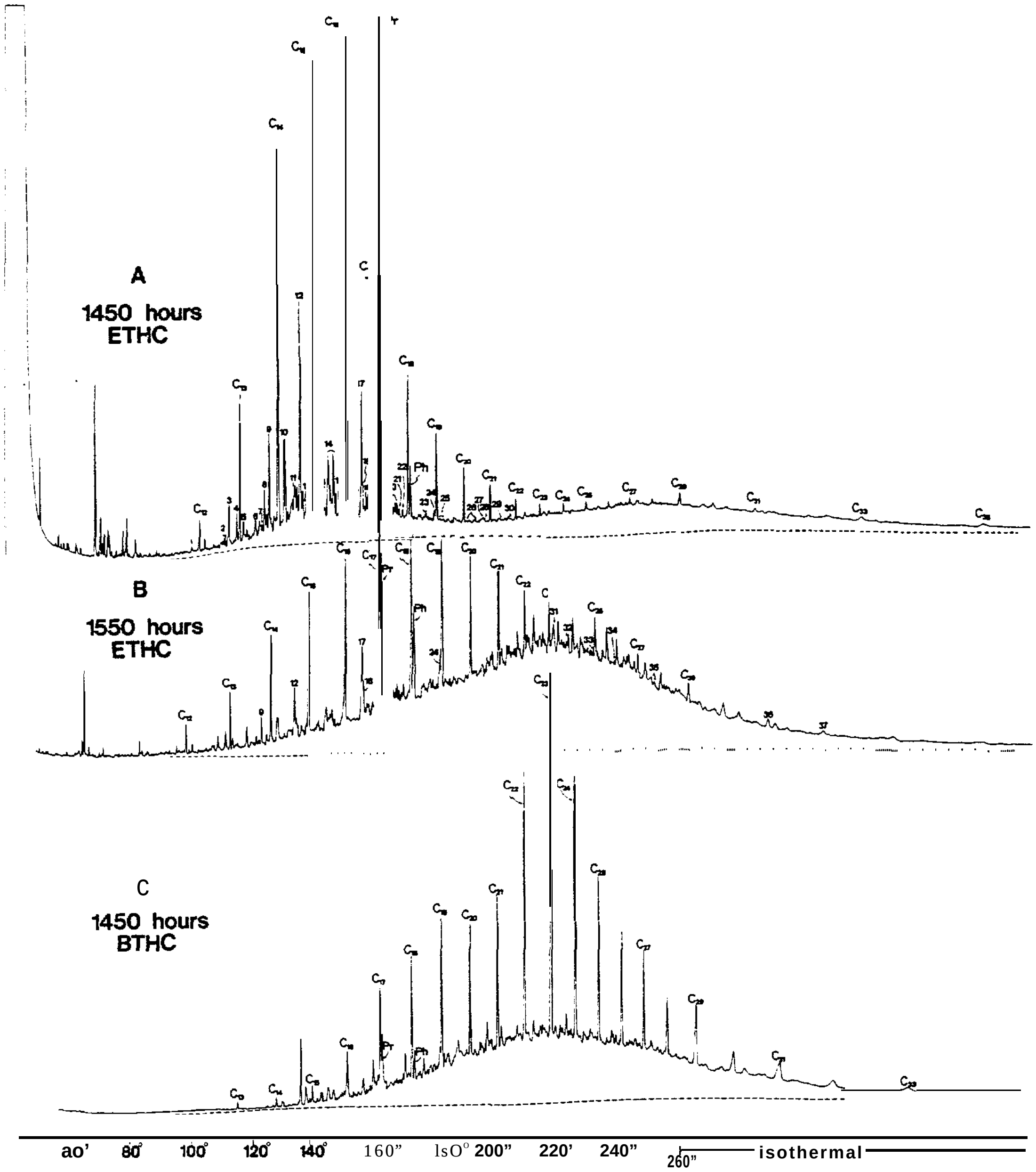

Figure 1. Gas chromatograms of total hydrocarbon fractions in storm runoff (A) 1450 hours (unfiltered sample); (B) 1550 hours (unfiltered sample); (C) 1450 hours (particulate). Peak identities are listed in Table II.

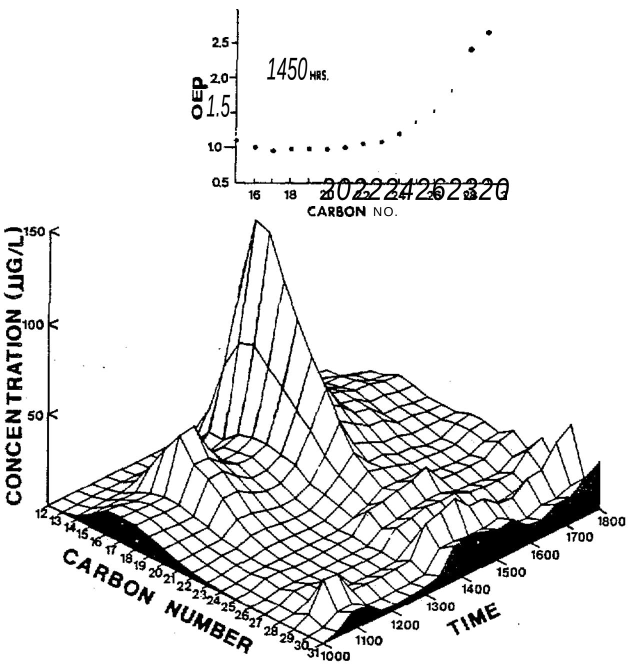

Figure 2. Distribution for normal hydrocarbons in unfiltered samples of storm runoff during the course of the storm along with running odd–even predominance values for the sample taken at 1450 hours.

the sample taken at 1000 hours, filtered samples contain reduced amounts of high molecular weight n-alkanes (relative to total n-alkanes; cf. Figure 3).

Bound hydrocarbons represent only a small fraction (<8%) of the total hydrocarbon burden (Table I). Normal alkane distributions for the BTHC are bi- or trimodal with maxima at n-C$_{17\sim18}$, n-C$_{23}$, and n-C$_{29\sim31}$ (Figure 3), and, in three of the five samples examined, the dominant mode is centered at n-C$_{23}$. OEP values for bound n-alkanes *are* not significantly different from those of the extractable hydrocarbons (Table I). Bound hydrocarbons in the range of n-C$_{13-21}$ were relatively depleted in comparison with their extractable-hydrocarbon counterparts (Figures 1C and 3), but the >n-C$_{24}$ hydrocarbons showed an enrichment.

Besides the normal alkanes, an assortment of branched, unsaturated, and cyclic compounds were identified (Figure 1A–C, Table II). Among the branched species, a homologous series of isoprenoids, C$_{14-21}$ (excluding C$_{17}$), were prominent. Also, with the exception of the C$_{15}$ homologue, C$_{13-19}$ isoalkanes were tentatively identified. Olefins were found in minor abundance; however, a number of polynuclear aromatic hydrocarbons were identified in both ETHC and BTHC fractions, including several homologous series. Among these were naphthalene plus C$_{1-5}$ homologies, biphenyl plus C$_{1-4}$, and phenanthrene/anthracene plus C$_{1-2}$ homologies. Fluoranthene, pyrene, chrysene, xanthene, and benzopyrene were also tentatively identified. No attempt was made to refine the separation of aromatic compounds; therefore, the present list is undoubtedly incomplete. As noted previously (4) aromatic compounds were enriched in filtered samples relative to unfiltered samples. Benzotbiophene and dibenzothiophene (plus alkylated homologies), found abundantly in Philadelphia storm waters (2), were detected only at trace levels here.

A series of alkyl cyclohexanes with side chains ranging in length from C$_8$ to C$_{15}$ (ETHC) "and from C$_{11}$ to C$_{18}$ (BTHC) were identified as major components. Other cyclic compounds included multiple homologous series of steranes, diterpanes, and triterpanes. The steranes found in all samples were complex; however, no sterenes were detected. Among the prominent constituents were the C$_{27-29}$ 5α-steranes with lesser amounts of methyl steranes (C$_{28-30}$). Extended tricyclic diterpanes (C$_{20-29}$) were also verified, where homologies from C$_{20}$ to C$_{24}$ have the inferred structure I (Figure 4), and those from C$_{26}$ to C$_{29}$ exist as diasteromeric pairs due to a methyl branch in the side chain.

Triterpanes were dominated by the 17a(H) -hopane series; neither triterpenes nor the 17β(H) compounds were found. The 17α(H) series consists of 17a(H) -trisnorhopane (II, R = H), 17a(H) -norhopane (II, R = C$_2$H$_5$), 17α(H)-hopane (II, R = C$_3$H$_7$), and an extended hopane series present as resolvable diastereomeric pairs in near 1:1 abundance, (22R, 22S) ranging from C$_{31}$ to C$_{35}$ (III). A C$_{28}$ triterpane identified as 17α(H),18α(H),21β(H)-28,30-bisnorhopane was also found (IV).

Fatty Acids. In general, the extractable normal fatty acids were bimodally distributed with maxima at 18:0 and 24:0 or 26:0 (Table III). Strong even-odd carbon-number predominance was observed in all cases. Palmitic acid (16:0) was the dominant species; however, the order of importance among the other major components (18:1, 180, and 16:1) was highly variable. Branched fatty acids including iso-14:0–17:0, anteiso-15:0, -17:0,-190, and one isoprenoid, 4,8,12 -trimethyltridecanoic acid, were detected in EFA fractions. Dehydroabietic acid (V) was found only in minor amounts. Various phthalates and adipates observed in all samples were present only in small quantities in procedural blanks. No triterpenoidal acids were detected.

On the basis of gravimetric data, the bound fatty acids constituted from 23 to 50% of the total acids. This amount is similar to that found by Barrington et al. (9) and Cranwell (*10*), who studied both marine and freshwater sediments, but is lower than that observed for Mississippi River waters (11). The general distribution features of bound and extractable fatty acids are similar to each other. No systematic differences in 16:1/16.0 or 181/18:0 ratios are apparent, but measurable differences include the 16:0/18:0 ratio (Table III), which is invariably higher for bound fatty acids, the ratio of even to odd carbon n-alkanoic acids, which is lower for the BFA fraction, and the percent of singly branched (i.e., iso and anteiso) acids which is 4-8 times higher in the bound fraction than for the corresponding extractable acids (cf. Table IV). The only isoprenoid identified in BFA fractions was 5,9,13 -trimethyltetradecanoic acid. Diterpenoidal and triterpenoidal acids were not detected.

Ketones. The ketone fractions were composed of relatively simple mixtures of compounds. In EKET fractions, a bimodal series of n-alkan-2-ones ranging from C$_{12}$ to C$_{27}$, maximizing at C$_{17}$ and C$_{25}$ and having a mean OEP of 1.3, was found only in trace amounts. The predominant compound was the isoprenoid 6,10,14 -trimethylpentadecan-2 -one; two isomers of phytenic acid γ-lactones were also found in abundance (structure VI).

A number of ketoaromatics including diphenyhnethanone, fluorenone, anthracenone, phenanthrenone, anthracenedione, phenanthrenedione (plus a C$_1$ homologue), and xanthenone were tentatively identified. Two ketosteroids were also found in minor amounts: cholesta-3,5-diene-7 -one and a C$_2$H$_5$ homologue (structure VII, strong peak at *m/z* 174).

The BKET fractions also contained a bimodal n-alkan-2-one series extending from C$_{10}$ to C$_{29}$ with a mean OEP value of 4.9, and maxima at C$_{17}$ and C$_{25}$. Again, the dominant ketone was the C$_1$s isoprenoid; however, only trace amounts of as yet unidentified ketoaromatics were detected, and these did not elute in the same regions as aromatics found in EKET fractions. In addition, the γ-lactone isomers of phytenic acid, found abundantly in the EKET fractions, were completely absent. Ketosteroids in the BKET fraction included a series of C$_{27-29}$ homologues of cholesta-3,5-dien-7 -one structure and C$_{28,29}$ triene homologue compounds (VII). Finally, a series of

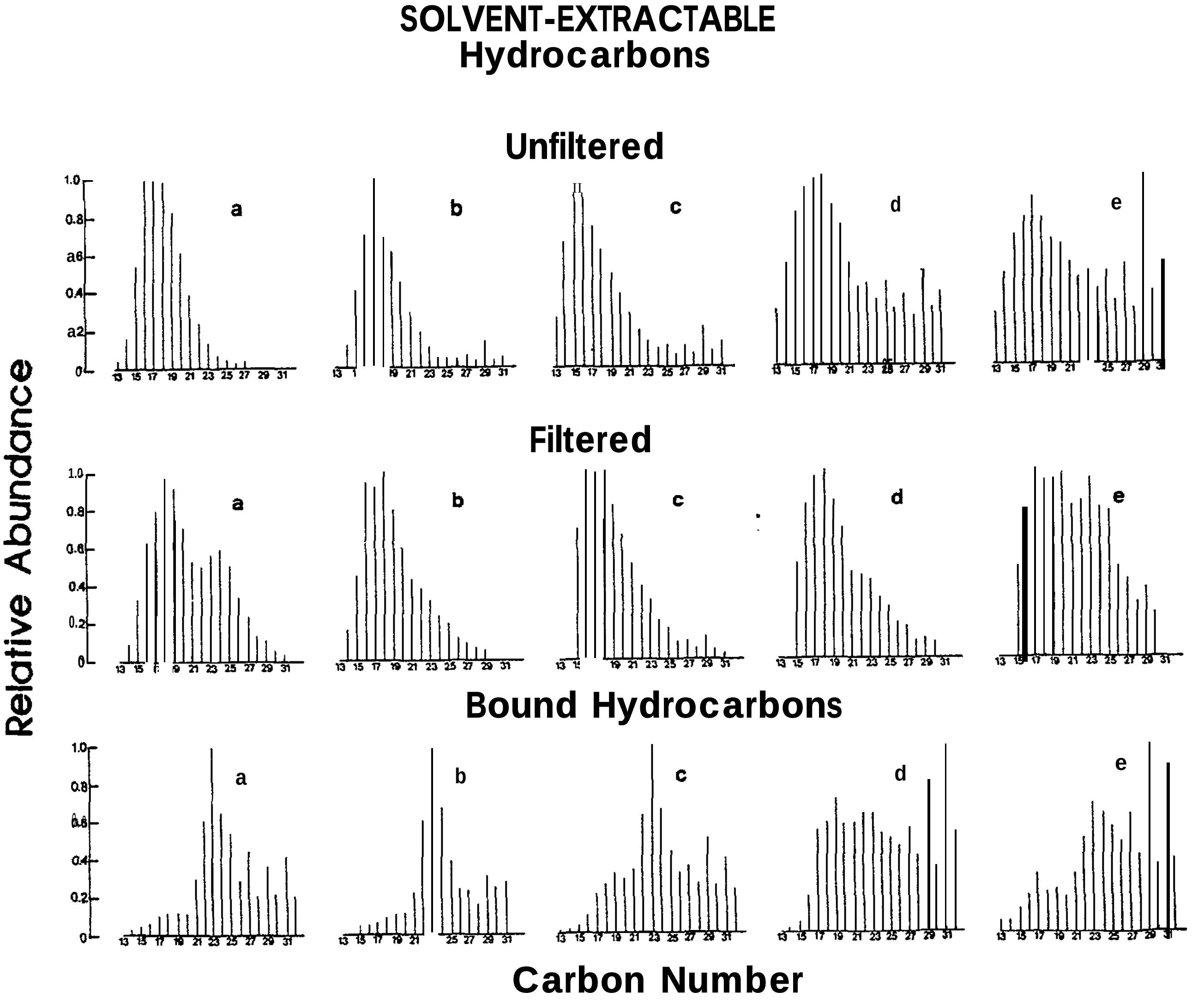

Figure 3. Normal alkane distribution plots for selected unfiltered, filtered, and particulate (bound) samples of storm runoff (a) 1000, (b) 1200, (c) 1450, (d) 1500, and (e) 1700 hours. Concentrations are normalized to that of most abundant *n*-alkane.

methoxy steroids (C_{27-29}, structure VIII) coeluted with the ketone band. These were identified by comparison with mass spectra of Idler et al. (*12*). The parent compound was 3-methoxycholesta-5-ene; lesser amounts of C_1- and C_2-substituted 3-methoxycholesta-5,22-diene homologies were also found. In the case of both keto- and methoxysteroids, the order of predominance was $C_{29} > C_{27} > C_{28}$ (steroid skeleton only).

Polar Compounds. The polar fraction representa a rather complex assemblage of molecular types. Gas chromatograms of the derivatized EPLR and BPLR fractions (1450 hours) show that the majority of the polar compounds are incorporated in a broad UCM extending from $<C_{14}$ to $C_{28}+$ (*n*-alkanols). In the EPLR fraction, the *n*-alkanol series is bimodal with maxima at C_{16} and C_{26} (Table V). Very minor amounts of α- and β-hydroxy acids were found, and α,ω-dicarboxylic acids, ω-hydroxy acids, and triterpenoidal alcohols were not detected. Conspicuous by their absence also were phytol and dihydrophytol. Authentic standards were used to verify that these isoprenoidal alcohols could be resolved from *n*-octadecanol and were not coeluting. Sterols identified in EPLR fractions included cholesterol, campesterol, stigmasterol, and β-sitosterol; stanols included coprostanol (structure 1X), epicoprostanol (structure X), and cholestanol (structure XI).

The BPLR fractions represent from 7 to 25% of the total recoverable polar compounds based on gravimetric results. Greater numbers of resolvable components in this fraction were identified chromatographically (Figure 5), including several homologous series such as the *n*-alkanols, α- and β-hydroxy acids, ω-hydroxy acids, α,ω-dicarboxylic acids, and sterols (Table V). The *n*-alkanols are bimodally distributed with maxima at C_{16} and C_{28}. The α- and β-hydroxy acids are distributed somewhat irregularly. Because α and β isomers coelute, separate distributions cannot be accurately determined. However, mass-spectral differences (*13*) allow one to estimate the respective amounts of these isomers in any given peak (Table II). In the present case, the α isomer predominates for compounds $>C_{20}$. In contrast, branched species, tentatively identified aa iso and anteiso C_{15} and C_{17} compounds, are principally in the form of the β isomer; the remaining members of the series have various isomeric compositions. The major constituents are C_{12}, C_{14}, "iso-C_{15}", C_{16}, C_{18}, and C_{24}.

The ω-hydroxy acids detected in BPLR samples are C_{20-26} even-carbon homologies. Except for C_{20}, which was present in small amounts, their relative abundances are roughly equivalent (Table V).

The α,ω-dicarboxylic acids were found in the range of C_{9-26}; however, in some samples the C_{9-19} compounds were com-

Table IL Selected Compounds identified in Los Angeies River Stormwaters[a]

peak no.	compd	peak no.	compd
	Hydrocarbons (Figure 1)		
	branched		aromatics
2	2-methyldodecane (*iso*-C_{13})	1	naphthalene
3	2,6, 10-trimethylundecane (isopr-C_{14})	4	1-methylnaphthalene
8	2-methyltridecane (*iso*-C_{14})	5	2-methylnaphthalene
9	2,6, 10-trimethyldodecane (isopr-C_{15})	6	triisopropylbenzene (internal standard)
12	2,6, 10-trimethyltridecane (isopr-C_{16})	7	biphenyl
17	2,6, 10-trimethylpentadecane (isopr-C_{18})	10	C_2 naphthalenes
24	2,6,10, 14-tetramethylheptadecane (isopr-C_{21})	13	Cl biphenyls
	cyclics	14	C_3 naphthalenes
11	*n*-octylcyclohexane (C_{14})	15	C_2 biphenyls
18	*n*-decylcyclohexane (C_{16})	16	C_4 naphthalenes
20	*n*-undecylcyclohexane (C_{17})	19	C_5 naphthalenes
23	*n*-dodecylcyclohexane (C_{18})	21	C_3 biphenyls
28	*n*-tetradecylcyclohexane (C_{20})	22	phenanthrene or anthracene
30	*n*-pentadecylcyclohexane (C_{21})	25	C_1 phenanthrene/anthracenes
31	$C_{23}H_{42}$ extended diterpane (structure 1, R = C_6H_{13})	26	C_2 phenanthrene/anthracenes
32	$C_{24}H_{44}$ extended diterpane (structure i, R = C_7H_{15})	27	pyrene
33	$C_{25}H_{46}$ extended diterpane (structure 1, R = C_8H_{17})	29	fluoranthene
34	$C_{26}H_{48}$ extended diterpane (structure 1, R = C_9H_{20})		
35	$C_{28}H_{52}$ extended diterpane (structure 1, R = $C_{11}H_{23}$)		
36	17α(H),21β(H)-30-norhopane (structure Ii, R = C_2H_5)		
37	17α(H),21β(H)-hopane (structure II, R = C_3H_7)		
	Polar Compounds[b] (Figure 4)		
	hydroxy acids		α,ω-dicarboxylic acids
1	α/β-hydroxydecanoic acid (*n*-C_{10})[c]	1	α,ω-nonanedioic acid (*n*-C_9)[e]
3	α/β-hydroxyundecanoic acid (n-C_{11})	6	α,ω-undecanedioic acid (*n*-C_{11})[e]
4	β-hydroxydodecenoic acid ($C_{12:1}$)	17	α,ω-hexadecanedioic acid (*n*-C_{16})
5	α/β-hydroxydodecanoic acid (*n*-C_{12})	21	α,ω-octadecanedioic acid (*n*-C_{18})
7	β-hydroxytridecanoic acid (*n*-C_{13})	23	α,ω-nonadecanedioic acid (*n*-C_{19})
8	α/β-hydroxytetradecanoic acid (*n*-C_{14})	25	α,ω-eicosanedioic acid (*n*-C_{20})
9	β-hydroxypentadecanoic acid ("*iso*-C_{15}")	31	α,ω-docosanedioic acid (*n*-C_{22})
10	α/β-hydroxypentadecanoic acid ("*ai*-C_{15}")	34	α,ω-tricosanedioic acid (*n*-C_{23})
11	α/β-hydroxypentadecanoic acid (*n*-C_{15})	37	α,ω-tetracosanedioic acid (*n*-C_{24})
12	β-hydroxyhexadecanoic acid ("*iso*-C_{16}")[c]	42	α,ω-pentacosanedioic acid (*n*-C_{25})
13	α/β-hydroxyhexadecanoic acid (*n*-C_{16})	44	α,ω-hexacosanedioic acid (*n*-C_{26})
14	β-hydroxyheptadecanoic acid ("*iso*-C_{17}")[c]		sterols and others
15	β-hydroxyheptadecanoic acid ("*ai*-C_{17}")[c]	2	diethyl phthalate
16	α/β-hydroxyheptadecanoic acid (*n*-C_{17})	18	1,2,3-propanetrioic acid, 2-(acetyloxy)-, tributylester
19	α/β-hydroxyoctadecanoic acid (*n*-C_{18})		
20	α/β-hydroxynonadecanoic acid (*n*-C_{19})	39	5β-cholestan-3β-ol (coprostanol, structure IX)
22	α/β-hydroxyeicosanoic acid (*n*-C_{20})	41	cholesta-5-ene-3β-ol (cholesterol)
24	α-hydroxyheneicosanoic acid (*n*-C_{21})[d]	43	24-methylcholesta-5-ene-3β-ol (campesterol)
26	ω-hydroxyeicosanoic acid (*n*-C_{20})	46	24-ethylcholesta-5-ene-3β-ol (β-sitosterol)
27	α-hydroxydocosanoic acid (*n*-C_{22})[d]		
29	ω-hydroxyheneicosanoic acid (*n*-C_{21})		
30	α-hydroxytricosanoic acid (*n*-C_{23})		
32	ω-hydroxydocosanoic acid (*n*-C_{22})		
33	α-hydroxytetracosanoic acid (*n*-C_{24})[d]		
35	ω-hydroxytricosanoic acid (*n*-C_{23})		
36	α-hydroxypentacosanoic acid (*n*-C_{25})		
38	ω-hydroxytetracosanoic acid (*n*-C_{24})		
40	α-hydroxyhexacosanoic acid (*n*-C_{26})[d]		
45	ω-hydroxyhexacosanoic acid (*n*-C_{26})		

[a] Major components and significant constituents are listed; identifications based on mass-spectral interpretation. [b] Normal and branched hydroxy acids listed; "*iso*-" snd "*ai*-" identifications based upon relative retention times and mass-spectral data. [c] Small amount of α-hydroxy acid isomer present. [d] Small amount of β-hydroxy acid isomer present. [e] Trace amount coeluting with another peak.

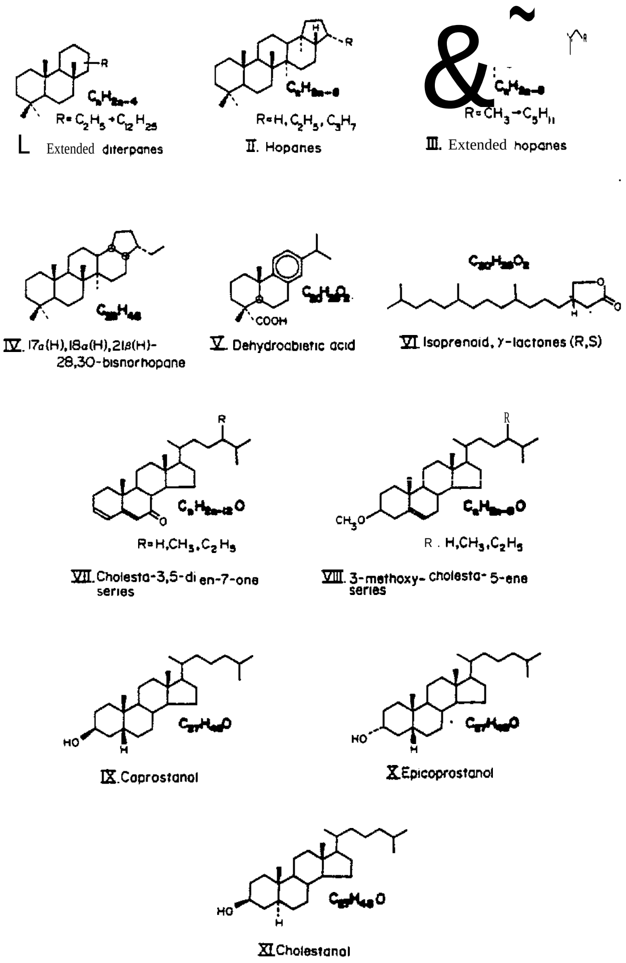

Figure 4. Structures **of organic compounds identified in storm runoff.**

pletely absent, whereas in others they constituted 99+’% of the total α,ω-diacids (Table V). Compounds greater than C_{18} showed strong even-odd predominance and maximized at C_{22}. Unsaturated species were not observed.

Bound sterols included cholesterol, campesterol, and β-sitosterol in the. order of predominance $C_{29} > C_{27} > C_{28}$. Cholestanol was the only stanol observed. As in the case of EPLR fractions, phytol, dihydrophytol, and triterpenoidal alcohols were not detected.

Discussion

Hydrocarbons. Hydrocarbons constitute roughly 60% of the total solvent-extractable organics in Los Angeles River stormwaters (4). The vast majority of these hydrocarbons (-94%) are associated with particulate matter and are primarily derived from petroleum residues. Molecular evidence presented here in support of this latter assertion includes the following: (1) a broad envelope of unresolved species extending from ≤n-C_{13} to n-C_{36}+ and comprising >80% of the total hydrocarbons (14),(2) a homologous series of normal alkanes (n-C_{13-24}) with OEP ≃ 1.0 (*14*), (3) abundant branched homologies including isoprenoids, iso- and anteisoalkanes, (*15, 16*), (4) multiple homologous series of alicyclic and polycyclic compounds such as the alkyl cyclohexanes, steranes, diterpanes, and triterpanes, and (5) a variety of parent polynuclear aromatic compounds in association with alkyl-substituted homologue assemblages.

In addition, the absence of 17β(H)-hopane isomers and the distribution of the 17a(H) -hopane series >C_{30} (i.e., 22R and 22S diastereomeric pairs occur in near 1:1 abundance) point to the ancient character of these hydrocarbons (17). An indication of the influence of locally produced/consumed petroleum was found in the molecule 17α(H),18α(H),21β(H)-28,30 -bisnorhopane, identified as a major terpenoid constituent of the Monterey shale off Santa Barbara, CA, and in California crude oils (*18*). More recently, it has been found in marine sediments and sediment-trap particulate collected in San Pedro Basin, located offshore from the mouth of the Los Angeles River (*19*, 20).

Biogenic hydrocarbons, in minor amounts, were evidenced by the high molecular weight n-alkanes (>n-C_{24}) with OEP values >1.0. These are presumably derived from bigher plant epicuticular waxes (*21*) and in no case exceed 1.6% of the total hydrocarbons (Table I). However, because bacteria have been known to display little or no carbon reference in metabolitally synthesized n-alkanes (22, *23*), we cannot exclude the possibility that minor amounts of bacterial hydrocarbons ‘might also be present in stormwater runoff. On the basis of the aforementioned assemblage of characteristics, we conclude that petroleum, not recent biogenic, hydrocarbons predominate.

A storm event not only removes but effectively homogenizes a diverse set of organic source materials (4). Distributions observed in the laboratory, then, must represent a composite of multiple inputs. Among the probable sources of hydrocarbons in the Los Angeles River basin are (1) vehicular exhaust particles, (2) lubricating oils, (3) atmospheric fallout (rain and dry, e.g., forest fires, combustion of fossil fuels, and eolian transport of bioorganics), (4) fuel oils, (5) spillage of crude and refined petroleum products during production, processing, or transportation, (6) leached/eroded pavement, (7) natural biogenic sources on land, (8) erosion of organic-bearing sedimentary rocks, and (9) others.

The difficulty in defining the composite arises from both the complexity of this input array and the possibility of postdepositional alterations (24, 25).

On the basis of GC, IR, and lead data, Zürcher et al. (*1*) suggested that automobile exhaust particulate were the primary contributors to hydrocarbon burdens in Swiss motorway runoff. These particulate contain hydrocarbons distributed essentially as a UCM from n-C_{22} to n-C_{34}+ and maximizing at n-C_{29} (26). We found a similar pattern in our samples, particularly during the later stages of the storm; however, n-alkanes, not generated to any great extent in combustion experiments (26), are quite abundant in stormwater samples. Dewaxed lubricating oils and transmission fluids consist essentially of high molecular weight UCMS with no detectable normal alkanes (27). Thus, the high molecular weight mode of the UCM which dominated the hydrocarbons in samples collected during later stages of the storm may have its origin in any combination of these materials.

The abundance of normal and isoalkanes and the relatively low UCM suggest that extensive biodegradation has not occurred, as it is generally agreed that microbial utilization of petroleum proceeds approximately in the following sequence normals, branched, cyclics, and aromatics (14, **24).** Normal and perhaps branched alkanes should have been greatly reduced or eliminated if intense microbial breakdown had taken place, leaving a strongly pronounced UCM. This type of distribution is common in petroleum-contaminated river and marine sediments (28–30) and biodegraded crude oils (31). The data also suggest that a minimum of physical weathering has occurred. Evaporative losses may be prevented by association of liquid hydrocarbons with particulate matter (32) or microencapsulation on/in pavement surfaces (e.g., solution of crankcase drippings into asphalt).

Attention should be drawn to a consistent change in the hydrocarbons that occurred during the storm. **Samples collected up to and including 1450 hours exhibited** bimodal

Table ill. Total Extractable Fatty Acids in Unfiltered Samples and Bound Fatty Acids in Particulate of Storm Runoff [a]

	1000		1200		1450				1700	
compd	EFA	BFA	EFA	BFA	EFA	BFA	EFA	❑FA	EFA	BFA
10:0	0.6		1.0		0.5	0.9		2.8	0.4	25
11:0	<0.1		0.1		0.2	0.5		0.9	0.1	0.1
120	6.6	0.5	3.4	0.6	3.4	17	6.9	30	2.0	16
13:0	<0.1	0.1	0.5	0.1	0.6	1.4	1.2	2.0	1.2	1.8
14:0	4.6	1.7	7.8	1.9	3.7	31	5.5	51	5.5	40
15:0	0.4	0.7	4.5	0.9	6.2	11	10	13	2.0	12
16:0	16	11	19	1.3	360	230	630	390	130	310
17:0	0.5	0.3	1.0	0.5	7.5	6.7	22	10	4.0	10
18:0	16	2.4	96	2.6	180	4.1	430	97	71	66
19:0	0.7	<0.1	1.3	0.1	2.6	0.8	4.6	1.4	1.9	3.0
20:0	0.6	0.2	1,4	0.3	10	4.3	14	7.0	7.2	13
21:0	0.1	0.1	0.4	0.1	1.6	0.9	1.9	1.3	1.5	2.8
22:0	0.6	0.4	1.6	0.5	7.1	6.0	9.0	9.3	8.9	22
23:0	0.2	0.1	0.3	0.1	1.6	1.4	2.4	2.0	2.1	5.8
24:0	0.6	0.6	1.6	0.6	6.2	5.9	8.6	9.2	10	24
25:0	0.1		0.3	0.1	1.4	0.9	1.6	1.6	1.7	3.5
26:0	0.2	0.4	1.2	0.3	3.4	2.8	4.1	4.2	7.6	12
27:0	<0.1		0.2	0.1	0.5	0.4	0.8	0.6	1.0	2.7
2ao	0.1	0.3	0.4	0.2	1.5	1.9	1.6	3.3	4.3	11
29:0					0.3		0.5		0.7	
30:0		0.1			0.8		0.8		2.6	
16:1	2.5	0.2	240	2.7	121	180	130	200	250	70
18:1	6.1	0.8	160	2.4	183	120	350	200	45	80
17:1[b]	<0.1		1.5	.0.1	1.4	2.2	3.3	1.3	6.6	4.3
19:1[b]			0.2	<0.1	0.8	1.0	3.5		1.4	5.5
i-13:0		<0,1	0.6	<0.1		0.8	0.7	1.2		1.6
ai-13:0		<0.1	0.8	<0.1		0.5	0.9	0.7		0.9
i-140		0.2	0.5	0.2	0.6	3.6	0.6	4.2	0.4	6.0
i-150	0.2	0.6	1.7	1.1	2.2	14	6.8	19	1.4	23
ai-15:0	0.2	0.5	2.6	1.0	2.2	13	5.0	19	1.4	21
i-16:0		0.2	1.6	0.1	1.6	1.0	3.2	1.1	0.4	1.4
i-17:0	0.2	0.1	0.4	0.2	0.3	2.4	0.9	3.4	1.2	5.4
ai-17:0	0.3	0.1	0.7	0.2	0.8	4.0	2.1	6.2	2.0	8.1
16:0/18:0	1.0	4.6	0,2	0.5	2.0	56	1.5	4.0	1.8	4.7

[a] Concentrations in μg/L. [b] Either cyclopropane or monounsaturated species.

Table IV. Percent Singly Branched and Unsaturated Acids and Even-to-Odd Ratios for Normal Fatty Acids in Extractable and Bound Fractions of Storm Runoff [a]

	% branched		O/. unsaturated		even/odd ratio [b]	
time	EFA	BFA	EFA	BFA	EFA	BFA
1000	1.6	8.4	15	5	22	14
1200	1.2	9.5	56	18	35	10
1450	0.8	5.6	38	43	27	14
1500	1.2	5.0	29	36	24	18
1700	1.2	8.3	53	20	15	13

[a] Based on gas-chromatographic analyses; EFA are for unfiltered samples. [b] Even/odd ratio = (Σeven carbon FAs)/(Σodd carbon FAs).

UCMS and pristane/n-C$_{17}$ ratios greater than unity (Table I). After 1450 hours, the UCMS were monomodal, and the pristane/n-C$_{17}$ ratios were less than 1.0. From the pristane/phytane and phytane/n-C$_{17}$ ratios, it is clear that pristane decreases with time (as opposed to n-C$_{17}$ increasing) and is related to the low molecular weight hump found in samples collected during the early phase of the storm. Furthermore, the n-alkane distribution plota (Figures 2 and 3) indicate that, in later stages of the storm, the lower molecular weight alkanes ($<n$-C$_{„}$) decrease in relative abundance. Vapor-pressure and volubility data demonstrate that branched/cyclic compounds are more susceptible to loss by evaporation and water washing than normal alkanes of the same carbon number (33). In addition, vapor pressure and volubility both decline with increasing molecular weight. Thus, samples collected after 1450 hours, probably represent partially weathered, older residues, whereas earlier samples were more recently deposited and, thus, are relatively unweathered.

Other subtle, but significant, physiochemical effects were observed during the storm. For example, the lower mean OEPS for n-alkanes of filtered samples are probably due to the attenuation of plant wax hydrocarbons (which contribute most to the odd-even predominance) because of their low solubilities. The selective partitioning of aromatics in fiitered samples (4) is a due to their greater molecular solubilities (33, 34).

Table V. Relative Abundances of Homologous Compound Series in Solvent-Extractable and Bound Separates of PLR Fractions (1450 hours) [a]

	n-alkanols		α/β-hydroxy acids		ω-hydroxy acids		α,ω-dicarboxylic acids	
carbon no. [b]	extr	bound	extr	bound	estr	bound	extr	bound
9								[c]
11				1.6				tr
12			tr	24.6				
13				0.6				
14	6.6	7.8	17.3	14.8				
15	5.0	2.6		2.0				
16	21.1	36.7	59.4	11.2				99.3
17	3.0	2.0	23.3	1.1				
18	7.5	21.0		9.6				0.19
19	2.2			1.2				0.04
20	8.7	7.0		1.2		3.1		0.10
21	0.2	0.9		1.0				0.02
22	5.7	4.5		5.9		32.6		0.18
23	0.1	0.7		4.7				0.02
24	6.6	4.6		15.5		31.0		0.08
25	1.0	0.4		2.4				0.02
26	10.2	5.0		2.2		33.3		0.04
27	0.2							
28	9.0	5.9						
30	7.8	1.8						
32	4.9							

[a] Abundances (%) determined by integration of total ion current for peaks obtained in GC/MS analysis; values relative to total current of all species. [b] Carbon number of carbon skeleton (prior to esterification or trimethylsilylation). [c] Unknown (minor) amount due to coelution with other compound(s).

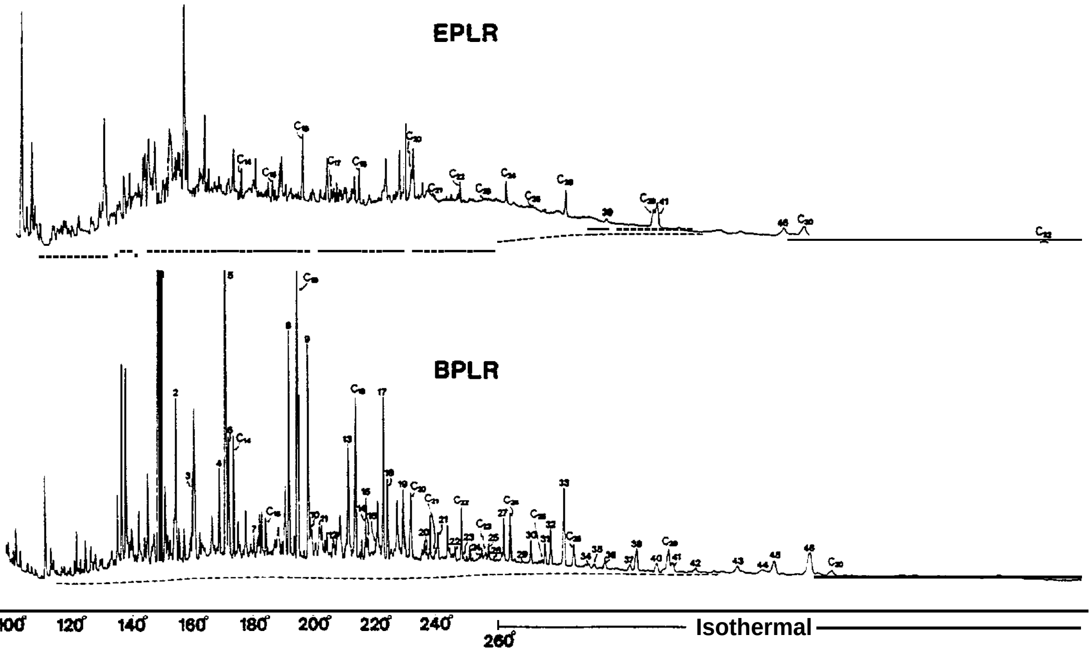

Figure 5. Gas chromatograms of derivatized extractable (unfiltered sample) and bound (particulate) polar compounde in stormwater runoff (1450 hours). Normal alkanols are designated on the figure: other peaks are identified in Table II.

The bound hydrocarbons represent only a small fraction (<8%) of the total recoverable hydrocarbons, an observation made previously for marine and river sediments (9, 28). The homologous series of normal, branched, and cyclic compounds and higher molecular weight *n*-alkanes suggest a mixed petrogenic/photogenic origin. However, the similarity of the *n*-alkane distribution plots (with a maximum at C_{23}) to those found by Cranwell (*10*) in lake sediments and Johnson and Calder (35) in a salt marsh environment may also indicate contributions from a microbial component. In studies of hydrocarbons in humic and fulvic acids, Schnitzer (36) and Khan and Schnitzer (37) have alluded to this possibility. Recent studies (38) have shown that degradation of microbial cellular components is reduced in soils by completing with humic acid-type phenolic polymers. Thus, stabilization of microbial residues may involve lipid incorporation into soil humus. The highly symmetrical UCMS centered roughly at n-C_{23} and the shift in n-alkane distributions to higher molecular weight (relative to ETHC distributions) could also reflect a size discrimination in the entrapment, retention, or microbial catabolism of hydrocarbons in the humic/fulvic cage structure (24, 37).

Fatty Acids. Fatty acids found in urban stormwaters are almost entirely biogenic. Petroleum, which is the dominant source of hydrocarbons in stormwaters, contains only minor amounts of long-chain carboxylic acids (39). It is, thus, an unlikely source of the fatty acids in runoff. The dominance of 160,180,181, and 161 compounds in EFA fractions suggests that hydrolyzed and glyceride-bound acids from cell walls of indigenous biota are the dominant source of acids in the range < 200 (20). Wax esters and free acids derived from higher plants are largely responsible for normal components above 20:0 (*21*). When summed, these high molecular weight acids constitute only a small fraction of the total fatty acids. The odd-carbon and iso and anteiso acids probably reflect a microbial component (40, 41), whereas dehydroabietic acid, found only in very small quantities in these samples, is a molecular marker of coniferous resins (42). This latter compound has also been preserved in sediment cores of southern California continental shelf basins (*19*). Introduction of dehydroabietic acid to the ocean via the Los Angeles River was probably mitigated, in this instance, by the rainfall pattern which was concentrated in nonforested, urban areas (4).

The bound fatty acids were a significant portion of the total recoverable (i.e., extractable plus bound) acids (25–50%). These compounds released by alkali hydrolysis can be lodged in several environments: (1) esterified in plant cutin (43, 44) and microbial cellular walls (45), (2) by linkage through ester and amide bonds to the surface and/or interior of humic/fulvic substances (9), and (3) physically entrapped in or adsorbed by, clay minerals and humic/fulvic substances (37, 46). In the present study, the enhanced occurrence of 16:0, iso, and anteiso acids and odd carbon number acids is suggestive of a large bacterial component (40, 47); however, it is impossible to say whether they are released from primary or secondary (38) sources. Higher plant wax residues (>20:0) are still present in BFA fractions, but in relatively small quantities; these are probably bound or adsorbed to humic/fulvic acids and clay minerals.

Ketones. The ketone fraction was only a minor constituent (4.3%) of the total solvent-extractable organics in stormwaters, and the bound ketones comprise from 12 to 24% of the total recoverable ketones. The only homologous series observed, the n-alkan-2-ones, are generally believed to be of terrestrial origin (48). They can be generated by β oxidation of fatty acids (followed by decarboxylation) or by direct oxidation of hydrocarbons (49). The patterns we observed do not match the n-alkane distributions. This is not surprising as these hydrocarbons have a variable distribution pattern and are dominated by petroleum, which, unlike plant wax residues, is not deposited primarily in soils. Furthermore, the petroleum hydrocarbons clearly have not undergone drastic biodegradation or weathering. The secondary maximum for the n-alkan-2-ones at C_{25} may originate from plant wax. The high relative abundance of these compounds in BKET fractions probably reflects the fact that humic/fulvic acids and n-alkan-2-ones are cogenetic, that is, contemporaneous products of soil chemistry.

Aromatic ketones in EKET fractions are almost certainly anthropogenic, although their exact source is unknown. Similar compounds were found by Benoit et al. (50) in Ottawa tap water; their origin was attributed to oxidation of polynuclear aromatic hydrocarbon precursors. This possibility seems unlikely in this instance because of the absence of alkyl-substituted homologue assemblages. Aromatic ketones were not found in BKET fractions probably because they do not originate in the natural soil environments where humic/fulvic materials form.

The isoprenoid γ-lactones (*51*) and C_{18} isoprenoid ketone (52, 53) were the only major known phytol degradation products found in runoff waters (excluding isoprenoid hydrocarbons). Phytol, dihydrophytol, and the isoprenoid acids (phytanic, pristanic, and phytenic) were not detected. The occurrence of the C_{18} isoprenoid in both EKET and BKET indicates that it probably is formed by microbial oxidation in soils where it may or may not become entrapped in humus. This compound has been found in marine sediments from Tanner Basin, CA (53), and in older sediments (54); however, its formation in subaerial environments has, until this time, not been reported. These findings indicate (1) that in situ diagenetic production of 6,10,14-trimethylpentadecan-2-one from chlorophyll under mild oxidative conditions as suggested by Ikan et al. (55) must include terrestrial as well as marine environments and (2) that phytol and dihydrophytol, if produced, are very rapidly transformed and/or removed.

The ketosteroid residues (cholesta-3,5-dien-7-one series) found in EKET and BKET fractions probably originate from autoxidation of sterol precursors (56). The pattern that we observed fits the sterol distribution in the PLR fraction, and, although we took every precaution to avoid oxidation of the isolated organics, we cannot rule out the possibility of technique-induced reactions. Whether they are artifacts or natural autooxidation products, it is surprising to find only these compounds among the many possible products known.

Methoxy steroids have, to our knowledge, not been reported in the literature as naturally occurring. In addition, microbial transformations leading from sterols to the methyl ethers are unknown (57). Thus, we suspect that these compounds may have been artificially produced. Confirmation of this hypothesis awaits further investigation.

Polar Compounds. At least two possibilities exist for the origin of the UCM, which dominates in PLR fractions (Figure 5). Petroleum contains polar heteroatomic materials commonly termed N-S–O compounds. Because of their polarity, these compounds elute much more slowly by our chromatographic technique than do true hydrocarbons. Hence, the UCM in polar fractions may simply be a procedural artifact consisting of the N-S-O fraction from urban petroleum residues. In the presence of oxygen, the natural decay processes result in oxidation and stepwise breakdown of organic molecules. Thus, the UCM fraction may also represent a highly complex mixture of natural and anthropogenic intermediate oxidation products.

Straight-chain alkanols are among the most prominent of the resolvable components in the EPLR fraction. These compounds exist as both free and esterified (to fatty acids) constituents of plant waxes, generally in the range of C_{24-34} showing even-odd predominance, and maximizing at C_{26} or C_{28} (*21*, 58). In rare instances they have been found as wax esters in microorganisms, but only compounds of carbon chain length less than C_{20} are known (59). We believe that the extractable high molecular weight n-alkanols in stormwaters are probably derived from higher plant waxes as free alcohols and esters; however, the origin of the lower series ($<C_{24}$) which maximizes at C_{16} may have multiple, and as yet undetermined, origins. The n-alkanol distributions in bound fractions were quite similar to those found in EPLR isolates. The higher molecular weight species which maximize at C_{28} represent plant residues, perhaps suberin (43), although their exact site of attachment in stormwater particulate is a matter of conjecture. The primary alcohols are generally absent from humic/fulvic acids (36) and are not known to exist in the

polyester matrix of cutin. Furthermore, they have not been reported as bound constituents of microbial membranes. Thus, we suspect that they maybe transported as plant detritus or by clay minerals. The bimodal character of the distribution suggesta a dual source, whereas the similarity of EPLR and BPLR patterns indicates a common derivation. In the presence of other indicators of chlorophyll degradation (e.g., C_{18} isoprenoid ketone and isoprenoid γ-lactones) the absence of phytol and dihydrophytol in EPLR fractions suggests that these are short-lived unstable compounds on land. Their absence in BPLR fractions signifies that chlorophyll breakdown with cleavage and transformation of the phytol side chain is extremely rapid.

The α- and β-hydroxy acids probably have diverse origins. Unlike their α-hydroxy analogues, normal and branched β-hydroxy acids less than C_{18} have been found in marine bacteria (60) and as microbial cell wall constituents (59). Their presence in" cutin and humic/fulvic materials, however, has not been reported. In studies of lake sediments, Eglinton et. al. (*13*) observed a suite of these acids ranging from C_{10} to C_{24}, and on the basis of similarities between fatty acid and α- and β-hydroxy acid distributions they suggested a microbially mediated pathway between these groups (i.e., oxidation of fatty acids). Our data suggest that compounds in the lower molecular weight range ($< C_{20}$), which are found in both EPLR and BPLR fractions, are derived from bacterial lipids and/or microbial cell walls. The origin and the binding site of the higher molecular weight hydroxy acids are unknown. If microbial oxidation of fatty acids from higher plants is the cause, oxidation of the α carbon appears to be favored; however, in this case, it is puzzling that these acids ($>C_{20}$) are apparently bound and not present as free acids or esters.

The ω-hydroxy acids, sometimes considered precursors for the production of the α,ω-dicarboxylic acids (*13*, 48), can exist in cutin primarily as the C_{16} or C_{18} species (43, 44) where they are usually found in association with 10,16 -dihydroxyhexadecanoic acid and other polyhydroxy and epoxide acids. In suberin, the corky layer of many plants, they are distributed in the range of C_{14-26}, but they have also been reported as ester polymers (four to six molecules) in epicuticular waxes (58). In these waxes, only homologies less than C_{20} in carbon chain length are found. Humic/fulvic sources of the ω-hydroxy acids are unknown, but they can be generated by diterminal oxidation of n-alkanes (*61*). The distribution that we observed in the BPLR fractions from storm runoff indicates that these compounds are probably derived from the polyester matrix of suberin.

The α,ω-dicarboxylic acids have been found in recent marine and lacustrine (60, 62) as well as older lake (13, 48) and ancient sediments (63). The diacids may be present in cutin in the range of C_{16-20} (44), in certain waxes (C_{16-26} (64)), and in suberin (C_{16-22} (43)), but generally they occur only as small molecules (primarily C_4) in humic/fulvic acids (36). Microbial oxidation of ω-hydroxy acids or terminal carbons of fatty acids (65) has, in some cases, been used to explain the diacid distributions although diterminal oxidation of n-alkanes is also considered a possibility (61). These compounds are not normal constituents of microbial cells; however, they have been found (66) as oxidation products of the insoluble cell debris of algae and bacteria (C_{6-18}).

We observed a distribution sometimes dominated by C_{16} with lesser amounts of higher homologies ranging up to C_{26}, but unsaturated species were not detected. In view of the reported low abundances of α,ω-C_{16} diacid in the polyester structure of cutin, we favor suberin or bacterial cell debris as the source of the C_{16-20} compounds. The distribution for compounds $>C_{19}$ resembles that found in a 5000-year-old lacustrine sediment by Eglinton et al. (*13*). They attributed the origin of diacids to ω oxidation of ω-hydroxy acids on the basis of similarities in compound distributions. Postdepositional oxidation of the ω-hydroxy acids is not indicated here because the distributions of these two groups are dissimilar (Table V). It seems more likely that the high molecular weight diacids in runoff arise through the activity of soil microbial factors on plant detritus such as higher plant wax esters.

Finally, sterols such as cholesterol, campesterol, stigmasterol, and β-sitosterol found in the EPLR and BPLR fractions are derived from higher plants (7), whereas coprostanol and epicoprostanol represent markers of mammalian fecal activity (67, 68). The absence of sterenes in the THC fractions indicates that these sterols have probably undergone little biodegradation.

Conclusions

Stormwaters carry complex materials of diverse origins; however, the two major sources of extractable organic substances transported to the ocean via stormwaters are anthropogenic and natural biogenic. The solvent-extractable organics are dominated by petroleum hydrocarbons (60%), whereas bound constituents are mostly biogenic. Fractionation of the extractable and bound components with subsequent molecular characterization has allowed us to speculate on the origins, alterations, and possible modes of introduction of various compound types in the Los Angeles River. Table VI summarizes these findings.

More than anything else, this study has pointed out the serious need for more detailed information regarding the distribution of compound classes in the natural (terrestrial) environment. In this context, the future use of molecular tracers in the marine environment will depend greatly on the ability to certify their origins.

Table VI. Summary of Molecular Markers Found in Storm Runoff Tabulated According to Their Presumed Sources

anthropogenic	recent biogenic
petroleum	microbial
1. n-alkanes, n-C_{13-24}	1. n-alkanes (?)
2. branched hydrocarbons	2. alkanoic acids
a. iso, anteiso	a. iso, anteiso series
b. isoprenoids	b. cyclopropane acids (?)
3. cyclic compounds	3. β-hydroxy acids
a. cyclohexane series	a. normal acids $< C_{20}$
b. steranes	b. iso, anteiso acids
c. diterpanes	4. α,ω-dicarboxylic acids (?)
d. triterpanes	
4. aromatic hydrocarbons	higher plants
5. unresolved complex mixture	1. n-alkanes $> n$-C_{24}
synthetics	2. n-alkanoic acids> 20:0
1. phthalates, adipates	3. dehydroabietic acid
2. aromatic ketones (?)	4. n-alkan-2-ones $> C_{25}$ (?)
	5. chlorophyll derivatives
	a. C_{18} isoprenoid ketone
	b. isoprenoid γ-lactones
	6. α,ω-dicarboxylic acids (?)
	7, ω-hydroxy acids
	8. n-alkanols $> C_{24}$
	9. phytosterols
	higher animals
	1. fecal sterols
	a. coprostanol
	b. epicoprostanol

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Literature Cited

(1) Zürcher, F.; Thüer, M.; Davis, J. A.`` Importance of Particulate Matteron the Load of Hydrocarbons of Motorway Runoff and Secondary Effluents"; in *Proceedings of the International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons,* Ontario, Canada, May 1978.
(2) MacKenzie, M. J.; Hunter, J. V. *Environ. Sci. Technol.* **1979,** *13,* 179.
(3) Hunter, J. V.; Sabatino, T.; Gomperte, R.; MacKenzie, M. J.J. *WaterPollut.Controlled. 1979,51,2129.*
(4) Eganhouse, R. P.; Kaplan, I. R. *Environ. Sci. Technol.*, preceding paper in this issue.
(5) Farrington, J. W.; Quinn, J. G. *Geochim. Cosmochim. Acta* **1971,** 35,735.
(6) Grob, *K.; Grob, K., Jr. J. High Resolut. Chromatogr. Chromatogr. Commun. 1978,57.*
(7) Gaskell, S. J. Ph.D. Thesis, University of Bristol, England, 1974.
(8) Scala, R. S.; Smith, J. E. *Geochim. Cosmochim. Acta* **1970,** *34,* 611.
(9) Farrington, J. W.; Henricks, S. M.; Anderson, R. *Geochim. Cosmochim.Acts 1977,41,289.*
(10) Cranwell, P. A. *Geochim. Cosmochim. Acta* **1978,** *42,* 1523.
(11) Hullett, D. A.; Eisenreich, S. J. *Anal. Chem.* 1979,51,1953.
(12) Idler, D. R.; Safe, L. M.; Safe, S. H. Steroids **1970,** *16,* 251.
(13) Eglinton, G.; Hunneman, D. H.; Douraghi-Zadeh, K. *Tetrahedron 1968,24, 5929.*
(14) Ehrhardt, M.; Blumer, M. *Environ. Pollut.* 1972,3,179.
(15) Johns, R. B.; Belsky, T.; McCarthy, E. D.; Burlingame, A. L.; Haug, P.; Schnoes, H. K.; Richter, W.; Calvin, M. *Geochim. Cosmochim.Acts 1966,30, 1191.*
(16) Bendoraitis, J. G.; Brown, B. L.; Hepner, L. S. *World Pet. Congr., Proc., 6th,* 19631963, Section 5, p 13.
(17) Dastillung, M.; Albrecht, P. Mar. *Pollut. Bull.* **1976,** *7,* 13.
(18) Seifert, W. K.; Moldowan, J. M.; Smith, G. W.; Whitehead, E. V. *Nature (London) 1978,271,436.*
(19) Sirnoneit, B. R. T.; Kaplan, I. R. *Mar. Environ. Res. 1980,3, 113.*
(20) Crisp, P. T.; Brenner, S.; Venkateeen, M. I.; Ruth, E.; Kaplan, I. R. *Geochim. Cosmochim. Acts 1979,43, 1791.*
(21) Eglinton, G.; Hamilton, R. J. *Science* **1967,156,1322.**
(22) Han, J.; Calvin, M. *Proc. Natl. Acad. Sci. U.S.A. 1969, 64, 436.*
(23) Jones, J. G. *J. Gen. Microbiol.* **1969,59, 145.**
(24) Reed, W. E. *Geochim. Cosmochim. Acts 1977,41, 237.*
(25) Clayton, J. L.; Swetland, P. J. *Geochim. Cosmochim. Acts 1978, 42,305.*
(26) Boyer, K. W.; Laitinen, H. A. *Environ. Sci. Technol. 1975,9, 457.*
(27) Dell'Acqua, R.; Egen, J. A.; Bush, B. *Environ. Sci. Technol.* 1975, 9, 38.
(28) Van Vleet, E. S.; Quinn, J. G. *Environ.* Sci. *Technol. 1977,11, 1086.*
(29) Farrington, J. W.; Tripp, B. W. *Geochim. Cosmochim. Acts 1977, 41, 1627.*
(30) Reed, W. E.; Kaplan, I. R. *J. Geochem. Explor.* 1977,7, 255.
(31) Seifert, W. K.; Moldowan, J. M. *Geochim. Cosmochim. Acts 1979,43,111.*
(32) Kilzer, L.; Scheunent, I.; Geyer, H.; Klein, W.; Korte, F. Chemosphere *1979,10, 75L*
(33) McAuliffe, C. *J. Phys. Chem. 1966,70, 1267.*
(34) Boylan, D. B.; Tripp, B. W. ***Nature (London)*** 1971,230,44.
(35) Johnson, R. W.; Calder, J. A. *Geochim. Cosmochim. Acts* **1973,** *37,* 1943.
(36) Schnitzer, M. In "Environmental Biogeochemistry"; Nriagu, J. O., Ed.; Arm Arbor Science Publishers: Ann Arbor, MI, 1976; Vol. 1, p 89.
(37) Khan, *S.* V.; Schnitzer, *M. Geochim. Cosmochim. Acts* **1972,36,** 745.
(3S) Nelson, D. W.; Martin, J. P.; Ervin, J. O. Soil Sci. Sot. *Am. J.* **1979,43, 84.**
(39) Seifert, W. K. *Prog. Chem. Org. Nat. Prod.* 1975,32, 1.
(40) Leo, R. F.; ***Parker, P. L. Science*** 1966,152,649.
(41) Boon, J. J.; deLeeuw, J. W.; Schenck, P. A. *Geochim. Cosmochim. Acts* 1975,39, 1559.
(42) Simoneit, B. R. T. *Geochim. Cosmochim. Acts 1977,41,463.*
(43) Kolattukudy, P. E. *Science* 1980,208,990.
(44) Eglinton, G.; Hunneman, D. H. *Phytochemistry* 1968,7,313.
(45) Shaw, N. *Ad.. Appl. Microbiol. 1974,17,63.*
(46) Meyers, P. A.; Quinn, J. G. *Geochim. Cosmochim. Acts* 1973, *37,* 1745.
(47) Simoneit, B. R. T. *Deep-Sea Res.* 1977,24, 813.
(48) Cranwell, P. A. *Chem. Geol.* 1977,20,205.
(49) Morrison, R. I. In "Organic Geochemistry Methods and Results"; Eglinton, G., Murphy, M. T. J., Eds.; Springer-Verlag New York, 1969; p 558.
(50) Benoit, F. M.; LeBel, G. L.; Williams, D. T. *Int. J. Environ. Anal. Chem. 1979,6, 277.*
(51) Brooks, P. W. Ph.D. Thesis, University of Bristol, England, 1974.
(52) DeLeeuw, J. W.; Correia, V. A.; Schenck, P. A. *Adv. Org. Geothem., Proc. Int. Meet., 6th, 19731974,993.*
(53) Ikan, R.; Baedecker, M. J.; Kaplan, I. R. *Nature (London) 1973, 244, 154.*
(54) Simoneit, B. R. T. *Chem. Oceanogr. (2nd cd.) 1975-19781978, 7,* 233.
(55) Ikan, R.; Baedecker, M. J.; Kaplan, L R. *Geochim. Cosmochim. Acts 1975,39, 187.*
(56) Smith, L. L.; Mathews, W. S.; Price, J. C.; Bachmann, R. C.; Reynolds, B. *J. Chromatogr. 1967,27, 187.*
(57) Charney, W.; Herzog, H. L. "Microbial Transformations of Steroids"; Academic Press: New York, 1967; p 14.
(58) Tulloch, A. P. In "Chemistry and Biochemistry of Natural Waxes"; Kolattukudy, P. E., Ed.; Elsevier: Ameterdarn, 1976; p 236.
(59) Albro, P. W. In" "Chemistry and Biochemistry of Natural Waxes"; Kolattukudy, P. E. Ed.; Elsevier: Amsterdam, 1976; p 419.
(60) Perry, G. J.; Volkman, J. K.; Johns, R. B. *Geochim. Cosmochim. Acts 1979,43, 1715.*
(61) Kester, A. S.; Foster, J. W. *J. Bacteriol. 1963,85,859.*
(62) Johns, R. B.; Odner, O. M. *Geochim. Cosmochim. Acts 1975,39, 129.*
(63) Haug, P.; Schnoee, H. K.; Burlingame, A. L. Science 1967,158, 772.
(64) Lamberton, J. A. *Aust. J. Chem.* 1961,14,.323.
(65) Kusonose, M.; Kusonose, E.; Coon, M. J. *J. Biol. Chem.* 1964. 239, 1374.
(66) Philp, R. P.; Calvin, M. *Nature (London) 1976,262,134.*
(67) Eneroth, P.; Helström, K.; Ryhage, R. *J. Lipid Res. 1964,5, 245.*
(68) Marker, R. E.; Wittbecker, E. L.; Wagner, R. B.; Turner, D. L. *J. Am. Chem. Sot. 1942,64,818.*

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Low $^{15}N/^{14}N$ in hydrothermal vent animals: ecological implications

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Low-trophic-level animal biomass from the Galapagos and 21 °N hydrothermal vents was found to have ^{15}N/ "N ratios which are lower than those previously reported for organic nitrogen [1–6], ammonium[1,2,5], and nitrate[1,2,7,8] in deep Pacific Ocean water. These nitrogen isotope ratios of vent animals are, however, near those of deep-oceanic N_2 (refs 1, 2, 7, 9) and resemble those of marine biota associated with N_2 fixation[2,10]. These observations suggest that organic nitrogen of nutritional importance to vent animals is initially synthesized within the vent environment and this synthesis may be preceded by N_2 fixation.

It has been argued''-" that local bacterial chemo-autotrophy is the primary source of biomass and energy for the dense invertebrate communities found at Pacific Ocean hydrothermal vents. Part of the evidence for vent primary production is the difference between the $^{13}C/^{12}C$ of vent animals and the $^{13}C/^{12}C$ of animals in the overlying pelagic environment[13,19]. It was reasoned that measurement of vent animal $^{15}N/^{14}N$ would provide further clues as to the base and the structure of these vent food webs.

A variety of animal tissues from hydrothermal vents were analysed including: trophosome and vestimentum from *Riftia pachyptila* Jones (a vestimentiferan worm), mantle tissue from *Calyptogena magnifica* Boss and Turner (vesicomyid clams), and crab muscle from *Bythograea thermydron* Williams (brachyuran crabs). These animals had been originally taken from either the Galápagos or the 21° N hydrothermal vent sites through the submersible Alvin, as indicated in Fig. 1. These tissues were dried at 60 'C and ground, and the nitrogen present in 5–10-mg replicate subsamples of these tissues was completely converted to N_2 using methods described by Stump and Frazer[20]. The "N/ "N relative to air (Fig. 1 legend) of these N_2 gas samples was determined by David Winter using a Varian MAT 250 ratio mass spectrometer.

Figure 1 shows vent animal $\delta^{15}N$ ranges from+ 1.8 to +9.8‰, with the values generally increasing as a function of the animal's assumed trophic level. This animal $\delta^{15}N$ increase with trophic status corroborates observations[2,4,10,21–25] that food chain/heterotrophic processes tend to increase ^{15}N relative abundance in the resultant animal biomass. Consequently, if vent animals were utilizing sedimentary organic nitrogen that had been produced and biologically processed on its journey through the more than 2 km of water overlying the vents, one would expect the $\delta^{15}N$ of vent animals: first, to exceed the $\delta^{15}N$ of plankton encountered in the surface layers of the Pacific Ocean, commonly 5–10‰ (refs 1, 2, 5, 10, 26), and second, to equal, if not exceed, the $\delta^{15}N$ of deep-ocean sedimentary organic nitrogen, 5-1 3‰ (refs 1-6). The relatively low $\delta^{15}N$ of assumed primary producer-consumer tissues from the vents, 1.8–4 .9‰ (Fig. 1), however, suggests that the organic nitrogen present in these tissues has undergone relatively little biological cycling and is, therefore, of local, rather than pelagic-sedimentary origin.

Additional y, the striking similarity between the $\delta^{15}N$ of low-trophic level vent animal tissues and the δ^{1} 'N of marine organisms associated with N_2 fixation (Fig. 1) suggests that the production of the organic nitrogen found in vent animals is preceded by N_2 fixation. Both the concentration and the low δ '⁵N of dissolved N_2 are relatively constant throughout the ocean[1,7,9], and little nitrogen isotopic fractionation is known to occur during fixation of N_2 and subsequent organic nitrogen synthesis[2,10,27–31]. The yet-to-be measured $\delta^{15}N$ of the NH_4^+ and the NO_3^- present32 in the vicinity of the vents may, however, prove these ions as likely as N_2 to be precursors to vent animal nitrogen. Large nitrogen isotope fractionation incurred during nitrate or ammonium assimilation and biomass production by some microbes and by some autotrophs in certain conditions[2,28,31,33–35] may also be factors causing vent organisms to be relatively depleted in ^{15}N.

Whatever the synthesis pathways and their inorganic starting compounds, the existing isotopic evidence indicates that the organic nitrogen as well as the organic carbon[13,19] found in vent animal biomass are largely produced by non-pelagic and non-photosynthetic processes.

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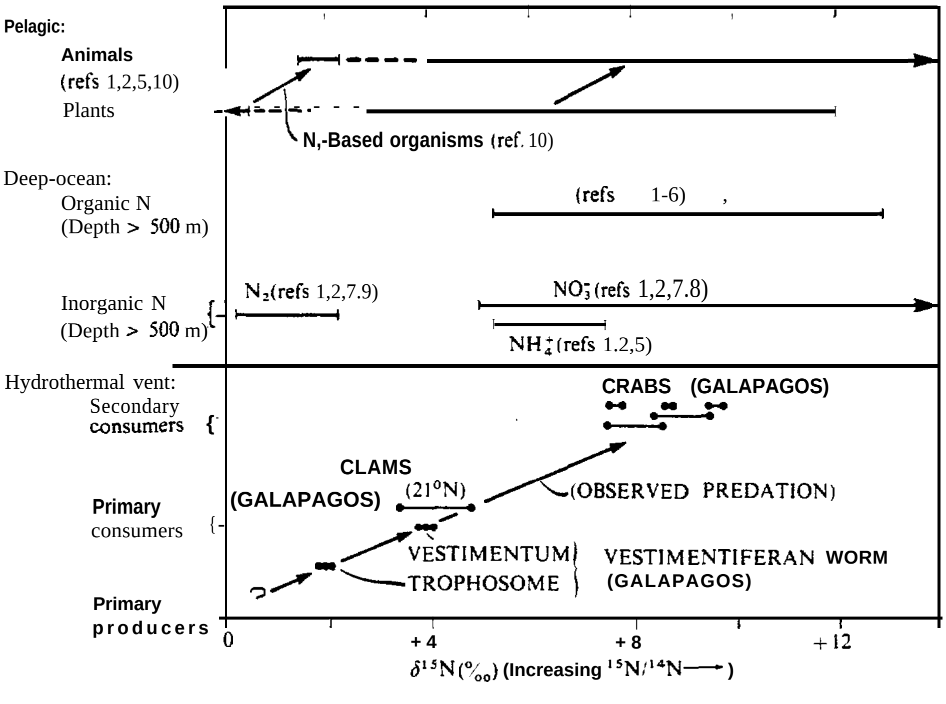

Fig, 1 The $\delta^{15}N$ of various Pacific Ocean nitrogen pools where:

$$\delta^{15}N = \{[\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{air}}] - 1\} \times 10^3\text{‰}$$

The vent sites, Galápagos (0.8° N, 86.1° W) and 21" N (20,9° N, 109.1° W), are located at ocean depths of 2.5 and 2.6 km, respectively. The assumed trophic levels and transfers (diagonal arrows) of hydrothermal vent animals/tissues are based on knowledge of related species, and on observations by Drs R. R. Hessler, G. N. Somero, H. Felbeck and J. J. Childress. The trophosome of the vestimerrtiferan worm is at least partly, if not largel y, composed of autotrophic tissues[16–18]. Replicate analyses of a single individual's tissue are connected by a horizontal line.

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1. Miyake, Y. & Wad a, E. *Rec. Oceanogr. Works Jap. 9, 137-152* (1967).
2. Wada, E., Kadonoga, T. & Matsuo, S. *Geochem. J. 9, 139-148 (1975).*
3. Peters, K. E.. Sweeney, R. E. & Kaplan, 1. R. *Limnol. Oceanogr.* 23, 598-604(197S 1.
4. Saino, T. & Hattori, A. *Nature* 283,752-754 (1980).
5. Sweeney, R. E.& Kaplan. L R. Mar. Chem.9,81-94 (1980).
6. Venkatesan, M. [.. Brenner, S., Ruth, E., Bonilla, J. & Kaplan, I. R. *Geochim. cosmochim. Acta* 44,789-802 (1980).
7. Cline, J, D. & Kaplan, 1. R. Mar. *Chem.* 3,271-299 (1975).

S. Li.. K. K. thesis, UCLA (1979).

9. Benson, B. B.& Parker. P. D. M. *Deep-Sea Res. 7,237-253 (1961).*
10. Wada, E. & Hattori, A. *Geochim. cosmochim. Acta 40,249-25* 1 *(1976).*
11. Corliss, J. B. *et al.* Science *203, 1073-1083 11979).*
12. Jannasch, H. W. & Wirsen, C. O. *Bioscience 29,592-598 (1979).*
13. Rau, G. H.& Hedges, J. L Science 203,648-649 (1979).
14. Karl, D. M., Wirsen, C. O. & Jannasch, H. W. Science 207, 1345-1347 (1980).
15. Hiatt, B. *Mosaic* 11, 15-21 [19801.
16. Cavanaugh, C., Gardiner, S. L., Jones, M. L., Jannasch, H. W. & Waterbury, J.B. Science (submitted).
17. Felbeck, H. Science (submitted).
18. Jones. M. L. Science (submitted).
19. Rau, G. H. Science (submitted).
20. Stump, R. K.& Frazer, J. W. *Nucl. Sci. Abstr.* 28, 746(1973).
21. Gaebler, O. H., Choitz, H. C., Vitti, T. G. & Vukmirovich, R. *Can. J. Biochem. Physiol. 41, 1089-1097 (1963).*
22. Gaebler, O. H., Vitti, T. G. & Vukmirovich, R. Can. *J. Biochem. 44, 1249-1257 (1966).*
23, Pang, P. C. & Nriagu, J. O. *Geochim. cosmochim. Acta* 41,811-814 (1977).
24. Steele, K. W. & Daniel, R. M. J. *Agric. Sci.* Carob. 90,7-9 (1978).
25. DeNiro, M. J. & Epstein, S. *Geochim. Cosmochim. Acta* (in the press).
26. Sweeney, R. E., Liu, K. *K. &* Kaplan, I.R. in *Stable Isotopes in rke Earth Sciences* (cd. Robinson, B. W.) 9-26 (DSIR, Wellington, 1978).
27. Hoering, T. C. & Ford, H. T. *J. Am. them. Sot.* **82,376-378 (1960).**
28. Delwiche, C. C.& Steyn, P. L. *Envir.* Sci. *Technol.* 4,929-935 (1970).
29. Delwiche, C. C.. Zinke, P. J., Johnson, C. M. & Virginia, R. H. *Bot.* Gaz. 140, SuppI. S65=S69(1,979)
30. Shearer, G.& Kohl, D. H. in *Recent Developments* in *Mass Spectrometry* in *Biochemistry and Medicine* Vol. 1 (cd. Frigerio, A.) 605-622 (Plenum, New York, 1978).
31. Kohl, D. H. & Shearer, G. *Plant Physiol.* *66,51-60* (1980).
32. Edmonds, J. M. *et al. Earth planet. Sci. Lett.* **46,** 19-36(1979).
33. Wada, E. & Hattori, A. *Geomicrobiol. J.* 1,85-101 (1978).
34. Kohl, D. J-1. & Shearer, G. in *Recent* Developments *in Mass Spectrometry* in *Biochemistry and Medicine Vol.* 1 (cd. Frigerio, A.) 623-640 (Plenum, New York, 1978).
35. Wada, E. in *Isotope Marine Chemistry* (eds Goldberg, E. D., Horibe, Y. & Saruhashi, K.) *375-398* (Uchida Rokakuho, Tokyo, 1980).

refer to granules within the trophosome cells having the dimensions of bacteria.

From the standpoint of the trophic structure of the vent community, the precise localization of the sulfur metabolism and Calvin-Benson cycle enzymes within the trophosome is of less importance than the fact that *R. pachyptila* may represent the first example of an autotrophic animal situated at the base of a food chain.

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References and Notes

1. K. Banse, *Prog. Oceanogr.* 2.53 (1964).
2. J. J. Childress, *Comp. Biochem. Physiol.* 50A. 787 (1975): K. L. Smith and R. R. Hess[cr. *Science* 184, *72 (1974): J. J.* Torres, B. W. Belman, J. J. Childress, *Deep-Sea Res.* 26A, 185 (1979).
3. P. Lonsdale, *Deep-Sea Res. 24.* 857 (1977); Galápagos Biology Expedition Participants. *Oceanus* 22.2 (1979).
4. J. B. Corliss *et* al., Science 203, 648 (1979}.
5. RISE Project Group: F. N. Spiess *et al., ibid.* 207, 1421 (1979).
6. H. W. Jannasch and C. O. Wirsen, *BioScience 29,592 (1979);* D. M. Karl. C. O. Wirsen, H. W. Jannasch, Science 207, 1345(1980).
7. J. M. Edmond et al.. *Earth Planet. Sci. Lett. 46.* 1, 1, 979).
8. M. L. Jones, Science 213, 333 (1981).
9. J. van der f-and and A. Nørrevang, Z. *Zool. Syst. Evolutionsforsch.*, Sonderheft 1, S6 (197 S): *K. Dan. Videnskr. Selsk. Biol. Skr.* 21 (No. 3), 1 (1977). Very recently a mussel has been found also lacking *a* digestive tract [R. G. B. Reid and F. R. Bernard, *Science 208. 609(1980)1.*
10. *M.* Caullery, *Bull. Sot. ZooL Fr. 39,350 (1914).*
11. A. J. Southward, E. C. Southward, T. Brattegard. T. Bakke. *J. Mar. Biol. Assoc. U.K. 59,* 133 (1979).
12. M. L. Jones, personal communication.
13. Rhodanese (E.C. 2.8. 1.1) was tested according to A. J. Smith and J. Lascelles [*J.* Gen. *Microbiol.* 42. 357(1966)1, and APS-reductase (adenosine phosphosulfate-reductase; E.C. 1.8.99.2) was tested according to H. D. Peck, Jr., T. E. Deacan, and J. T. Davidson [*Biochim. Biophys. Acts %, 429 (1%5)]. The* ATP-sulfurylase (E.C. 2.7.7.4) was tested in a continuous photometric test in which the ATP formed was used to phosphorylate glucose and the glucose 6-phosphate formed was oxidized with NADP$^+$ and glucose 6-phosphate dehydrogenase. The test mixture contained: triethanolamine-HCl buffer, 0.1 mole/liter. *p*H *7.3:* magnesium acetate. 2.5 mmole/liter; glucose, 25 mmole/liter; NADP$^+$. 0.5 mmole/liter; sodium pyrophosphate, 25 mmole/liter; adenosine 5′-phosphosulfate (obtained from Sigma Chemical), 0.5 mmole/liter; Ap$_5$A [*P*^{1}, *P*^{5}-di(adenosine-5′) -pentaphosphate, an inhibitor of aden ylate kinase] [G. E. Lienhard and I. I. Secemski. *J. Biol. Chem. 248. 1121 (]973)], 0.25* mmole/liter; hexokinase, 5 unit/ml; glucose-6-phosphate dehydrogenase 2.5 unit/ml in a final volume of 2 rrd. The test could be started with pyrophosphate, APS, or extract. In addition, controls were made by dividing the continuous test into two steps. the *first one* being at the level of glucose-6-phosphate. which was tested subsequently in the neutralized perchloric acid extract according to G. Lam? and G. Michal, in *Me thoden der enzymatischen Analyse*, H. U. Bergmeyer, Ed. (Verlag Chemie, Weinheim, 1974). vol. 2. p. 1283.
14. Specimens were frozen immediatel y after recovery: worm 1, in March 1979 at - 15°C and stored at – 15°C; worm 2, in December 1979 at -78°C and stored at - 80°C.
Is. Homogenization was in triethanolamine-HCl buffer. 0.1 mole/liter, *p*H 7.3, I: 4 (weight to volume). Trophosome was homogenized gently in a glass-Teflon Potter Elvehjem homogenizer with large gap; muscle tissue in a glass-glass homogenizer with conical rough contact area. The supernatant of a homogenate centrifuged for 10 minutes at 27000*g* was used as extract. Grinding trophosome tissue extensively with a motor-driven homogenizer (like the one used for muscle) did not increase the yield of enzymes compared to gentle homogenization.
16. Yellow Springs Instrument Co. The test mixture contained: triethanolamine-HCl buffer. 0.1 mole/liter, *p*H 7.3; magnesium acetate, 2.5 mmdz/liter: Na_2S, 10 mmole/liter. The reaction could be started with Na_2S or extract. After boiling the extract for 5 minutes in a water bath, the reaction velocity decreased significantly.
17. E. Latzko and M. Gibbs, *Plant Physiol.* 44, 295 (1969).
18. E. Racker, *Arch. Biochem. Biophys. 69. 300 (1957);* M. Wishnick and M. D. Lane, *Methods Enzymol. 23.571 (1971).*
19. *The* pyrophosphate used for this reaction could be provided by a reversed reaction of the inorganic pyrophosphatase [P. W. Robbins and F. Lipmann, *J. Biol. Chem.* .233, 686 (1958)].
20. E. N. Powell, M. A. Crenshaw, R. M. Rieger, *J. Exp. Mar. Biol. Ecol. 37.57 (1979): Mar. Ecol. Prog. Ser.* 2,169 (1980).
21. H. D. Peck. Jr., in *The Enzymes*, P. Boyer, Ed. (Academic Press, New York, 1974), vol. 10, p. *651:* J. Westley, *Adv. Enzymol. 39, 327 (1973):* R. M. Lyric and I. Suzuki. *Can. J. Biochem. 48,* 344 (1970).
22. P. D. Trudinger, *Adv. Microbiol.* 3, 111 (19691.
23. J. J. Childress, personal communication.
24. Also in the Pogonophora a "spongy tissue'" is found in the trunk comparable to the trophosome of the Vestimentifera [(8, 9); A. V. Ivanov, *Pogonophora*, D. B. Carlisle, Transl. and Ed. (Consultants Bureau. New York, 1963)].
25. G. H. Rau and J. I. Hedges, *Science* 203, 648 (1979); G. H. Rau, *ibid.* 213.338 (1981).
26. J. F. Siebenaller and G. N. Somero, personal communication.

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Hydrothermal Vent Clam and Tube Worm ^{13}C/^{12}C: Further Evidence of Nonphotosynthetic Food Sources

Abstract. *The stable carbon isotope ratios in clam mantle tissues taken from both Galápagos and 21°N hydrothermal vent sites were similar to the unusually low ratios of carbon-13 to carbon-12 previously reported for a Galápagos hydrothermal vent mussel. In marked contrast to these bivalves, vestimentiferan worm tissues from a Galápagos vent had isotope ratios that were higher than those of open ocean biota. These observations suggest that more than one nonpelagic and nonphotosynthetic carbon fixation pathway is of nutritional importance to vent animals, and that at least one of these pathways is common to two geographically separated vent* sites.

After dense animal communities were discovered near Pacific Ocean hydrothermal vents (*1*), on-site microbial chemosynthesis was implicated as the primary source of reduced carbon for these organisms. The locally large standing crop and apparent rapid growth (2) of some of these animals require a food base that is much more abundant than is normally available to deep-sea benthos. These circumstances, however, do not preclude the possibility that the relatively sparse food resource sedimenting from the ocean's euphotic zone is being physically concentrated or entrained by advective currents near the vents (3). Still, high rates of microbial carbon fixation can occur in vent waters (4), and this chemosynthetic primary production could conceivably be an important source of energy and biomass for higher trophic levels. Support for the concept that vent animals do not rely on imported, photosynthetically derived food sources was found in the striking dissimilarit y between the ^{13}C/^{12}C of a vent mytilid mussel and the ^{13}C/^{12}C of nonvent marine organisms (5). Further isotopic evidence for vent food web autochthony is presented in this report.

Portions of mantle tissue from whole, frozen vesicomyid clams, *Calyptogena magnifica* Boss and Turner, collected by the *Alvin* submarine from the Rose Garden site (Galápagos Rift) and from the 21°N site (East Pacific Rise), were obtained from Dr. George Somero, Scripps Institution of Oceanography. Also removed were samples of frozen vestimentum and trophosome of a vestimentiferan worm, *Riftia pachyptila* Jones, originally collected from Rose Garden. All of the above samples were dried for several days at 60°C and then ground or pulverized. A 50-mg portion of the dried, ground vestimentum was submerged in 8 percent HCl and the solution was then gently heated to dryness. Subsamples (5 to 10 mg) of all of the above tissues were then combusted and the resultant CO_2 was purified, collected, and isotonically analyzed by previously described methods (6). The ^{13}C/^{12}C of each sample is reported as δ^{13}C, the relative per mil difference between the ^{13}C/^{12}C of the sample and the ^{13}C/^{12}C of the PDB carbonate standard (7).

The δ^{13}C of clam mantle tissues from both Galápagos and 21°N vents are quite similar to the previously reported δ^{13}C of a Galápagos vent mussel (Table I). This earlier study *(5)* pointed out that such δ^{13}C values are lower than those of animals sampled from other marine envi-

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Table 1, The replicate $\delta^{13}C$ values of vesicomyid clam and vestimentiferan worm tissues taken from the hydrothermal vent sites indicated. For comparison, the $\delta^{13}C$ ranges of previously analyzed marine organisms are also listed,

Animal	Hydrothermal vent site	$\delta^{13}C$, per mil (±0.2 per roil)
Clam (mantle)	21°N (East Pacific Rise)	-32.6, -32.7
Clam (mantle)	Rose Garden (Galápagos)	-32.0, -32.1
Mussel (foot and mantle)*	Clambake I (Galápagos)	−32.7 to -33.6
Vestimentiferan worm	Rose Garden (Galápagos)	
Vestimentum (muscle)		-10.8, -[0.8, −11.0
Vestimentum (acid treated)		−10.9, −11.0
Trophosome		-10.9, -il.]
	Nonvent data	
Nonvent marine organisms	Temperate and tropical waters	-8 to -25

*Data from (5). †Data from (5, 8, 10, 11, 14, 17)

ronments. Pressure or depth effects apparently cannot explain the ^{13}C-depleted condition of these vent animals because the $\delta^{13}C$ of bathypelagic organisms and detritus, taken from depths comparable to the vents, are usually similar to the $\delta^{13}C$ of the organic material existing near" the ocean surface (8). Metabolic isotope fractionation effects, which would significantly lower a clam's or mussel's $\delta^{13}C$ below that of its food source, are unlikely in view of controlled invertebrate experimentation (9, *10*) and analyses of naturally occurring bivalve specimens (5, *10, 11*). It is therefore concluded that the consistently low $\delta^{13}C$ of vent bivalves results from the utilization of food sources whose derivation (and hence. stable carbon isotope ratio) is unlike that of the organic material found in the overlying ocean.

As to the nature of this isotopically different food source, chemoautotrophic bacteria are present in vent waters (4, *12*) and seem likely food items for filter feeding animals. A limited number of analyses suggest that some chemoautotrophic bacteria preferentially fix $^{12}CO_2$ to a greater extent than do photoautotrophs, thus producing biomass whose $\delta^{13}C$ can be lower than that of available inorganic 'carbon by 30 per mil or more (*13, 14*). It is therefore possible to explain the approximate 28 per mil difference between bivalve $\delta^{13}C$ and the $\delta^{13}C$ of vent water ΣCO_2, $\geq$ -4 per mil (*15*), as entirely due to carbon isotope fractionation incurred during chemosynthesis of organic matter and preservation of the resultant isotope abundances in higher trophic level biomass. Microbial fixation of carbon sources other than $C0_2$ (*16*), as well as carbon fixation driven by the oxidation of elements or compounds other than the most obvious one, hydrogen sulfide, may also merit consideration. At present, the carbon i sotope abundances produced by chemoautotrophs are in almost all cases unknown.

That more than one type of autotrophy exists at the vents is indicated by the relatively high $\delta^{13}C$ of *R. pachyptila* tissue (Table 1). By comparison with acidified worm tissues (Table 1), these elevated $\delta^{13}C$ values cannot be the result of ^{13}C-rich carbonate contamination. Although littoral animal $\delta^{13}C$ values less negative than -15 per mil are not uncommon {10, II, *17*), such values are interpreted as resulting from the utilization of near-shore C_4 plant material as a food source. The C_4 plants produce biomass whose S ^{13}C values typically range from –6 to -15 per mil (*18*). It is not evident from $\delta^{13}C$ values of open-ocean animals, plants, or detritus (8) that ^{13}C-enriched material produced by C_4 photoautotrophs is an important food source for pelagic organisms and, subsequently, deep-sea benthos. Therefore, possessing an internal autotrophic capability (*19*, 20) and evidently lacking a way of ingesting particulate food sources (*21*), vestimentiferan worms found at the Galápagos and other vent sites apparently rely on organic carbon produced (i) within their bodies and (ii) by pathways that fractionate carbon isotopes in a way different from those pathways supplying hydrothermal vent bivalves.

The presence in *R. pachyptila* of carbon isotope abundances resembling those of C_4 plants—in spite" of the apparent lack of a crucial C_4 enzyme in the worm's autotrophic trophosome (*20*)—presents an anomaly also recently found in the marine seagrass *Thalassia testudinum*. In this C_3 plant, $\delta^{13}C$ values also near -11 per mil are explained by Benedict *et al.* (22) as arising from a CO_2 limitation that occurs within the plant forcing the carboxylation of ribulose bisphosphate to be less isotopically selective in the use of $^{13}CO_2$ or $^{12}CO_2$. Consequently, unlike other C_3 autotrophs, relatively little isotopic fractionation is exhibited between the inorganic carbon available to this plant, -10 per roil, and the bulk organic carbon the plant produces, – 11 per mil. A limited internal supply of $C0_2$ relative to internal demand by carbon-fixing processes may then also explain the unexpectedly high $\delta^{13}C$ values observed in i?. *pachyptila*.

In any case, the unusual stable carbon isotope abundances found in Galápagos and 21°N hydrothermal vent animals indicate that their primary sources of organic carbon are unlike those commonly used by marine animals. On-site carbon fixation, at the Expense of chemical rather than light energy, is apparently the ultimate source of this isotonically distinctive animal biomass- Furthermore, the large isotopic dissimilarity between vestimentiferan worm and bivalve tissues suggests that at least two different, locally produced food sources are being utilized by vent organisms. Use of autochthonous sources of food is also borne out by recent measurements of ^{15}N (*23*) and ^{14}C (*24*) natural abundances in vent animals.

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References and Notea

1. J. B. Corliss and R. D. Ballard, *Natl. Geogr.* 1S2. 441 (1977); P. Lonsdale, *Nature (London) 281. .531 (1979):* RISE Project Group: F. N. Spiess *et al.*, *Science* 20)7, 1421 (1980):
2. K. K. Turekian. J. K. Cochran, Y. Nozaki, *Nature (London)* 208. 385 *(1979).*
3. P. Lonsdale, *Deep-Sea Res. 24.857 (1977):* J. T. Enright, W. A. Newman, R. R. Hessler. J. A. McGowan, *Nature (London) 2S9, 219 (1981).*
4. H. W. Jannasch and C. O. Wirsen, *BioScience* 29.592 (1979): D. M. Karl, C. O. Wirsen, H. W. Jannasch, *Science* 2117, .1345 (1980).
5. G. H. Gau and J. I. Hedges, *Science* 203.648 (1979).
6. Combustion and CO_2 isolation methods: R. K. Stump and J. W. Frazer, *Nucl. Sci. Abstr. 2S,* 746 (1973). Isotope analysis was done by D. Winter, UCLA, using a Varian MAT 250 ratio mass spectrometer.
7. $\delta^{13}C = \{[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB}] - 1\} \times 10^3$ per roil. PDB refers to belemnite from the Peedee Formation, South Carolina [H. Craig. *Geochim. Cosmochim. Acta* 12, 133 (1957)].
8. P. M. Williams and L. 1. Gordon. *Deep-.Sea Res.* 17, 19(1970); B. J. Eadie and L. M. Jeffrey, *Mar. Chem:* 1.200 (1973).
9. M. J. DeNiro and S. Epstein. *Geochim. Cosmochim. Acta 42, 495* (1978): J. A. Teeri and D. A. Schoeller, *Oecologia* 39.197 (1979).
10. E. B. Haines and C. L. Montague. *Ecology* 60, ! 48 (1979).
11. M. L. Keith, G. M. Anderson. R. Eichler, *Geochim. Cosmochim Acta 28.* 1757 (1964); P. L. Parker, ibid.. p. 1155; B. N. Smith and S. Epstein. *Plant Physiol.* 46.738 (1970): H. Erlenkeuser, *Naturwissenschaften 63.338 (1976);* E. B. Haines, *Estuarine Coastal Mar. Sri. 4.* 609 *(1976):* T. McConnaughey and C. P. McRoy, Mar. *Biol. 53, 263 (1979):* A. V. Botello, E. F. Mandelli, S. Macko, P. L. Parker, *Geochim. Cosmochim. Acta* 44, 557 (1980).
12. J. B. Corliss *et al.*. Science 203. 1073 (1979): Galápagos Biology' Expedition Participants. *Oceanus* 22.2 (1979).
13. E. T. Degens, R. R. L. Guillard, W. M. Sackett, J. A. Hellebust, *Deep-Sect Res. 15.1 (* 1968): G. Fuchs. R. Thauer, H. Ziegler. W. Sticler, *Arch. Microbiol.* 120.135 (1979).
14. E. T. Degens, in *Organic Geochemist?.* G. Eglinton and M. T. J. Murphy. Eds. (Springer-Verlag, New York. 1969). pp. 304-329.
15. H. Craig. J. A. Welhan, K. Kim. R. Poreda. J. E. Lupton, *Eos* 61.992 (1980).

16. E. Broda, *The Evolution of the Bioenergetic Processes* (Pergamon, New York, 1978); G. Gottschalk, *Bacterial Metabolism* (Springer-Verlag, New York, 1979).
1 P. L. Parker and J. A. Calder, in *Organic Matter in Natural Waters*, D. W. Hood, Ed. (Univ. of Alaska Press, Fairbanks, 1970), pp. 107-127: E. B. Haines, *Limnol. Oceanogr.* 21, 880 (1976); G. W. Thayer, P. L. Parker, M. W. LaCroix, B. Fry, *Oecologia* 35, 1 (1978).
18. B. N. Smith and S. Epstein, *Plant Physiol.* 47, 380 (1971); T. Whelan, W. M. Sackett, C. R. Benedict, *ibid.* 51, 1051 (1973).
19. C. M. Cavanaugh, S. L. Gardiner, M. L. Jones, H. W. Jannasch, J. B. Waterbury, *Science* 213, 340 (1981).
20. H. Felbeck, *ibid.*, p. 336.
21. M. L. Jones, *ibid.*, p. 333.
22. C. R. Benedict, W. W. L. Wong, J. H. H. Wong, *Plant Physiol.* 6S. 512 (1980).
23. G. H. Rau, *Nature (London)* 289, 484 (1981).
24. P. M. Williams *et* rd., in preparation.

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Prokaryotic Cells in the Hydrothermal Vent Tube Worm *Riftia pachyptila* Jones: Possible Chemoautotrophic Symbionts

Abstract. *The existence of a symbiotic association between vestimentiferan tube worms from deep-sea hydrothermal vents and chemoautotrophic sulfur-oxidizing prokaryotes, based on histological and enzymatic evidence, is suggested.*

A major recent biological discovery is that of the dense benthic animal populations clustered tightly around the newly explored deep sea hydrothermal vents at the Galápagos Rift and East Pacific Rise ocean spreading centers (f, 2). The primary or sole base of the food chain in these communities appears to be the chemoautotrophic production of bacterial biomass with hydrogen sulfide emitted from the vents as the geothermic source of energy (3).

The most conspicuous animal of these vent communities is the large red-plumed vestimentiferan tube worm, *Riftia pachyptila* Jones (4), of the phylum Pogonophora (5). Observations from the submersible *Alvin* indicate that the tubes of *Riftia* are attached to rocks situated directly in the flow of sulfide-rich seawater from the vent (H_2S, up to 160 μM) (2). *Riftia* is superficially similar but much larger (up to 1.5 m in length and a diameter of 38 mm) than other related benthic pogonophorans (4). The most striking feature of this phylum is the lack of mouth and gut. *Riftia*'s large size is astonishing because speculation on the mode of nutrition of the Pogonophora has centered on the uptake of dissolved organic material via the epidermis (6). However, uptake rates of dissolved amino acids at ambient concentrations by the pogonophoran *Siboglinum fiordicum* were shown to be insufficient to account for the animal's metabolic requirements (7). Thus, the mechanism of nutrition of this group remains unclear.

Specimens of *Riftia* were collected at a number of geothermal vents in the Galapagos Rift and East Pacific Rise. The body of the animal consists of four regions (Fig. 1A). The cavity of the trunk, the third and most extensive region (at least 50 percent of the total length in postjuvenile specimens), is occupied by the gonads and the trophosome. The latter, of irregular and variable development along its length, is compact, of many lobules, and is well-supplied with vascular elements. Prior to this study the function of the trophosome in vestimentiferans was unknown. In *Lamellibrachia luymesi* it was suggested to serve as a source of nutrition for developing sperm or as a detoxifying organ (8, 9). In 21 of 31 specimens of *Riftia* examined, crystals of elemental sulfur up to 100 μm in size were found within the trophosomal tissue (10). This observation suggested a capacity for using the chemoautotrophic oxidation of sulfide as an internal source of nutrition. We report here a number of subsequent observations demonstrating the presence of prokaryotic cells within the trophosomal tissue of *Riftia pachyptila* Jones.

In stained paraffin sections the trophosomal tissue is granular (Fig. 1A) (11). The granules are usually aggregated in lobelike accumulations. There are few nuclei present, and the majority of these are associated with blood vessels and the squamouslike covering of the lobular surfaces. Juveniles as small as 1.44 mm long and 0.33 mm in diameter have a trophosome identical in appearance to that of post-juveniles (Fig. 1A). A trophosomal tissue homogenate stained with 4′,6-diamidino-2-pheny lindole (a specific and sensitive DNA stain) and examined with epi-fluorescence microscopy (12) revealed that the morphologically distinct granules (3 to 5 μm in diameter) uniformly produced a brilliant blue fluorescence. This is interpreted as their being either prokaryotic cells or eukaryotic organelles (such as mitochondria). Direct counts of this trophosome homogenate indicated that there were 3.7 x 10^9 cells measuring 3.0 μm or more per gram of tissue (wet weight) (13).

The trophosomal tissue available for examination by electron microscopy was collected at the Rose Garden geothermal vent (14) and had been fixed in 5 percent Formalin (in seawater) as a general preservative: Consequently, the fixation for transmission electron microscopy is not of the highest quality but is sufficient to resolve important structural features. Scanning electron microscopy revealed that the characteristic lobes of the trophosomal tissue consist of densely packed spherical bodies (Fig. 1 B). Transmission electron microscopy (TEM) of the same tissue (15) indicated that these bodies are prokaryotic cells varying in size between 3 and 5 μm (mean = 4.20 ± 0.64 μm; $n = 16$) and having a cell wall resembling that of gram-negative bacteria (Fig. 1C). To date we have been unable to determine if the prokaryotic cells are located within, or outside the trophosomal cells.

The presence of lipopolysaccharide (LPS), a compound characteristic of the outer cell wall of gram-negative bacteria, was confirmed in frozen trophosomal tissue by the *Limulus* amoebocyte lysate test (16). The result of the assay was strongly positive (0.8 μg of LPS per milligram of wet tissue) indicating the presence of a large population of gram-negative prokaryotic cells far in excess of what could be attributed to bacterial contamination of the frozen sample.

Felbeck (17) found in the trophosomal tissue high activities of enzymes used in generating adenosine triphosphate (ATP) from the oxidation of reduced sulfur compounds, that is, thiosulfate sulfurtransferase (rhodanese), APS reductase, and ATP sulfurylase. In addition, high activities of RuBP carboxylase and ribulose 5-phosphate kinase (enzymes of the Calvin-Benson cycle of CO_2 fixation) have been measured in the trophosome in activities comparable to those of spinach leaves (17). The prokaryotic cells make up a major portion of the trophosome in *Riftia*. This suggests strongly that they are responsible for these enzymatic activities and are symbiotic chemoautotrophic bacteria that are capable of generating ATP by way "of sulfide oxidation and reducing CO_2 to organic matter. Preliminary studies by Rau (18) on $^{13}C/^{12}C$ ratios in *Riftia* lend support to

V. MANUSCRIPTS IN PREPARATION

THE SOURCE OF POLYCYCLIC AROMATIC HYDROCARBONS AS IMPLIED FROM THEIR DEPTH PROFILES[1]

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ABSTRACT

The concentration and distribution pattern of polycyclic aromatic hydrocarbons (PAH) in two sediment cores from the California Bight area (San Nicolas and Tanner Basins), in two cores from pristine areas (Alaska and Walvis Bay) and in a core from Hula Peat Basin were determined by gas chromatographic-mass spectrometric analysis. Considerable amounts of PAH were found in the California Bight cores and the surface samples contain a higher concentration relative to deeper samples. The PAH concentration in the Walvis Bay core is very low, as was expected; however, a core from Alaska was surprisingly enriched in PAH. No trend was observed in the PAH concentration of these cores as a function of depth of burial. High amounts of PAH were found in the peat sample which differs from the other samples mainly in its low perylene content. The appearance of PAH at depths corresponding to negligible human activity indicates that they could be natural derivatives and not anthropogenic products, although high concentration in the San Nicolas surface sample is probably due to anthropogenic input. Preferential enrichment in the parent PAH relative to the alkylated species suggests combustion products rather than petroleum, as the source of the PAH in the cores studied. However, the input mechanism to the ocean could be from an atmospheric as well as stream soil erosion source.

INTRODUCTION

Most polycyclic aromatic hydrocarbon (PAH) assemblages of recent sediments in the world are characterized by a higher abundance of-the parent compounds relative to their corresponding alkylated homologs, and by a relatively constant ratio of phenanthrene, fluoranthene, pyrene, the $C_{18}H_{12}$ and the. $C_{20}H_{12}$ species (e.g., the ratio of fluoranthene to pyrene is approximately 1.0; LaFlamme and Hites, 1978). This similarity in PAH distribution pattern and their increase in abundance with proximity to urban centers point to anthropogenic activities *as* the major source of these compounds. in Recent sediments (LaFlamme and Hites, 1978; Wakeham et al., 1980a).

A complex mixture of PAH in recent sediments may also be attributed to petroleum contamination (Giger and Blumer, 1974; Lake et al., 1979; Wakeham, 1977; Youngblood and Blumer, 1975). In this case, the mixture will be deficient in the parent, rather than in their corresponding alkylated homologs, and the alkyl homologs with three and four carbon atoms will be the most predominant (Speers and Whitehead, 1969).

Retene and perylene are also abundant among the PAH compounds in Recent sediments. These compounds are natural products; however, the mode of generation of perylene is still debatable (Arizenshtat, 1973; Orr and Grady, 1967; Simoneit, 1977; Prahl and Carpenter, 1979; Wakeham et al., 1979; 1980b).

The substantial increase in PAH concentration in the very Recent sediments relative to older ones could be attributed to anthropogenic combustion (Hites et al., 1977; Müller et al., 1977; Prahl and Carpenter, 1979). However, the presence of the same PAH assemblage, although in minor quantities, at a depth corresponding to the time interval in which human activity was still undeveloped, indicates that PAH with similar pattern as that of anthropogenic combustion, would also be derived from a natural source. Youngblood and Blumer (1 975) suggest that PAH is produced through natural forest fires and are later dispersed by air currents to the sediments.

The carcinogenic nature and persistence of PAH in sediments have considerable environmental impact. Whether they are natural products which have always been incorporated into the sediment or have an anthropogenic origin, their contribution to the sediments is of great importance.

The purpose of this work is to examine the distribution of PAH in basins close to human centers, in pristine areas, and in peat basins in which self-ignition could occur. Changes in the concentration of PAH in the different environments with depth were determined. Such information should be helpful in deciding whether the source of PAH in specific basins is mainly anthropogenic or natural.

'The California Bight samples were chosen as representative of polluted environments; petroleum residues derived from natural seepage and/or shale erosion have been found in the deeper sediments in this area (Simoneit and Kaplan, 1980) . The Alaska and Walvis Bay samples represent pristine areas. One peat sample was obtained from a core at Hula (Israel).

SAMPLES AND ANALYTICAL TECHNIQUES

Gravity cores of sediment from the San Nicolas and Tanner Basins, and box cores from Walvis Bay and Alaska were frozen immediately after collection and kept frozen until analysis. The Hula swamp core was kept refrigerated. Sample locations are given in Table 1.

The defrosted sediments were extracted on a shaker table with methylene chloride several times until the extract became pale in color. After methylation with BF_3-MeOH and removing the sulfur on copper column, the hexane dissolved fraction was chromatographed on a Sephadex LH 20 column and eluted with methanol. The aromatic fractions was collected and further purified by chromatography on an alumina-silica gel column with methylene chloride according to Giger and Blumer (1974).

The GC/MS analyses were carried out on a Finnigan Model 4000 quadruple mass spectrometer directly interfaced with a Finnigan Model 9610 gas chromatograph equipped with a 30m x 0.25mm SE 54 glass capillary column. The mass spectrometric data acquired was processed using a Finnigan INCOS Model 2300 data system. The concentrations of the compounds were calculated by integrating peak area of mass fragmentograms, and the data are represented by the peak intensity units per gram dry sediment.

RESULTS

Concentrations of PAH in two cores from the California Bight, one from a basin closer to the coast {San Nicolas Basin) and the other in the offshore (Tanner Basin) are given in Table 2.

In both basins, alkylated and parent PAH were found. Although in the Tanner Basin, the PAH concentration is much lower, the species of the PAH and the pattern of their distribution are generally similar to those of the San Nicolas Basin.

It appears that in most samples analyzed in these two basins, the parent PAH are more prominent than their corresponding alkylated compounds except for methyl phenanthrenes (m/z 192) which are more abundant than phenanthrene (m/z 178,

Fig. 1). Naphthalenes and alkylnaphthalenes were detected in all the samples; however, in the analytical procedures, an uncontrollable loss of these compounds occurs and their quantitative consideration is meaningless. The interrelations among the various parent PAH compounds are similar in principle. Phenanthrene is the most prominent compound of the 178 mass compounds, although some anthracene is always present. Concentration of pyrene is always higher than that of fluoranthene. Of the 252 mass compounds, perylene, benzo(e)pyrene and benzofluoranthene are present in all sections of the cores with perylene as the most, and benzo(e)pyrene, as the least abundant (Fig. 1). It is interesting to note that the carcinogenic compound, benzo(a)pyrene, was not found in any of the analyzed samples, except in one station (Tanner Basin, 50-55 cm depth) and only in traces. Minor quantities of benzo(a)anthracene are present in all the California Bight samples.

No change with depth was observed in the concentration and mode of distribution of the PAH in the Tanner Basin core (Fig.2). All compounds, alkylated and parent, including perylene, follow the same distribution pattern. Unfortunately, because of experimental losses, the type and the amount of PAH in the upper 5 cm of the core could not be established. PAH compounds in the San Nicolas core show changes in their concentration with depth (Fig. 2). The surface sample is the richest, the 10-15 cm depth samples are the most depleted, and the deepest samples from the 35-55 cm depth are again somewhat enriched in the alkylated, as well as the parent PAH. In general, all species except phenanthrene show the same depth profile. A notable enrichment in pyrene content was observed in the surface sample.

The PAH distributions in two cores from pristine areas, Alaska and Walvis Bay in West Africa, were also studied (Table 2). In the Walvis Bay samples, the PAH concentration is very low as expected; however, it is surprisingly high in the Alaska core samples. The principal PAH compounds of the California Bight samples were also found to be predominant in both of these two areas. The Alaska samples differ from the California Bight samples in having a very high content of perylene (ten times higher), and also higher amounts of the alkylated homologs of fluoranthene and pyrene, relative to their corresponding parent hydrocarbons. Almost all of the PAH (∿ 80-90%) in the Alaskan core. is due to the mass 252 compounds.

There is no definite trend in the PAH distribution pattern in the Alaska core as a function of depth (Fig. 2). However, two important observations must be emphasized: first, there is a depletion, rather than an increase, in most PAH components in the surface sample compared to the deepest.sample. Secondly, the perylene distribution pattern down the core is different from that of the other PAH compounds.

In the Walvis Bay samples, whether surface or subsurface, PAH concentration is very small and does not show any change in depth" (Fig. 2). Although the concentrations are low, the interrelation among the alkylated and the corresponding parent compounds, as well as among parent hydrocarbons themselves, is different from those of the California Bight and of the Alaska cores. A higher ratio of fluoranthene to pyrene (in some samples ∿ 3.0) is observed compared to other areas (Table 3). Relatively higher concentrations of anthracene was observed, which was found only in trace amounts in the Califoria Bight and is absent in the Alaskan samples.

PAH concentration in the peat sample from the Hula Basin is relatively high and as in most of the other samples, the concentration of the parent PAH is generally higher than their corresponding alkylated compounds. However, perylene is relatively low and the fluoranthene to pyrene ratio is two to three times higher than that found in the California and Alaska samples (Table 3), but similar to the global average (LaFlamme and Hites, 1978).

DISCUSSION

The surface sample from the San Nicolas Basin in the California Bight, in which anthropogenic input has been demonstrated (Venkatesan et al., 1980a), contains PAH with proportions of non-alkylated PAH not far from the cited global average except that the ratio of fluoranthene to pyrene is less than 1.0 (Table 3).

The content of PAH in the surface sample of the San Nicolas Basin is significantly higher than found at lower depths. Because the organic carbon content along the entire core is similar, the increase in the PAH concentration in the surface sample does not appear to be caused by changes in the nature of the sediment, but rather is a result of addition of PAH. The increase is also reflected in some change in the ratios between the major non-alkylated components. The relatively larger PAH concentration in the surface sample of San Nicolas Basin might be attributed to an anthropogenic combustion as found in cores from Buzzards Bay (Hites et al., 1977), Constance Lake (Müller et al., 1977) and Dabob Bay (Prahl and Carpenter, 1979). We believe that this distribution is not due to biotrubation, because previous studies by Bruland et al. (1 979) on San Nicolas Basin show animal reworking down to only 14 cm from the surface.

Simoneit and Kaplan (1980) found triterpenoids in California Bight samples, which indicate paleoseepage in the Recent sediments. however, no evidence was found, either in the San Nicolas Basin core samples or in the Tanner Basin samples, for petroleum-derived PAH.

TheAlaskan sample which represents a pristine area (Venkatesan et al., 1980) also contains a 'relatively high PAH content. Perylene in this sample contains about 90% of the non-alkylated compounds (Table 3) and in this respect is remarkably different from all the other areas 'studied here, and also from that of the global values of LaFlamme and Hites (1978); yet, the concentrations of the species which are most abundant in Recent sediments (for example, phenanthrene, fluoranthene, pyrene, etc.), are of the same order in Alaska and in San Nicolas Basin (Table 2). Similar PAH distribution in various other locati ons in Alaska have been reported by Venkatesan et al. (1980b). Differences 'among the various samples are mainly reflected by the abundance of the alkylated homologs, the fluoranthene/pyrene ratio and the perylene concentration. Our results for the Alaska area, taken together with those of LaFlamme and Hites (1978) and of Venkatesan et al. (1980b) imply that the PAH is not uniformly distributed in the Alaskan area and that the presumably pristine areas do not necessarily lack PAH.

Unlike samples from Alaska, the Walvis Bay samples contain a small content of PAH in accord with the results from LaFlamme and Hites (1978). These marine basins, whether rich (Alaska) or depleted (Walvis Bay, Tanner Basin) in PAH, exhibit no significant trend in the PAH concentration with depth; this indicates that the PAH in these basins were derived from a constant natural source. The predominance of the non-alkylated homologs points to natural combustion.

The interpretation of a natural source for the Alaskan samples is supported by the following consideration. The rate of sedimentation in the area from which the core was taken is between 18-33 cm/1000 years (Nelson and Creager, 1977). Even if the slowest sedimentation rate figure (18 cm/1000 years) is taken into account, the sample from a depth of 90 cm would have been deposited about 5000 years ago. At. that time, the area should have been free of industrial activity.

That the source of PAH in the Hula Basin sample is natural, is also quite clear. An age of about 20,000 years is estimated for this sample based upon correlation to equivalent peat strata reported by Cogwill (1965). Since human activity at this time is questionable and as there was no industrialization during that period, the source of PAH must be exclusively natural.

The possibility of selective enrichment of non-alkylated PAH in the sediments due to microbial degradation of the alkylated compounds is discussed by Teal et al. (1978). They concluded that biochemical degradation of petroleum PAH to a pyrolytic distribution pattern is unlikely. Thus, it seems that the "presence of PAH is not the result of petroleum contamination (Speers and Whitehead, 1969; Coleman et al., 1973), either natural or anthropogenic.

In all the marine cores, perylene, which is considered a biogenic derivative, was not only present, but was frequently the predominant compound. High perylene concentration is particularly notable in the Alaskan sample, which was collected from nearshore Norton Sound, where terrestrial input is considerable. It contains ten times more perylene than each of the other compounds, and ten times more perylene than in all the other basins studied. There are fluctuations in the perylene depth profile in this Alaskan core, but it is not clear whether there is a significant increase in its concentration as a function of depth. Fluctuations in the quantity of precursor input may be a reason for this depth profile (Wakeham et al., 1980b). Since perylene was found relatively more abundant in nearshore than in offshore sediments in Norton Sound (and in other locations in the Bering Sea [Venkatesan et al., 1980b]), a terrigenous precursor can be reasonably assumed for perylene in this area.

In the Walvis Bay core samples, perylene concentrations are relatively low and no significant changes in its concentration with depth was noticed. These results are totally incompatible with those if Wakeham et al. (1979) who found in the Walvis Bay area, a rather high concentration of perylene, claim an increase in perylene concentration with depth and *suggest* that it is formed by diagenesis of diatomaceous ooze.

The presence of perylene in the Hula swamp sample again indicates a terrestrial origin. However, its absence in peat from Chatham Island (New Zealand, unpublished data) indicates that it does not necessarily form in every terrestrial environment, and that peat may" be a source of perylene precursor only. Perylene generation is still debatable; it is considered a natural, non-combustion-derived PAH formed within the sediments (Orr and Grady, 1967; Aizenshtat, 1973; Wakeham et al., 1980b) or, naturally-derived, but incorporated into the sediment as a pre-formed hydrocarbon (Prahl and Carpenter, 1979).

Another biogenic PAH, retene, present in all the marine cores except that of Walvis Bay, is absent in the peat samples. Retene might be generated from resinous plants (Simoneit, 1977; Windsor and Hites, 1979) and thus may indicate a terrestrial biogenic input to the marine sediments. The lack of retene in the Hula peat might indicate the lack of resinous plants. The predominance of marsh vegetation, pollen and the paucity of arboreal pollens in the Hula pollen in the Hula Basin has been noted (Horowitz, 1973).

CONCLUSIONS

In all the cores analyzed, non-alkylated PAH are more abundant than their corresponding alkylated homologs. The PAH species which are predominant in most Recent sediments of the world (LaFlamme and Hites, 1978) are also the most abundant in these cores. Differences in PAH concentration are apparent in different geographic locations. In samples from Norton Sound, Alaska, which is considered to be a pristine area, a relatively high amount of PAH and particularly perylene, was identified. No trend was observed in the PAH depth profiles.

The PAH distribution pattern of the surface sediments in all the areas studied, points to a combustion source. Their presence at depth in the time period in which human activity was still undeveloped, suggests a natural, rather than anthropogenic combustion as the main source of these compounds. Biosynthesis of many of these compounds cannot be yet ruled out.

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REFERENCES

Aizenshtat, Z. (1973). Perylene and its geochemical significance. Geochim Cosmochim. Acts 37, 559-567.

Bruland, K.W., R.P. Franks, J. Bellows and A. Soutar (1979). The age dating of box cores. Southern California Baseline Study, Befit.hit, Year 2, Vol. 2, Final Report, Rept. No. 12.0 SAI-77-917-LJ.

Cogwill, U.M. (1969). The waters of Merom: A study of Lake Huleh. Arch Hydrobiol. 66; 249-272.

Giger, W. andM. Blumer (1974). Polycyclic aromatic hydrocarbons in the environment: Isolation and characterization by chromatography, visible, ultraviolet and mass spectrometry. Anal. Chem. 46; 1663-1671.

Hites, R.A., R.E. LaFlamme and J.W. Barrington (1977). Sedimentary polycyclic aromatic hydrocarbons: The historical record. Science 198; 829-831.

Horowitz, A. (1973). Development of the Hula Basin, Israel. Israel J. Earth Sci. 22; 107-139.

LaFlamme, R.E. and R.A. Hites (1978). The global distribution of polycyclic aromatic hydrocarbons in Recent sediments. Geochim. Cosmochim. Acts 42; 289-303.

Lake, J.L., C. Norwood, C. Dimrock and R. Bowen (1979). Origin of polycyclic aromatic hydrocarbons in estuarine sediments. Geochim. Cosmochim. Acts 43; 1847-1854.

Müller, G., G. Grimmer and H. Böhnke (1977). Sedimentary record of heavy metals and polycyclic aromatic, hydrocarbons in Lake Constance. Naturwissenschaften 64; 427-431.

Nelson, H. and J.S. Creager (1977). Displacement of Yukon-derived sediment from Bering Sea to Chukchi Sea during Holocene time. Geology 5; 141-146.

Orr, W.L. and J.R. Grady (1967). Perylene in basin sediments of southern California. Geochim. Cosmochim. Acts 31; 1201-1209.

Prahl, F.G. and R. Carpenter (1979). The role of zooplankton fecal pellets in the sedimentation of polyclic aromatic hydrocarbons in Dabob Bay, Washington,. Geochim. Cosmochim. Acts 43; 1959-1972.

Simoneit, B.R.T. (1977). Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim Cosmochim. Acts 41; 463-476.

Simoneit, B.R.T. and I.R. Kaplan (1980). Triterpenoids as molecular indicators of paleoseepage in Recent sedimdnts of the Southern California Bight. Mar. Env. Res., in press.

Speers, G.C. and E.V. Whitehead (1969). Crude Petroleum, in Organic Geochemistry (G. Eglinton and M.T. Murphy, Eds.), p. 638-675, Springer.

Teal, J.M., K. Burns and J. Barrington (1978). Analyses of aromatic hydrocarbons intertidal sediments resulting from two spills of No. 2 fuel oil in Buzzards Bay, Massachusetts. J. Fish. Res. Bd. Can. 35; 510-520.

Venkatesan, M.I., S. Brenner, E. Ruth, J. Bonilla and I.R. Kaplan (1980a). Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochim. Cosmochim. Acts 44; 789-802.

Venkatesan, M.I., M. Sandstrom, S. Brenner, E. Ruth, J. Bonilla and W.E. Reed (1980b). Organic geochemistry of surficial sediments from Eastern Bering Sea. Chapter 25-in: Oceanography of the Bering Sea: With Emphasis on Renewable Resources, (D.W. Hood, Ed.).

Wakeham, S.G. (1977). Synchronous fluorescence spectroscopy and its application to indigenous and petroleum-derived hydrocarbons in lacustrine sediments. Env. Sci. Tech. 11; 272-276.

Wakeham, S.G., C. Schaffner, W. Giger, J.J. Boon and J.W. Leeuw (1979). Perylene in sediments from the Namibian Shelf. Geochim. Cosmochim. Acta 43, 1141-1144.

Wakeham, S.G., Schaffner, C. and W. Giger (1980a). Polycyclic aromatic hydrocarbons in recent lake sediments - I. Compounds having anthropogenic origins. Geochim. Cosmochim. Acts 44; 403-413.

Wakeham, S.G., C. Schaffner, and W. Giger (1980b). Polycyclic aromatic hydrocarbons in recent lake sediments - 11. Compounds derived from biogenic precursors during early diagenesis. Geochim. Cosmochim. Acts 44; 415-429

Windsor, J.G., Jr. and R.A. Hites (1979). Polycyclic aromatic hydrocarbons in Gulf of Maine sediments and Nova Scotia soils. Geochim. Cosmochim. Acta 43; 27-33.

Youngblood, W.W. and M. Blumer (1975). Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and Recent marine sediments. Geochim. Cosmochim. Acts 39; 1303-1314.

Table 1. Sample location, and percentage of carbonates and organic carbon

Sample	Location	Carbonates %	Organic Carbon %
San Nicolas Basin	33° 06' N 119° 02' W	35 – 60	2.66 – 4.3≥
Tanner Basin	32° 4≥ W 119° 30' W	41 – 56	4.42 – 5.65
Alaska	63° 39' N 161° 17' W	15 – 16	0.94 – 1.01
Walvis Bay	22° 34' S 13° 50' E	59 – 63	7.11 – 7.99
~~Chatham Island~~			
Hula	33° 5' 35° 34'		

Table 2 - PA}{ found **in** the San **Nicolas,** Tanner, **Alaska** and **Walvis** Bay cores In **arbitrary** peak **intensity units/** gram dry **sediment**

compound name	m. w.	San Nicolas Basin						Tanner Basin			
		o-5 cm	5-1o cm	10-15 cm	1s -20 cm	35-40 cm	50-55 cm	5-1o cm	10-15 cm	35-40 cm	50- 5 cm
naphthalene	128	+	+	+	+	+	+	-		+	-
methyl naphthalene	142	+	+	+	+	+	+			+	
dimethyl "	160	+	+	+	+	+	+			+	
tri " "	170	+	this table	+	+	+	+			+	
fluorene	166	+	+	+	+	this table	tr	tr	ir	*475*	
phenanthrene	178	34557	G029	10792	*14325*	35920	*36638*	5174	*3299*	*9344*	1338
anthracene	178	tr	tr	tr				474	*475*		
tetramethyl naphthalenes	184	this table	this table	+	tr	tr	tr	588	tr	*tr*	nd
methyl phenanthrene	192	51308	13773	18802	21938	41120	*45796*	35663	4681	*14023*	3541
dimethyl phenanthrene	206	41397	1199	14721	16060	31120	*34601*	7279	4465	*11752*	4208
fluoranthene	202	35134	22863	9060	8563	17340	*17980*	6923	2315	*7191*	2499
pyrene	202	108719	29396	17669	25858	23840	30060	11332	4190	*11486*	3599
methyl fluoranthene and pyrene	216	54072	40088	20513	18390	38160	36743	8846	4085	*13846*	5029
benzo- ghi -fluoranthene	226	10494	8030	4186	4726	6540	9217	2183	838	*3153*	1295
chrysene	228	41152	24667	8205	9612	16460	21612	8944	3010	*7474*	3702
benzo-a-anthracene	228	+	tr	tr	?	?	tr	tr	518	*3332*	?
methyl chrysene	242	335s6	20146	12661	?	16180	17644	7163	2489	*9746*	2400
benzofluoranthene	252	30346	21431	7382	7514	9400	13741	8085	2005	*9835*	2344
benzo-e-pyrene	252	11595	9410	3424	4063	6560	6629	3989	tr	*4402*	1688
perylene	252	85997	42464	14447	31001	37020	51903	26925	7477	*17771*	2993
dimethyl benzo phenanthrene	256	22463	7	11997	6783	15480	13912	7178	*1994*	8881	1812
methyl fluoranthene, pyrene & perylene	266	+	17598	7928	?	ir	tr	10994	*1793*	11684	1167
retene	234	tr	?	886	tr	this table	tr	1350	*G38*	*2056*	790

Table 2: (Continued)

Compound name	m, w.	Alaska					Walvis Bay		
		0 - 2 cm	10 - 15 cm	15 - 20 cm	20-29 cm	90 cm	Surfaces 4 cm, 15 cm 20 cm	10 cm	44 cm
naphthalene	128	+	+	+	+	+			
methyl naphthalene	142	+	+	+	+	+			
dimethyl naphthalene	156	+	+	+	+	+			
trimethyl naphthalene	170	+	+	+	+	+	-		
fluorene	106	+	+	+	+	+			
phenanthrene	17'8	56238	*91283*	37124	31170	96596	tr	tr	3113
anthracene	17a						+	+	2600
tetramethyl napntna lene	184	+	tr	this table	tr	+			
methyl phenanthrene	192	high, may contain sulfur				116139			7743
dimethyl phenanthrene	206	68546	75398	80183	106548	96354			5026
fluoranthene	202	11777	10G64	12393	14346	14518	tr	1309	3256
pyrene	202	24960	25811	29891	39847	37858	tr	498	3436
methyl fluoranthene and pyrene	216	40634	45721	*58516*	69305	67587	tr	tr	1320
benzo-ghi-fluoranthene	226	1000	649	this table	1106	991	tr	491	444
chrysene	228	48252	42934	54191	65372	72534	tr	2278	1066
benzo-a-anthracene	228					·	tr	tr	tr
methylchrysene	*242*	45259	49000	62782	?7390	63798	tr	2077	tr
benzo fluoranthene	*252*	28811	27555	35500	36470	50157	tr	2341	
benzo-e-pyrene	*262*	21541	19326	25905	30790	38545	tr	623	397
perylene	252	960890	1017756	1261317	629113	1120526	tr	5275	4333
dimethyl benzo phenanthrene	256	87637	47502	96897	101210	79833	tr	3719	-
methyl fluoranthene, pyrene & perylene	2G6	37084	37064	45566	?	81076	tr	tr	
retene	234	15791	?	15204	28164	26277			?

tr = trace

+ . detected, not determined

TABLE 3. Concentration of Non-alkylated PAH

Sample	Phenanthrene %	Fluoranthene %	Pyrene %	Chrysene %	$C_{20}H_{12}$ %	Fluoranthene / Pyrene
San Nicolas Basin						
0 - 5 cm	10	10	30	15	35	0.33
5- 10. cm	4	15	19	16	46	0.79
10-15 cm	15	13	25	12	35	0.52
15-20 cm	14	8	26	1.0	42	0.31
35 -4.0 cm	25	12	16	11	36	0.75
50 - 55 cm	20	10	17	12	41	0.59
Tanner Basin						
5 - 10 cm	7	10	16	13	54	0.63
10-15 cm	15	10	19	14	42	0.53
35-40 cm	14	11	-17	11	47	0.65
50-55 cm	7	14	20	20	39	0.70
Alaska						
O-2 cm	4.8	1.0	2.1	4.1	88.0	0.48
10-15 cm	7.5	0.9	2.1	3.5	87,8	0.43
15-20 cm	3	0.9	2.1	3.7	90.3	0.43
20 -25 cm	3.7	1.7	4.7	7.6	82.3	0.36
~ 90 cm	6.7	1.1	2.6	5.1	84.5	0.39
Walvis Bay						
4 cm		11	4	18	67	2.75
44 cm	20	21	22	7	30	0.95
Hula						
35 cm	13	28	25	11	24	1.14
Global abundance*	12	16	15	23	35	1.0

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*from La Flamme and Hites (1978)

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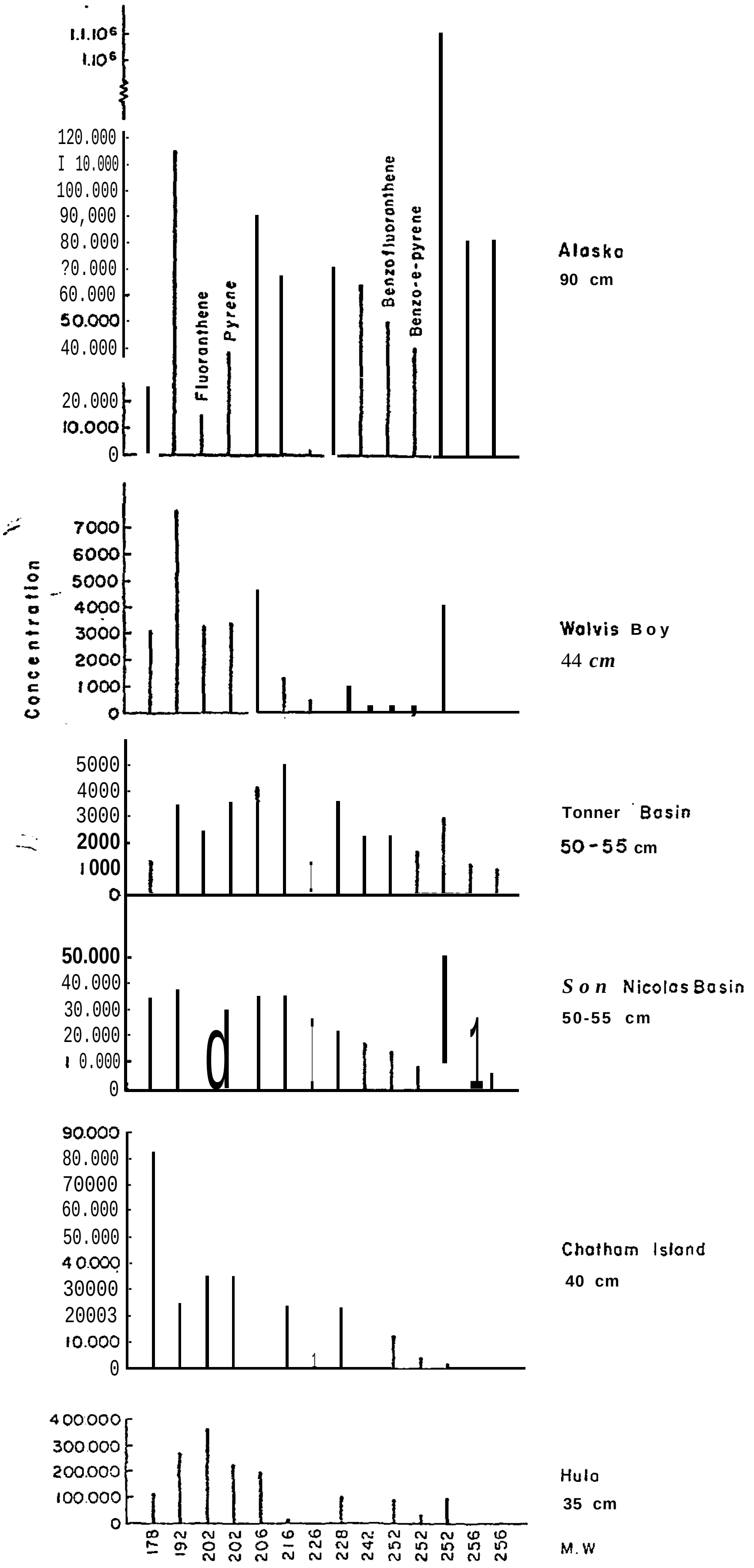
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1.10⁶
120.000
I 10.000
100.000
90,000
80.000
?0.000
60.000
50.000
40.000
20.000
10.000
0
Fluoranthene
Pyrene
Benzofluoranthene
Benzo-e-pyrene
Alaska
90 cm
Concentration
7000
6000
5000
4000
3000
2000
1000
0
Walvis Boy
44 cm
5000
4000
3000
2000
1000
0
Tonner Basin
50-55 cm
50.000
40.000
30.000
20.000
1 0.000
0
Son Nicolas Basin
50-55 cm
90.000
80.000
70000
60.000
50.000
40.000
30000
20003
10.000
0
Chatham Island
40 cm
400.000
300.000
200.000
100.000
0
Hula
35 cm
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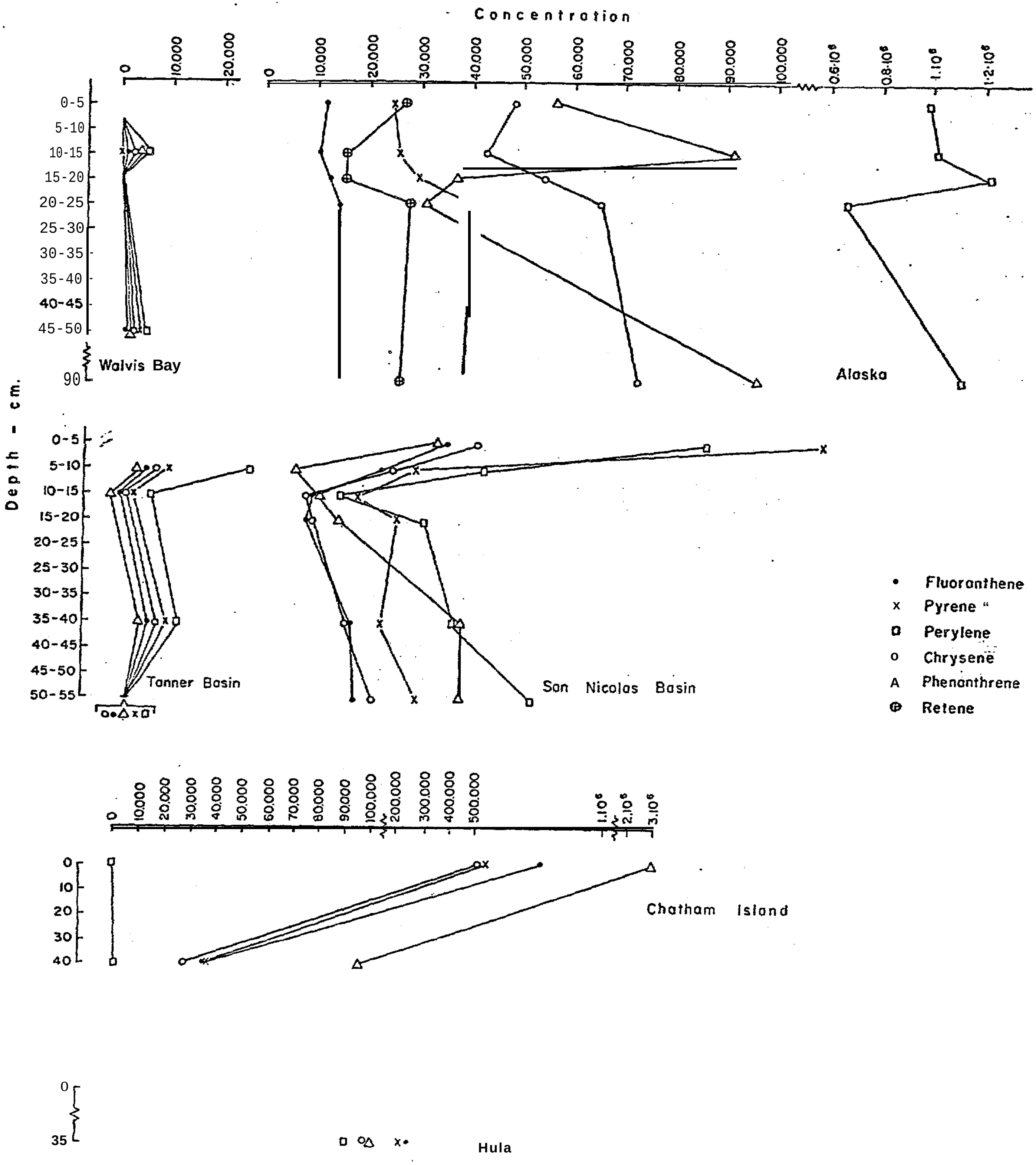
202
202
206
216
226
228
242
252
252
252
256
256
M.W


Concentration
0
10,000
20,000
0
10,000
20,000
30,000
40,000
50,000
60,000
70,000
80,000
90,000
100,000
0.6·10⁶
0.8·10⁶
1.10⁶
1.2·10⁶
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
90
Walvis Bay
Alaska
Depth - cm.
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-45
45-50
50-55
Tanner Basin
San Nicolas Basin
• Fluoranthene
x Pyrene "
□ Perylene
o Chrysene
A Phenanthrene
⊕ Retene
0
10,000
20,000
30,000
40,000
50,000
60,000
70,000
80,000
90,000
100,000
200,000
300,000
400,000
500,000
1.10⁶
2.10⁶
3.10⁶
0
10
20
30
40
Chatham Island
0
35
Hula

ELEMENTAL AND STABLE ISOTOPIC COMPOSITION OF TERRESTRIAL ORGANIC MATTER IN STORM RUNOFF

Robert P. Eganhouse, Shari-Tan Lu and I.R. Kaplan

ABSTRACT

Suspended particulate matter from Los Angeles River stormwaters was isolated and separated into three organic fractions: $CHCl_3$ extractable, humic acids and insoluble organic matter. Elemental (C,H,N) and isotopic ($\delta^{13}C$,δD, $\delta^{15}N$) analyses were performed on the particulate and organic fractions to determine their natural variability and potential sources for these materials. The composition of the. recovered organic matter varied continuously throughout the storm. However, for a given fraction, the variations of measured parameters were small compared with differences between fractions, The $CHCl_3$ extractable material appears to be largely petrogenic, in agreement with molecular information. Humic acids, found only in small abundance, are most likely derived from soil and freshwater algal debris. The insoluble organic matter has unique, but consistent, isotopic charact'eri'sties.(6~ ^{3}'C ≃-26.4 ‰, δD≃ -69.4°/00 , $\delta^{15}N$ ≃ 12.8 ‰) and its origin is, as yet, unknown. Possible sources include: tire wear debris, fossil fuel combustion particles, forest fire ash, partially-degraded lignin, relict kerogen, terrestrial "proto-kerogen" and plastic residues. Limitations on the use of elemental and stable isotope data in the source differentiation of organic matter in coastal sed ments are discussed in the context of the foregoing data.

INTRODUCTION

Stable isotope ratios ($\delta^{13}C, \delta^{15}N$) have frequently been used to differentiate marine and terrestrial sources of organic matter in estuarine and coastal sediments (Sweeney and Kaplan, 1980, Tan and Strain, 1979; Peters et al., 1978). Their use is based upon observations that: 1) terrestrial and marine plants exhibit distinct isotope ratio distributions (Sweeney et al., 1978; Craig, 1953) and 2) isotope ratios of sedimentary organic matter change systematically across estuarine traverses where mixing of these source materials would presumably occur (Shultz and Calder, 1976; Hunt, 1968; Sackett and Thompson, 1963). Unfortunately, a number of variables relating to photosynthetic fixation and plant metabolism, as well as the subsequent breakdown of biosynthetic compounds, tend to reduce the discrimination value of isotopic measurements (Estep and Hoering, 1980; Eadie and Jeffrey, 1973; Smith and Epstein, 1971; Degens et al., 1968). As a result, there has been an increasing tendency for use of multiple source indicators in environmental studies (Sweeney et al., 1980; Stuermer et al., 1978; Hedges and Parker, 1976).

Certain end products of photosynthesis which survive biodegradation (e.g., lignin, refractory algal debris, humic acids) may display source-specific elemental compositions. These variations form the basis for using elemental ratios and abundances to distinguish between marine and terrestrially-derived organic matter (Plockington and Leonard, 1979; Plockington, 1976; Tissot et al., 1974). Again, there are large natural variations within and between organisms in each environment which tend to make quantitative assessments in sediments difficult.

These geochemical tools have been applied almost exclusively to studies of original source materials and sedimentary deposits. Very little information presently exists on the isotopic/elemental composition of suspended matter in rivet-s and virtually none on their distribution among various organic phases. The present study involves the measurement of elemental and isotopic abundances of several organic fractions isolated from suspended particulate matter in Los Angeles River stormwaters. These particulate represent well--homogenized terrestrial erosion products which were collected just prior to their injection into the marine environment. Previous molecular studies of stormwaters have shown that natural terrestrial organics transported in the river are superimposed by a complex array of anthropogenic components derived from the intense human activities in the basin (Eganhouse et al., 198?). Our specific objectives were to:

1) define the limits of natural elemental and isotopic variations of runoff-borne particulate organic matter during the course of a storm event,

2) establish elemental/isotopic distributions between various fractions of suspended organic matter and attempt to identify their possible sources, and

3) develop baseline information for a major southern California drainage system to be used in future coastal sediment modelling efforts.

This research is part of a larger study of the sources of terrestrial organic matter and its fate in. the marine environment:

Study Area

The Los Angeles River, a predominantly man-made system of channels terminating at San Pedro Harbor, drains a 2100 km^2 basin. Both rugged mountainous areas and a large portion of highly-urbanized Los Angeles are contained within the basin. Unlike many previously-studied (Gearing et al., 1977; Shultz and Calder, 1976; Hunt, 1968), this river system if highly seasonal. During most of the year (May to December) there is very little precipitation, and dry weather flow (comprising ∿ '30% of the yearly total) is made up by controlled reservoir releases, discrete industrial and treatment plant waste discharges and agricultural/domestic water runoff (LACFCD 1976). Under storm conditions, which occur sporadically during the remainder of the year, highly variable flows are regulated by a number of reservoirs within the basin. Due to the low rain infiltration in paved areas, peak flows can be large.

EXPERIMENTAL

Sampling and Extraction

Eleven sequential samples of stormwater runoff were collected at a location 4 km upstream from the mouth of the Los Angeles River channel. This is just above the highest high tide zone. Water samples were obtained over the full range of flow conditions during the second storm event of the 1978-1979 rainy season. Details of the sampling methodology and dynamic properties of the storm are given elsewhere (Eganhouse and Kaplan, 1981).

After poisoning the water samples with $HgCl_2$ and removing homogenized aliquots for molecular analysis, the suspended particulate were concentrated by gravitational settling for 48 hours. The supernatant was then decanted, and the solids were stored frozen until organic group separations could be performed.

The frozen particulate samples were lyophilized and extracted exhaustively with $CHCl_3$ at ambient temperatures using a mechanical shaker table. Extraction efficiency was monitored by the UV fluorescence of aromatic hydrocarbons in the extracts (Eganhouse _et_. _al_. 1981) and assured by extracting 2-3 times after cessation of fluorescence. The combined extracts for each sample were concentrated by rotary evaporation (∿ 200 mm Hg, < 35°C), and total $CHCl_3$-extractable organic contents (TEO) were quantified gravimetrically using a Mettler ME 22 microbalance. After esterification of extractable acids, esters and glycerides in TEO extracts, five subfractions were separated by thin-layer chromatography: 1) THC (total hydrocarbons) 2) FA (fatty acids, methyl esters), 3) KET (ketones), 4) PLR (polar compounds), 5) NEP (non-elutable polar compounds). For details see Eganhouse and Kaplan (1981).

Humic/fulvic acids were extracted from the TEO-free residues using 0.2 N NaOH under a nitrogen atmosphere according to the procedure of Stuermer et al. (1978). After precipitation of the humic acids (HA) at pH = 2, the fulvic acid-bearing supernatant was discarded. The content of fulvic acids appeared to be minor compared with that of the humic acids. The HA precipitate was then washed with doubly-distilled water, lyophilized, weighed and stored in a vacuum-dessicator.

Silicate minerals were removed from the solid residue using an HCl/HF treatment regimen (Stuermer et al., 1978) in order to concentrate the insoluble organic matter (IOM). After acid treatment, this fraction was washed, dried, weighed and stored in the same manner as the humic acids. Ash contents, not measured for the HA "fractions due to extremely low yields, were determined on IOM fractions by weight difference upon combustion at 900°C.

Elemental and Isotopic Analyses

Elemental and isotopic analyses of non-volatile organic fractions (i.e., particulate, HA and IOM) were performed in virtually the same manner as described by Stuermer et al. (1978). In the case of the TEO fractions and the five TEO subfractions, special care was taken to prevent evaporative losses during preparation of the combustion vessels. Approximately 1 mg (solvent-free) samples were weighed into pre-combusted boats and then placed in dry quartz combustion tubes. After cooling the tubes with liquid nitrogen briefly, the samples were sealed under vacuum. HA and IOM fractions were evacuated for ≥ 24 hours to insure complete removal of absorbed water.

All samples were combusted at 900°C in the presence of CuO and Ago. Water generated during combustion was reduced to hydrogen gas in a uranium furnace

(800°C) to permit separation from N_2 and CO_2 by vacuum line techniques (Kaplan et al., 1970). Elemental abundances were determined manometrically, while isotope ratios, presented here in the standard "δ" notation, were measured with a Varian MAT 250 isotope ratio mass spectrometer. isotope standards for C, H and N were Chicago Pee Dee Belemnite, atmospheric nitrogen and "standard mean ocean water" (SMOW), respectively.

Because we were especially interested in examining the variability of our samples, a preliminary study was done to measure the precision of elemental/ isotopic analyses for both volatile and non-volatile sample types. The results, presented in Tablel, are for replicate samples of carbonate-free sediment homogenates from Tanner Basin and $CHCl_3$-extractable organics of the same. For comparison, previous data by others for different sediment samples from Tanner Basin are provided. Discrepancies between the elemental results from the present study and those from the literature are due to different extraction methodologies and variation in the samples which were collected at different times and locations. The isotopic results are in excellent agreement. The greatest variability occurred for %N in $CHCl_3$-extractables. All other measurements, with one exception, showed coefficients of variation < 7%. The hydrogen content of sediments may be more variable due to the problem of sample homogeneity since hydrogen is not only bound to organic matter but also occurs as interlayer water in clays.

RESULTS

General Features.

Table 2 lists data for the levels of suspended solids, %C, %N, N/C atomic ratios and $\delta^{13}C$ for carbonate-free stormwater particulate. There are no correlations among these parameters. However, a noticeable increase in clay mineral content of the particulate occurred from 1550-1800 hours. This coincided with a decline in C, N and H abundances of both particulate and organic fractions (HA, IOM--Table 3) during this time. X-ray diffraction analysis of five of the samples revealed that the mineralogy was dominated by quartz, muscovite, chlorite and feldspar with smaller amounts of hematite and calcite.

Because of the low masses involved, there is some error associated with gravimetric measurements of TEO, HA and IOM yields. Nevertheless, these data (Figure 1) indicate that the HA fraction was in low abundance throughout the storm; TEO and IOM fractions together comprised 81-94% of the total recovered organic matter. Furthermore, the TEO fraction predominates until the very latest stages of the storm. The apparent similarity of the HA and TEO trends was confirmed by linear regression analysis (r = 0.83).

Elemental Composition of Organic Fractions

A summary of C, N and H abundances and atomic ratios for TEO, HA arid IOM fractions is given in Table 3. The most striking feature of these data is the uniformity of the values. Variations for all parameters are at or near the level of experimental error (cf., Table 1). The large variations in the measurement of nitrogen in TEO isolates are due to the extremely small quantities of gas evolved. Much less variable are the elemental ratios, suggesting a high degree of molecular" homogeniety.

The hydrogen content in the TEO fraction is very high due to the dominance of hydrocarbons (∿ 60%, Eganhouse and Kaplan, 1981), whereas the mean H/C ratio of 1.9 indicates that these solvent-extractable organics are largely aliphatic. Such findings are consistent with previous results (Eganhouse and Kaplan, 1981; Eganhouse et al., 1981).

The C, N and H contents of the HA fraction are difficult to compare with literature values because data of this type are normally presented on an ash-free basis. Since ash contents of humic acids are normally < 10%, the tabulated abundances are probably fairly accurate. The H/C ratios are similar to those sometimes found for soil humic acids (Nissenbaum and Kaplan, 1972; Brown et al., 1972;

Stevenson and Gob, 1971; Rashid and King, 1970; Schnitzer and Skinner, 1969). However, lacustrine (Ishiwatari 1970; Otsuki and Hanya, 1967) and marine humic acids (Hue and Durand, 1973; Nissenbaum and Kaplan, 1972; Brown et al., 1972; Rashid and King, 1970) are known to have broad ranges which overlap terrestrial values. The N/C values obtained for stormwater HA are higher than most data accumulated for terrestrial, lacustrine (algal) or marine environments with the exception of work done by Stuermer et al., (1978). They found that plotting data for humic acids from marine and terrestrial environments on an N/C versus H/C grid not only gave a good correlation (r = 0.77), but also there appeared to be a group separation between algally- and terrestrially-derived HAs. When plotted on such a diagram the present data falls in line with points of Stuermer et al. (1978) and intermediate between algal and terrestrial groups (Fig. 2a). However, the data fall outside the bulk of those reported by others for a variety of environments.

The carbon, hydrogen and nitrogen abundances in the IOM fraction are reasonably uniform and fall within an acceptable range for terrestrial "proto-kerogens", but in general, values of %N and %H are lower than normal for recent algal sources (Stuermer et al., 1978). The low H/C ratios indicate a highly-aromatized structure, perhaps similar to that of "humic kerogens" (Dow, 1977) or kerogen which has undergone a moderate degree of thermal alteration (Tissot et al., 1974). Simoneit and Mazurek (1980) recently reported residual organic carbon fractions of marine aerosols with H/C ratios in the same range. The N/C ratios are somewhat lower than is commonly found for recent "proto-kerogens" (Stuermer et al., 1978) and higher than most ancient kerogens (McIver, 1967). Similar N/C values have, however, been found for TEO-free vehicle aerosols collected in tunnels (Pierson 1978). When plotted on an N/C versus H/C diagrem (Fig. 2b) the data for stormwater IOM fractions fall in line with those Stuermer et al. (1978) obtained, but due to the low hydrogen and nitrogen contents they are on the extreme "terrestrial" end of the distribution.

Stuermer et al. (1978) found that when elemental ratios for "proto-kerogens" (H/C, N/C) were plotted against those of humic acids from the same samples, a good correlation was obtained. On this evidence, they inferred a common source or genesis for these organic fractions. The data obtained here do not conform to the correlations found by Stuermer et al (1978). Assuming their interpretation is correct, this indicates that stormwater HA and IOM fractions are genetically unrelated.

Finally, the variation in elemental abundance between stormwater organic fractions are noteworthy. For example, there is a two-fold difference in H/C values between TEO and IOM fractions and a twenty-fold variation in N/C between HA and TEO fractions. A graphical presentation of the average elemental distribution among these fractions (Fig. 3) illustrates these points. Carbon is clearly lodged in the TEO and IOM fractions (TEO + IOM ≃ 94%) with the THC subfraction dominating the organic solvent-extractable material. The same is true for hydrogen which is enriched in the more aliphatic, less condensed phases. Nitrogen, however, is in very low abundance in the TEO fraction. Owing to the high relative concentrations of the IOM in stormwater particulate and the nitrogen. content of the HAs, roughly 95% of the nitrogen is bound in these latter two fractions where it is essentially unavailable for utilization by microorganisms.

Stable Isotopic Compositions of Organic Fractions

Measured values of $\delta^{13}C$, $\delta^{15}N$ and δD for organic isolates are given in Table 4. $\delta^{15}N$ values for TEO samples were not measured because of insufficient yields of nitrogen gas during combustion.

The $\delta^{13}C$ values of TEO fractions are remarkably uniform and near the level of experimental error (cf., Table 1). Table 5 lists $\delta^{13}C$ and %C for the five TEO subfractions, calculated composite TEO values based upon elemental and isotopic mass balances and the corresponding measured TEO data. Calculated and measured values of %C and $\delta^{13}C$ are in good agreement, verifying that significant losses and fractionation were probably not produced by the chromatographic technique. The small differences are more likely to be due to errors in the mass recoveries than the isotopic measurements. Additionally, it is obvious that the value of $\delta^{13}C_{TEO}$ is dependent upon the isotopic composition of the hydrocarbons because this is where the majority of the carbon is found (Fig. 3). The $\delta^{13}C$ values obtained for the THC fractions (-26.8 to -26.3‰) are typical of petroleum, but depleted in ^{12}C relative to terrestrial plant lipids (Grizzle *et al.*, 1979; Fuex, 1977; Hoering, 1974). Molecular analysis indicates that these hydrocarbons have a petrogenic origin (Eganhouse *et al.*, 1981). By comparison, the other TEO subfractions are depleted in 12C relative to the hydrocarbons and terrestrial plant lipids (Smith and Epstein, 1970; Park and Epstein, 1961). This suggests different origins for THC and the other lipid fractions. Eganhouse *et al* (1981) hypothesized that the PLR constituents, which occur largely as an unresolved complex mixture in gas chromatograms, might have included N-S-O compounds from petroleum. The $\delta^{13}C_{PLR}$ values (-23.7 to -25.6 ‰) obtained here are depleted in I*C by roughly 1.3 ‰ relative to the hydrocarbons (-26.3 to -26.8 ‰). Such a depletion is consistent with data for petroleum fractions (Stahl, 1978) but is not unequivocal evidence for a petrogenic origin for the PLR isolates.

δD values for the TEO fractions (Table 4) are also uniform. The data fall within the range found for seven petroleums by Hoering (1974) and are generally enriched in deuterium relative to higher plant lipid fractions (Estep and Hoering, 1980; Hoering, 1974).

The humic acids in these stormwaters exhibit very small $\delta^{13}C$ variations. The data seem to fit marginally with values found for some terrestrial environments (Stuermer *et al.*, 1978); however, they are depleted in ^{12}C relative to most soil humic acids (Goh *et al.*, 1977; Wakeham and Carpenter, 1976; Nissenbaum, 1974; Nissenbaum and Kaplan, 1972; Brown *et al.*, 1972; Degens, 1969). On the other hand, they are enriched in ^{12}C compared with many marine humic acids (Crisp *et al.*, 1979; Stuermer *et al.*, 1978; Ishiwatari *et a?.*, 1977; Stuermer and Harvey 1974; Nissenbaum, 1974; Hoering, 1973; Nissenbaum and Kaplan, 1972). $\delta^{15}N$ values for the humic acids were highly variable and on the average appear to be intermediate between reported terrestrial and marine values (Crisp *et al.*, 1979; Stuermer *et al.*, 1978; Sweeney *et al.*, 1978). The stormwater HA data for $\delta^{13}C$ and $\delta^{15}N$ are consistent with those obtained by' Peters *et al.* (1978). They found a linear correlation between $\delta^{15}N$ and $\delta^{13}C$ for organic matter from river and coastal sediments in which the slope paralleled that of the presumed inorganic nutrients (N_2, CO_2-land; NO_3^-, HCO_3^- ocean).. The authors suggested that such a correlation reflects the mixing of marine and terrestrial organic matter. The data points for stormwater HA fall very near the empirical correlation line they obtained, most of them clustering near those of undisturbed natural rivers and an oligotrophic lake. The δD values of the HA were consistently around -100 ‰.

The IOM fraction has uniform $\delta 13C$ values very near those of the TEO and THC measurements. This may indicate a genetic relationship. By comparison with the data of others (Stuermer *et al.*, 1978; Goh *et al.*, 1977), these IOM fractions are isotonically similar to recent terrestrial source materials. However, they appear to be depleted in ^{13}C relative to kerogens isolated from" other rivers in California (peters *et al.*, 1978). The $\delta^{15}N$ are anomalously and 'consistently heavier than reported terrestrial kerogens and "proto-kerogens" (Stuermer *et al.*, 1978; Peters *et al.*, 1978). Atmospheric nitrogen has a $\delta^{15}N$ value of

0‰ and refractory terrestrial organic matter is generally thought to be near this value (Sweeney *et al*., 1978). Thus, it appears that nitrogen in the IOM fraction is most likely derived from sources other than recent natural plant debris and stable breakdown products. The δD values are extremely heavy relative to the other stormwater organic fractions and completely unlike any found in the recent environments studied to date. These data clearly show that significant isotopic variations occur between different fractions of organic matter in the suspended solids of this river.

DISCUSSION

The elemental and stable isotopic compositions of estuarine and marine sediments are usually measured with respect to the total organic matter (TOM). The present data indicate that this practice can yield misleading results because these compositions are determined principally by two variable fractors: 1) the elemental/isotopic characteristics of specific organic fractions and 2) the composition of the TOM in terms of these individual fractions.

In the case of stormwater particulate, most measured parameters for any one organic fraction are strikingly uniform during the storm. Thus, fraction-specific variations do not contribute much to variations in the properties of the TOM. However, significant differences in elemental/isotopic characteristics were noted between individual fractions. Furthermore, the relative abundances of the fractions fluctuated continuously throughout the storm. Therefore, if meaningful comparisons are to be made between or within environments, it is clear that isolation procedures must be used to fractionate the organic matter before measurement. The alternative is a severe loss of information due to mixing of complex and sometimes unrelated source materials.

Another consideration is the behavior of continentally-derived organic matter in the estuary. In a dynamic system such as this, marine and terrestrial organic materials are mixed concurrent with dramatic changes in physico-chemical conditions. Ongoing microbial degradation is intensified upon contact with the water-sediment interface. Because solvent-extractable organics exhibit marked differences in their physical, chemical and biochemical properties (eg., volatility, volubility, biological uptake and catabolism, adsorption by particulate matter, and elemental/isotopic distributions), they could experience considerable fractionation in the estuarine and marine environments. Thus, as a class, they are unlikely candidates for elemental/isotopic source differentiation because they do not maintain their identities except on a trace molecular basis. The same processes of dispersion, sedimentation and biodegration that profoundly affect the TEO fractions are virtually unimportant in the case of refractory organic matter such as the HA and IOM fractions. Consequently, these components hold greater promise in studies involving quantitative estimates of terrestrial contributions to marine sediments.

The results for the TEO fraction (especially the hydrocarbons) essentially agreed with what was, found in prior detailed molecular analyses (Eganhouse et al., 1981). The extractable organics are probably derived from two distinct reservoirs: petroleum and recent biogenic organic matter. Separation of the extractable organic' matter revealed a diversity in the distribution of carbon and its isotopes among molecular groups.

The stormwater humic acids-appear to be of mixed terrestrial and algal origins. This is based upon comparison of elemental data (H/C, N/C) with that of Stuermer et al (1978). Because the samples were collected beyond the influence of marine waters, a partial recent marine origin for these humic acids is not possible. The most likely source of algal ly-derived humic material are the numerous reservoirs which are used to help regulate flows in the drainage channels during storm conditions. Presumably, this input could be affected by a flush-type action in the reservoir and storm channel sediments.

Stuermer *et al.* (1978) combined the H/C ratio and $\delta^{13}C$ values and showed that terrestrial and marine humic acids might be differentiated into clusters. Figure 4 plots these and other literature data along with that for stormwater humic acids. The present data appear to fall near the approximate boundaries for marine and terrestrial clusters. Because marine humic acids cannot be present in the stormwaters, the conclusion that stormwater humic acids represent a mixture of marine and terrestrial contributions would clearly be erroneous. This example illustrates the fact that considerable discretion must be exercised in interpreting elemental and isotopic data in the absence of outside corroborative evidence.

Perhaps the most interesting results of this study were obtained for the insoluble organics.. Optical and scanning electron microscopy showed this material to be a black, amorphous, highly-cohesive aggregate reminiscent of diesel combustion particles (Vuk *et al.*, 1976) with minor amounts of (< 5%) plant structural remains (Fig. 5). Both elemental and isotopic data suggest that the major portion of this material bears no relation to the humic acids. Possible sources (in order of suggested probability) include: tire wear particles, fossil fuel combustion particulate, forest fire ash, lignin, relict kerogen and plastic debris. The low nitrogen and hydrogen contents indicate an extremely carbon-rich material; however, the carbon isotope data, although similar to that of the hydrocarbons, are ambiguous. In view of the dominance of petrogenic constituents among extractable organics, the rainfall pattern (which was restricted to heavily-developed areas), and the low yields of presumably biogenic humic acids, it seems highly probable that these materials have originated from vehicular use (i.e., diesel combustion and tire debris) and/or power plant combustion of fossil fuels. If this is true, the heavy $\delta^{15}N$ and δD values may have resulted from preferential loss of the lighter isotope during pyrolytic breakdown. Until a variety of source materials can be analyzed, these statements will remain speculative. However, if refractory nitrogen in stormwater particulate proves to have a fossil fuel origin, nitrogen isotope measurements might be used to estimate the contribution of anthropogenic organic nitrogen to terrestrial aerosols.

Some final comments regarding the unique nature of this river system must be made. The observed $\delta^{15}N$ enrichment in IOM fractions seems in conflict with the idea that light nitrogen is generally lodged in the most refractory portion of terrestrially-derived organic matter (Peters et al., 1978)”. Similarly, combined use of $\delta^{13}C$ and $\delta^{15}N$ to characterize the origin of the IOM is seriously jeopardized in this instance by the anomolous $\delta^{15}N$ results. These discrepancies are probably related to the overwhelming influence of man’s activities in the drainage basin. Because this river contributes roughly 28% of the total surface runoff to southern Californiats coastal waters, however, it can scarcely be considered a minor exception.

CONCLUSIONS

Collectively, these data indicate that interpretation of elemental and isotopic data in terms of source differentiation can be extremely difficult and in the absence of independent corroborative data must be approached with the utmost caution. Particularly in urban areas, more data are urgently needed on potential source materials. Existing models which have been successfully applied in certain undisturbed environments and in locations heavily-inundated by a point-source ‘discharge of natural terrestrial’ organic matter may be invalid for locations where contributions from unknown and diverse sources occur. In these cases, more detailed analysis of individual organic components is not only desirable, but necessary.

ACKNOWELDGEMENTS

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REFERENCES

Brown, F.S., Baedecker, M.J., Nissenbaum, A. and Kaplan, I.R.(1972). Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia--I II. Changes in organic constituents of sediment. Geochim. Cosmochim. Acts 36, 1185-1203.

Craig, H. (1953). The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acts 3, 53-92.

Crisp, P.T., Brenner, S., Venkatesan, M.I., Ruth E. and Kaplan, I.R.(1979). Organic chemical characterization of sediment-trap particulate from San Nicolas, Santa Barbara, Santa Monica and SanPedro Basins, California. Geochim. Cosmochim. Acts 43, 1791-1801.

Degens, E.T. (1969). Biochemistry of stable carbon isotopes. In Organic Geochemistry (eds., G. Eglinton and M.T.J. Murphy), pp. 304-329, Springer-Verlag.

Degens, E.T., Guillard, R.R.L., Sackett, M.W. and Hellebust, J.A. (1968). Metabolic fractionation of carbon isotopes in marine plankton--I. Temperature and respiration experiments. Deep-Sea Res. 15, 1-9.

Dow, W.G. (1977). Kerogen studies and geological interpretations. J. Geochem. Explor. 7, 79-99"

Eadie, B.J. and Jeffrey, L.M. (1973). $\delta^{13}C$ analyses of oceanic particulate organic matter. Mar. Chem. 1, 199-209.

Eganhouse, R.P. and Kaplan, .R. (1981). Extractable organic matter in urban stormwater runoff.. 1. Transport dynamics and mass emission rates. Environ. Sci. Technol. 15, 310-3 5.

Eganhouse, R.P., Simoneit, B.R.T. and Kaplan, I.R. (1981). Extractable organic matter in urban stormwater runoff: 2. Molecular characterization. Environ. Sci. Technol. 15, 315-326.

Estep, M.F. and Hoering, T.C. (1980). Biogeochemistry of the stable hydrogen isotopes. Geochim. Cosmochim. Acts 44, 1197-1206.

Fuex, A.N. (1977). The use of stable carbon isotopes in hydrocarbon exploration. J. Geochem. Explor. 7, 155-188.

Gearing, P., Plucker, F.E., and Parker, P.L. (1977). Organic carbon stable isotope ratios of continental margin sediments. Mar. Chem. 5, 251-266.

Gob, K.M., Stout, J.D. and Rafter, T.A. (1977). Radiocarbon enrichment of soil organic matter fractions in New Zealand soils. Soil Sci. 123, 385-391.

Grizzle, P.L., Coleman, H.J., Sweeney, R.E. and Kaplan, I.R. (1979). Correlation of crude oil source with nitrogen, sulfur and carbon stable isotope ratios. In: Proceedings Joint Meeting Am. Chem. ______ Soc. Japan, Honolulu, April 1-6, 1979, pp. 39-51. ‘oc-;chem’’

Hedges, J.I. and Parker, P.L. (1976). Land-derived organic matter in surface sediments from the Gulf of Mexico. Geochim. Cosmochim. Acts 40, 1019-1029.

Hoering,T.C. (1973). The isotopic composition of the carbon and hydrogen in organic matter of recent sediments. Cam. Inst. Yrbk. 73, 593-595.

Hoering, T.C. (1974). The biogeochemistry of the stable hydrogen isotopes. Cam. inst. Yrbk. 74, 598-604.

Hunt, J.M. (1968). The significance of carbon isotope variations in marine sediments. In: Carbon in Biochemisty (ed. G.D. Hobson), pp. 27-35, Pergamon Press.

Hue, A.Y. and Durand, B. (1973). Étude des acides humiques et de l'humine de sédiments récents considérés comme précurseurs des kérogènes. In: Advances inorganic Geochemistry 1973 (eds. B. Tissot and F. Bienner), PP.-53-72, Editions Technip.

Ishiwatari, R. (1970). Structural characteristics of humic substances in recent lake sediments. In: Advances in Organic Geochemistry 1970, (eds. G.D. Hobson and G.C. Speers), pp. 283-311, Pergamon Press.

Ishiwatari, R., Ishiwatari, M., Rohrback, B.G. and Kaplan, I.R. (1977). Thermal alteration experiments on organic matter from recent marine sediments in relation to petroleum genesis. Geochim. Cosmochim. Acts 41, 815-828.

Kaplan, I.R., Smith J.W. and Ruth, E. (1970). Carbon and sulfur concentration and isotopic composition in Apollo 11 and lunar samples, Proc. Apollo 11 Lunar Sci. Conf. Geochim. Cosmochim. Acts Suppl. 2, 1317-1329.

Los Angeles County Flood Control District (1976). Hydrologic Report 1974-1975.

McGiver, R.D. (1967). Composition of kerogen--clue to its role in the origin of petroleum. Seventh World Petroleum Congress 2, 25-36.

Nissenbaum, A. (1974). The organic geochemistry of marine and terrestrial humic substances: implications of carbon and hydrogen isotope studies. In: Advances in Organic Geochemistry 1973 (eds. B. Tissot and F. Bienner), pp. 39-52, Editions Technip.

Nissenbaum, A. and Kaplan I.R. (1972). Chemical and isotopic evidence for the in situ origin of marine humic substances. Limnol. Oceanogr. 17, 570-582.

Otsuki, A. and Hanya, T. (1967). Some precursors of humic acid in Recent lake sediment suggested by infra-red spectra. Geochim. Cosmochim. Acts 31, 1505-1515.

Park, R. and Epstein, S. (1961). Metabolic fractionation of ^{13}C and ^{12}C in plants. Plant Physiol. 36, 133-138.

Peters, K.E., Sweeney, R.E. and Kaplan, I.R. (1978). Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23, 598-604.

Pierson, W.R. (1978). Particulate organic matter and total carbon from vehicles on the road. In: Proc. Conf. Carbonaceous Particles in the Atmosphere, Berkeley, California, March 20-22, 1978.

Plockington, R. (1976). Terrigenous organic matter in surface sediments from the Gulf of St. Lawrence. J. Fish. Res. Bd. Can. 33, 93-97.

Plockington, R. and Leonard, J.D. (1979). Terrigenous organic matter in sediments of the St. Lawrence Estuary and the Saguenay Fjord. J. Fish. Res. Bd. Can. 36, 1250--1255.

Rashid, M.A. and King, L.H. (1970). Major oxygen-containing functional groups present in humic and fulvic acid fractions isolated from contrasting marine environments. Geochim. Cosmochim. Acta 34, 193-201.

Sackett, W.M. and Thompson, R.R. (1963). Isotopic organic composition of recent continental derived elastic sediments of eastern Gulf Coast, Gulf of Mexico. Bull. Amer. Assoc. Petrol. Geol. 47, 525-531.

Schnitzer, M. and Skinner, S.I.M. (1969). Free radicals in soil humic compounds Soil Sci. 108, 383-390.

Shultz, D.J. and Calder, J.A. (1976). Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments. Geochim. Cosmochim. Acts 40, 381-385.

Simoneit, B.R.T. and Mazurek, M.A. (1980). Natural background of biogenic organic matter in aerosols over rural areas. In: Proc. Fifth Internat. Clean Air Congress, Buenos Aires, Argentina.

Smith, B.N. and Epstein, S. (1970). Biogeochemistry of the stable isotopes of hydrogen and carbon in salt marsh biota. Plant Physiol. 46, 738-742.

Smith, B.N. and Epstein, S. (1971}. Two categories of $^{13}C/^{12}C$ ratios for higher plants. Plant Physiol. 47, 380-384.

Stahl, W.J. (1978). Source rock-crude oil correlations by isotopic type-curves. Geochim. Cosmochim. Acts 42, 1573-1577.

Stuermer, D.H., Peters, K.E. and Kaplan, I.R. (1978). Source indicators of humic substances and proto-kerogen. Stable isotope ratios, elemental compositions and electron spin resonance spectra. Geochim. Cosmochim. Acts 42, 989-997.

Stuermer, D.H. and Harvey, G.R. (1974). Humic substances in seawater. Nature 250, 480-481.

Stevenson, F.J. and Gob, K.M. (1971). Infrared spectra of humic acids and related substances. Geochim. Cosmochim. Acts 35, 471-483.

Sweeney, R.E. and Kaplan, I.R. (1980). Natural abundances of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. Mar. Chem. 9, 81-94.

Sweeney, R.E., Kalil, E.K. and Kaplan, I.R. .(1980). Characterization of domestic and industrial sewage in southern California coastal sediments using nitrogen carbon, sulphur and uranium tracers. Mar. Environ. Res. 3, 225-243.

Sweeney, R. E., Liu, K.K. and Kaplan, I.R. (1978). Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: Stable Isotopes in the Earth Sciences. DSIR Bull. 220, (cd. B.W. Robinson], pp. 9-26, Wellington, New Zealand.

Tan, F.C. and Strain, P.M. (1979). Organic carbon isotope ratios in recent sediments in the St. Lawrence Estuary and the Gulf of St. Lawrence. Estuar. and Coastal Mar. Sci. 8, 213-225.

Tissot, B., Durand, B., Espitalié, J. and Combaz, A. (1974). Influence of nature and diagenesis of organic matter in formation of petroleum. Bull. Amer. Assoc. Petrol. Geol. 58, 499-506.

Vuk, C.T., Jones, M.A. and Johnson, J.H. (1976). The measurement and analysis of the physical character of diesel particulate emissions. Trans. Sot. Autom. Eng. Paper 76031, 556-597”

Wakeham, S. and Carpenter, R. (1976). Aliphatic hydrocarbons in sediments of Lake Washington. Limnol. Oceanogr. 21, 711-723.

Table 1. Precision of elemental and isotopic analyses on Tanner Basin sediments ($CO_3^{=}$-free) and $CHCl_3$-extractable organics[a]

Sample	% Carbon	% Hydrogen	%Nitrogen	N
Sediments	13.90±0.62	1.63±0.18	1.7130.10	5
$CHCl_3$-extractable	74.52±4.92 (62.5)[c]	11.52±0.57 (7.54)[c]	1.86±0.65 (3.83)[c]	5
	$\delta^{13}C$	δD	$\delta^{15}N$	
Sediments	-21.25±0.09 (-21.5)[d]	-110.8±4.6	8.22±0.09 (7.62)[d]	6
$CHCl_3$-extractables	-24.71±0.09 (-24.3)[c]	-168.9±7.7	-----	5

[a] Values from this study given as mean ± one standard deviation; isotope data in units of per mil (%).

[b] Samples too small for isotopic analysis.

[c] Ishiwatari et al. (1977).

[d] Peters et al. (1978).

Table 2. Suspended solids, % carbon, % nitrogen, N/C ratios and $\delta^{13}C$ in carbonate-free particulate from Los Angeles River stormwaters

Time Sample	Suspended Solids (mg/l)	% Carbon.	% Nitrogen	N/C	$\delta^{13}C$ (‰)
1000	23.6	15.2	1.48	.083	-25.20
1100	150	18.1	0.73	.035	-25.12
1200	47.0	14.5	0.79	.047	-24.35
1300	95.3	13.0	0.70	.046	-25.13
1400	216	14.1	1.08	.071	-24.80
1450	266	14.6	0.61	.036	-24.84
1500	280	15.7	0.73	.040	-24.51
1550	321	13.0	0.56	.037	-24.74
1600	362	10.2	0.36	.030	-24.93
1700	663	3.8	0.18	.041	-24.92
1800	1,520	3.9	0.18	.040	-25.00
$\overline{X} \pm 1\sigma$	358±424	12.4±4.6	0.67±.38	.046±.016	-24.86? 0.26

Table 3. Elemental compositions of organic components in suspended stormwater particulates

Sampling Time	SOLVENT EXTRACTABLE ORGANICS %C	%N	%H	Atomic Ratios H/C	N/C	HUMIC ACIDS %C	%N	%H	Atomic Ratios H/C	N/C	INSOLUBLE ORGANIC MATTER[a] %C	%N	%H	Atomic Ratios H/C	N/C	Ash%
1000	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1100	72.7	0.55	11.6	1.91	.006	38.0	4.95	4.22	1.33	.112	64.7	2.22	3.54	0.66	0.29	[illegible].4
1200	66.4	0.52	10.5	1.90	.007	--	--	--	--	--	--	--	--	--	--	--
1300	71.6	0.35	11.2	1.88	.004	42.3	5.33	4.78	1.36	.108	--	--	--	--	--	--
1400	75.2	--	11.7	1.87	--	37.5	4.46	4.18	1.34	.102	56.7	2.[illegible]	4.47	0.95	.032	[illegible].6
450	68.1	--	[illegible]9	1.92	--	39.3	4.75	4.34	1.33	.04	--	--	--	--	--	--
1500	75.6	0.38	11.5	1.83	.004	41.7	5.00	4.75	1.37	.03	61.2	1.83	4.73	0.83	.026	2.6
1550	74.9	0.25	11.4	1.82	.003	38.9	4.66	4.32	1.33	.103	66.6	2.11	4.71	0.85	.027	4.3
1600	78.6	--	12.8	1.96	--	41.3	4.53	4.61	1.34	.094	67.5	2.23	5.01	.89	.028	4.0
1700	77.4	--	12.7	1.96	--	33.2	3.53	3.53	1.28	.091	60.5	2.43	4.65	0.92	0.34	5.4
1800	73.6	--	11.9	1.95	--	26.6	2.81	3.06	1.38	.090	56.5	1.86	3.93	.84	.028	32.1
$\overline{X} \pm 1\sigma$	73.4± 3.9	0.41± 0.12	11.6± 0.7	1.90± 0.05	.005± .002	37.6± 5.0	4.45± 0.79	4.20± 0.57	1.34± 0.03	0.101± 0.008	62.0± 4.5	2.13± 0.19	4.36± 0.50	0.85± 0.09	.029± .003	

a = Data for insoluble organic matter calculated on an ash-free basis.

Table 4. Stable isotopic compositions (‰) of organic components in suspended stormwater particulate

	TOTAL EXTRACTABLE ORGANICS[a]		HUMIC ACIDS			INSOLUBLE ORGANIC MATTER		
Sampling Time	$\delta^{13}C_{PDB}$	δD_{SMOW}	$\delta^{13}C_{PDB}$	$\delta^{15}N_{AIR}$	δD_{SMOW}	$\delta^{13}C_{PDB}$	$\delta^{15}N_{AIR}$	δD_{SMOW}
1000	-26.15	-111.8	--	--	--	--	--	--
1100	-25.81	-112.6	-24.31	9.03	-90.8	-26.62	11.70	-62.4
1200	-26.02	-114.7	--	--	--	--	--	--
1300	-26.13	-109.1	-24.47	5.49	-104.9	--	--	--
1400	-26.05	-116.4	-24.04	5.31	-103.0	-26.88	11.71	-71.3
1450	-26.21	-113.7	-23.50	3.74	-97.3	--	--	--
1500	-25.92	-121.7	-23.13	3.76	-101.6	-26.48	11.04	-71.4
1550	-26.03	-115.7	-28.56	3.95	-102.5	-25.57	14.18	-62.0
1600	-26.09	-112.3	-23.97	3.94	-97.5	-25.74	14.32	-64.6
1700	-25.95	-116.4	-24.53	4.51	-101.9	-25.80	10.53	-77.4
1800	-26.36	-118.8	-24.67	5.81	-107.2	-27.53	16.1	-76.6
$\overline{X}$ ± 1σ	-26.07±0.15	-114,.8*3.5	-24.02±0.53	5.06±1.69	-100.7±4.9	-26.37±0.71	12.80*2.07	-69.4±6.5

a = $\delta^{15}N$ values were not obtained due to insufficient sample size.

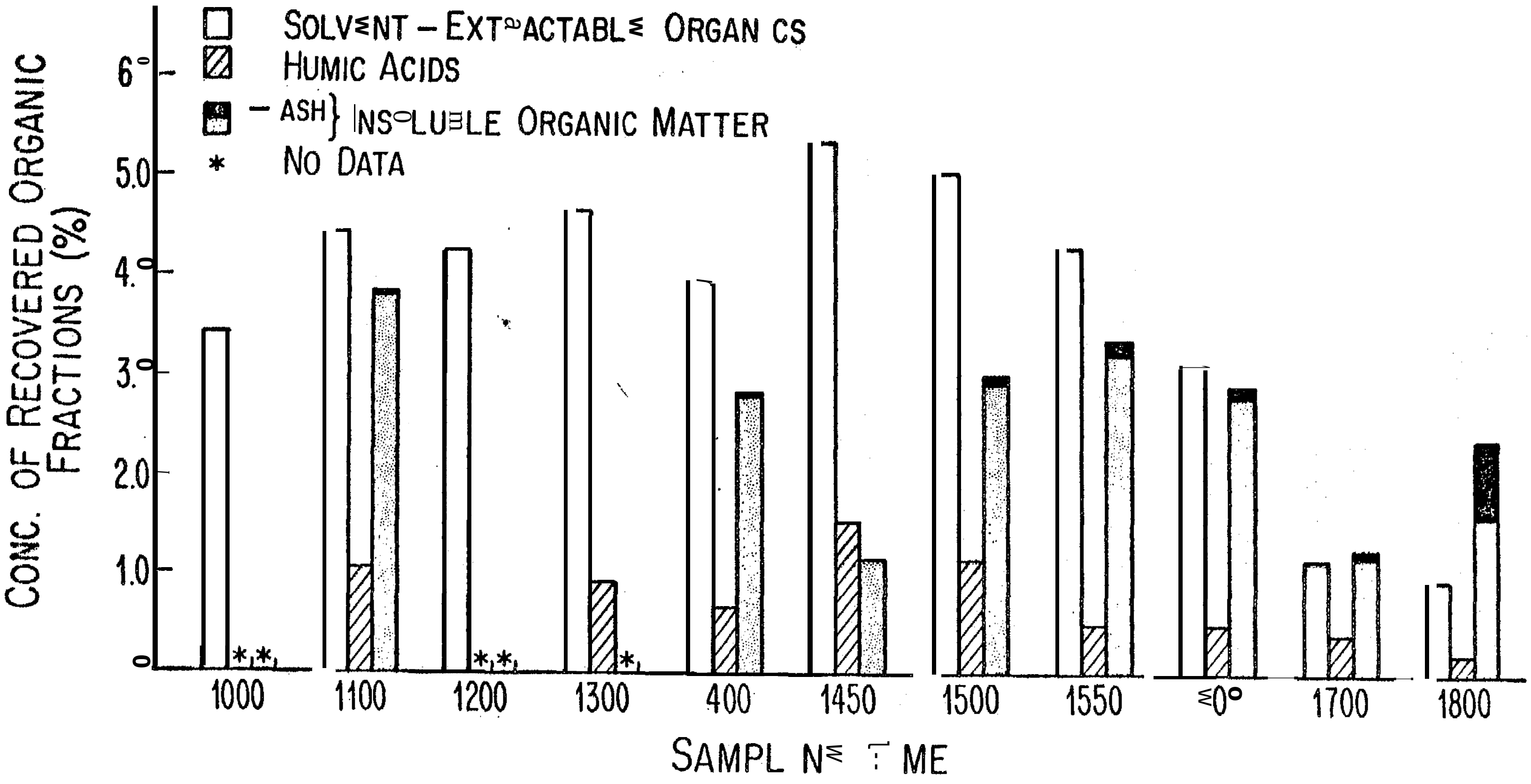
Table 5. Carbon content and isotopic composition (in units ‰) of lipid subfractions

Fraction	1000 hours $\delta^{13}C$	1000 hours %C	1450 hours $\delta^{13}C$	1450 hours %C	1700 hours $\delta^{13}C$	1700 hours %C
Total hydrocarbons	-26.30	80.8	-26.83	85.1	-26.67	84.6
Fatty Acids	--[a]	71.2	-25.02	87.7[b]	-25.94	79.0
Ketones	-22.48	71.5	-24.89	66.7	-24.09	77.4
Polar Compounds	-23.69	36.6	-25.64	48.0	-25.51	65.8
Non-elutable polar compounds	-25.04	62.8	-24.76	69.7	-25.09	67.6
Composite value	--	--	-25.62	71.9	-26.00	77.4
TEO	-26.15	--	-26.21	68.1	-25.95	77.4

a = insufficient sample

b = questionable value

LIST OF FIGURES


CONC. OF RECOVERED ORGANIC FRACTIONS (%)
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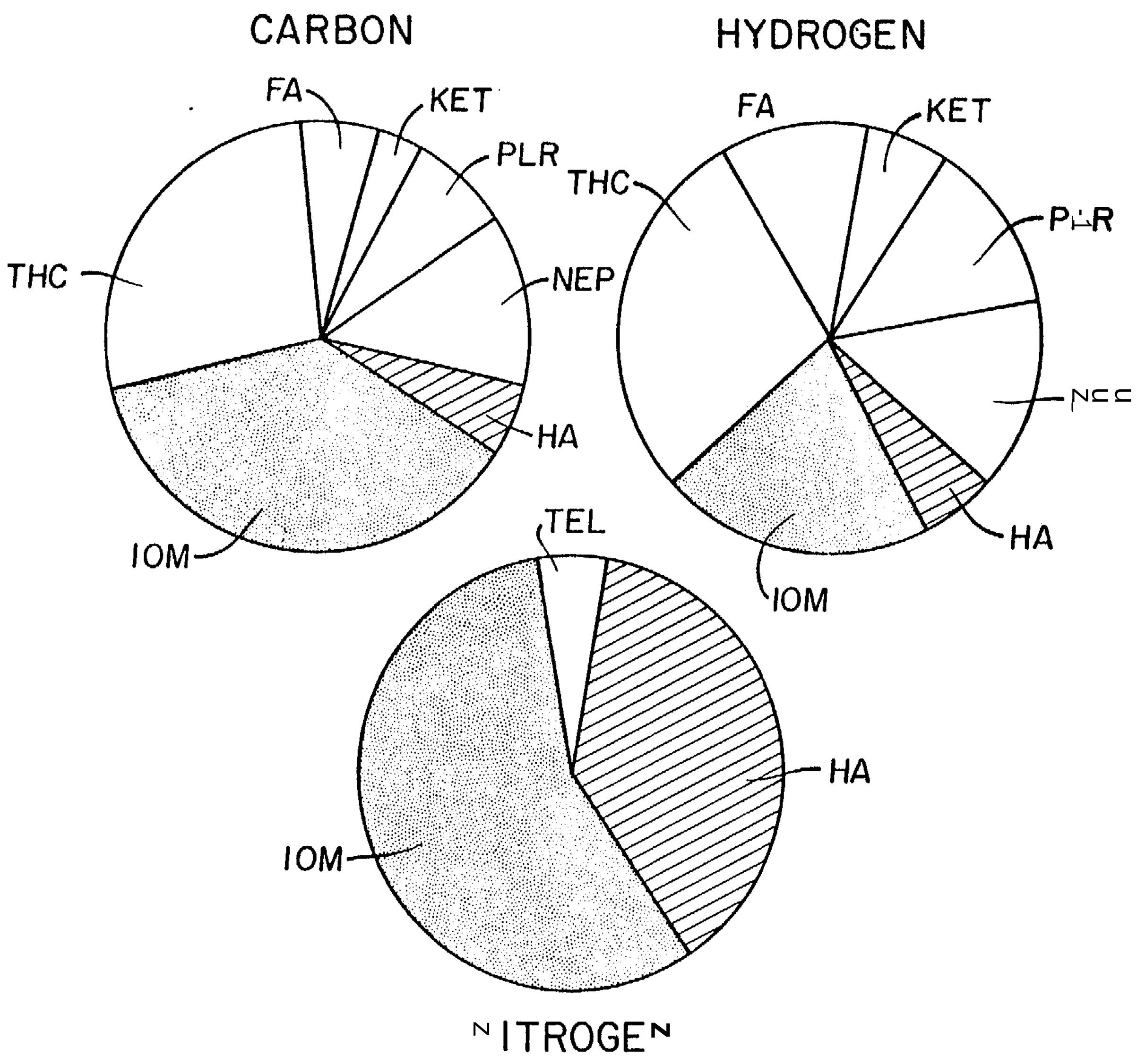
5.0
4.0
3.0
2.0
1.0
0
SOLVENT - EXTRACTABLE ORGANICS
HUMIC ACIDS
- ASH
INSOLUBLE ORGANIC MATTER
* NO DATA
1000
1100
1200
1300
400
1450
1500
1550
1600
1700
1800
SAMPLE TIME

Figure 1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NITROGEN

Figure 2

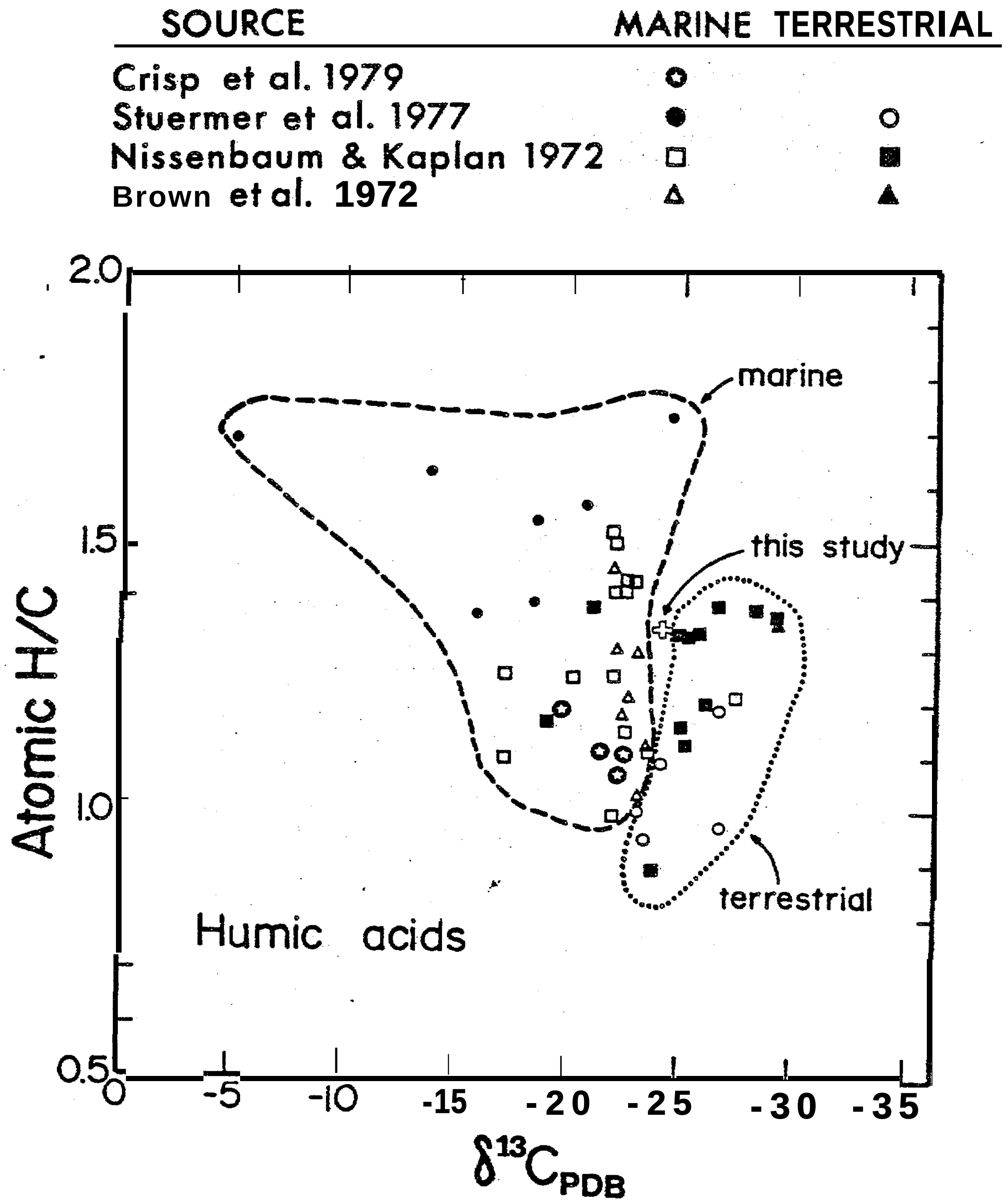
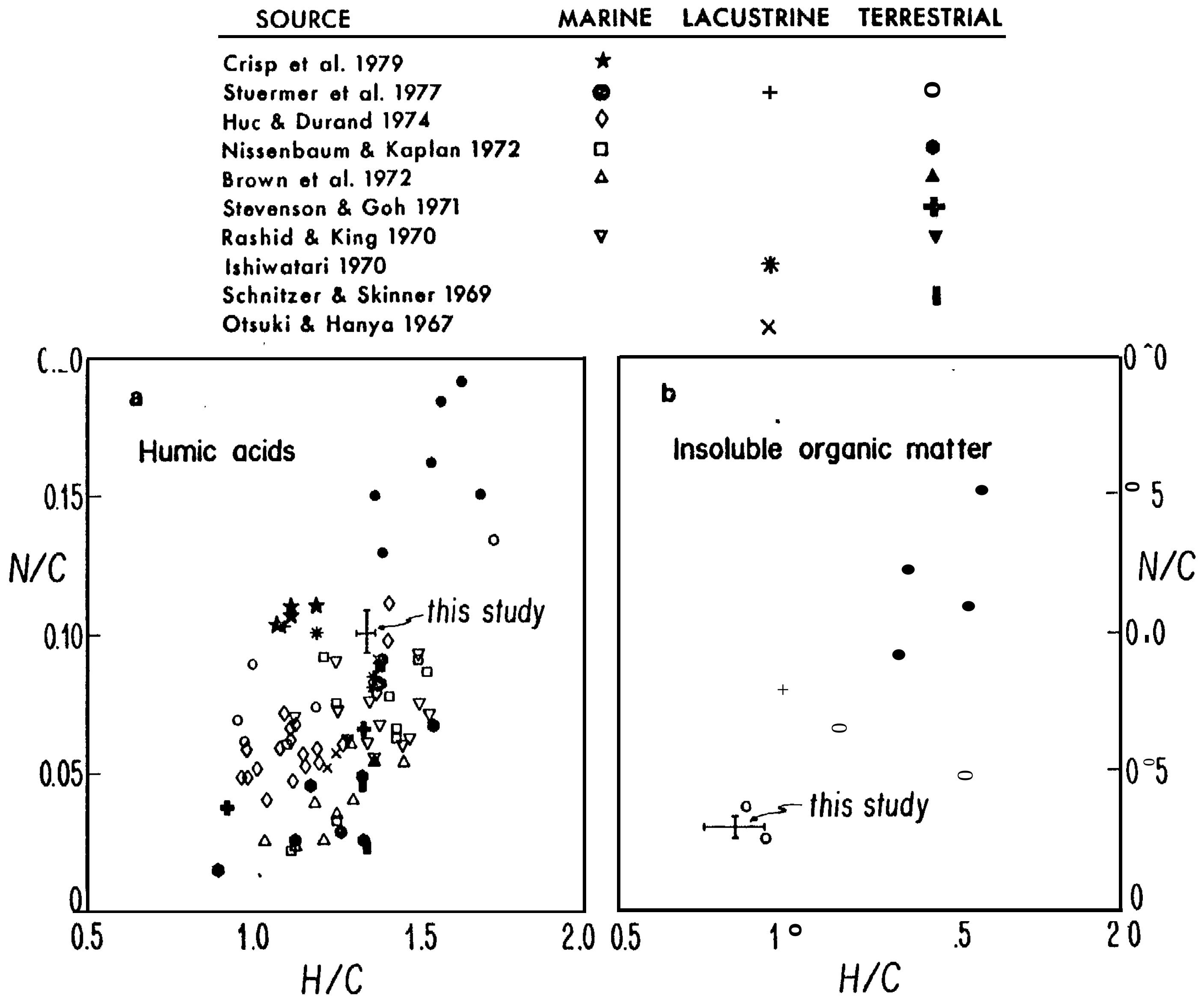

SOURCE
MARINE TERRESTRIAL
Crisp et al. 1979 ✪
Stuermer et al. 1977 ● ○
Nissenbaum & Kaplan 1972 □ ■
Brown et al. 1972 △ ▲
Atomic H/C
2.0
1.5
1.0
0.5
0
-5
-10
-15
-20
-25
-30
-35
$\delta^{13}C_{PDB}$
marine
this study
terrestrial
Humic acids

Figure 3


SOURCE
MARINE
LACUSTRINE
TERRESTRIAL
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Stuermer et al. 1977
Huc & Durand 1974
Nissenbaum & Kaplan 1972
Brown et al. 1972
Stevenson & Goh 1971
Rashid & King 1970
Ishiwatari 1970
Schnitzer & Skinner 1969
Otsuki & Hanya 1967
a
Humic acids
this study
N/C
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0.10
0.05
0
0.5
1.0
1.5
2.0
H/C
b
Insoluble organic matter
this study
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1.0
1.5
2.0
H/C

Figure 4

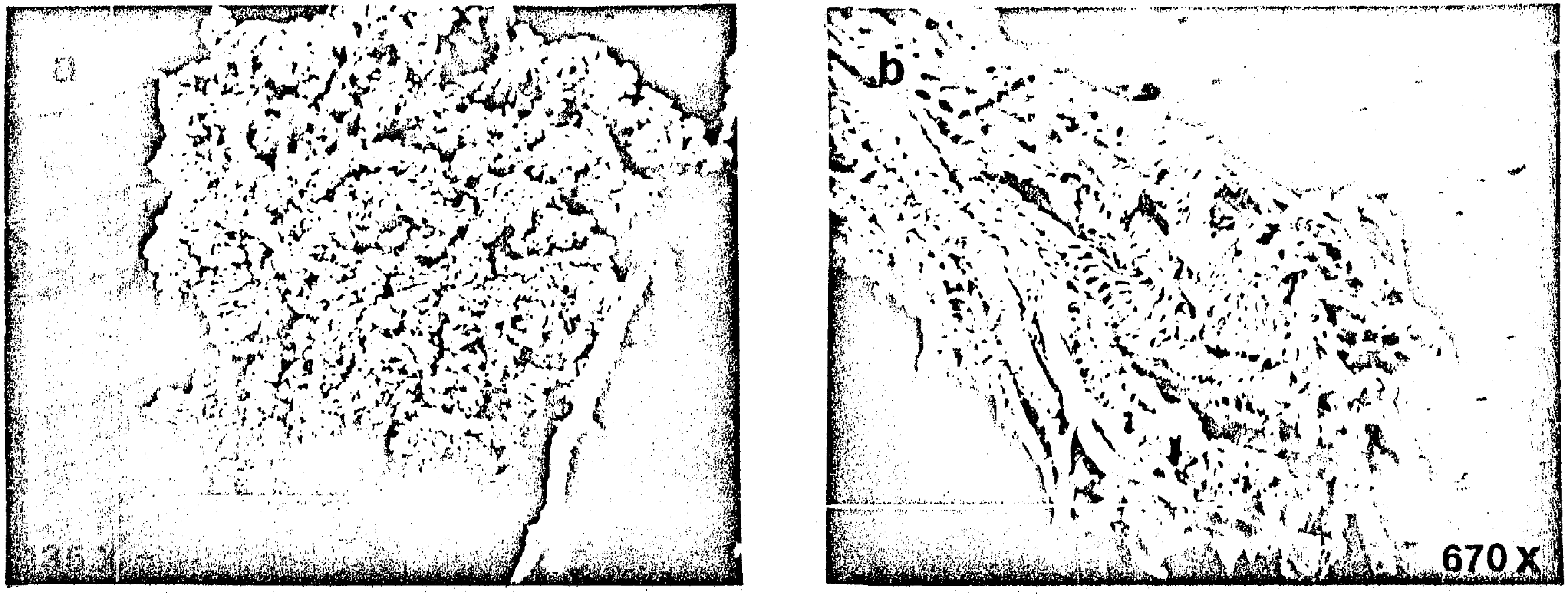

Figure 5

COMPOSITION OF EXTRACTABLE ORGANIC MATTER
IN MUNICIPAL WASTEWATERS

Robert Eganhouse
and
I.R. Kaplan

ABSTRACT

Wastewater effluents sampled from southern California's four largest treatment plants were analyzed for their extractable organic (oil and grease) contents. Subsequently, five organic fractions were isolated for the purpose of determining compositional and concentrational changes of the wastewaters with time. The mean levels of variation for major compound classes were low (12-22%}, the dominant class of organics being the fatty acids. Somewhat greater than half of the total extractable substances in non-sludge effluents were filterable, whereas > 93% were retained for sludge samples., Dissolved and particulate phases of the effluents differed greatly in their extractable organic compositions. This is a consequence of partitioning during the solution process.

INTRODUCTION

Organic matter extracted from wastewaters by solvents such as chloroform, trichlorotrifluoroethane or hexane is commonly termed oil and grease. This mixture of compounds is known to be an exceedingly complex (1,2) and variable component of municipal wastes (3,4). More importantly, it comprises many of sewage's most offensive, recalcitrant and toxic constituents (5,6). Hence, "oil and grease" represents a major challenge to plant engineers who must be concerned with the effectiveness of its removal *in* waste streams.

Many of the substances thought to be most biologically deleterious survive treatment and are ultimately discharged to the environment (7,8). Usually, rivers or the ocean serve as the primary repositories in which organics are either biochemically transformed (sometimes to more or equally dangerous species), taken up by organisms, exchanged with atmosphere or deposited in sediments. Surprisingly, very little is known about the detailed molecular nature, input rates and environmental fate of the vast majority of wastewater-derived organics, and only recently has this subject received serious attention (9,10). However, it is clear from available information that more comprehensive data are urgently needed.

In the present study, final effluents from the four largest municipal wastewater treatment plants in southern California were anlayzed for their extractable organic content and composition. The plants under consideration serve an estimated population of 9.8 million, and their effluents (which receive mainly primary treatment) are currently being discharged to the ocean via submarine outfall systems at a rate of 4 billion l/day. Our objective here is to present data on the temporal variability and phase partitioning of organic compound groups for these effluents. The results, which are the most extensive of their kind, should provide a baseline against which other wastewaters and future changes in the wastewaters of southern California can be compared. The detailed molecular characteristics of' extractable from these effluents will be discussed separately (11).

EXPERIMENTAL

Sampling

Duplicate (3ℓ) flow-proportioned 24-hour composite samples of final effluent were collected by plant personnel at each of the four treatment "facilities during 1979. A sampling protocol and descriptions of the effluents are given in Table 1. The dischargers sampled were: 1) JWPCP-CLASD) (Joint Water Pollution Control Plant--County of Los Angeles Sanitation Districts), 2) Hyperion City of Los Angeles, 2 effluents, cf. Table 1), 3) OCSD (Orange County Sanitation Districts) and 4) CSD (City of San Diego}. More detailed characteristics of these effluents treatment procedures and plant locations can be found elsewhere (4).

Upon collection, one of the two (3ℓ) samples was preserved at pi-i 1 (HCl) with 200 ml hexane and refrigerated (10'C). pending return to the laboratory. After homogenization of the other sample, two liters were filtered using precombusted GF/A glass fiber filters, the filtrate being preserved and refrigerated as before. The remaining effluent was stored frozen for subsequent elemental/ isotopic analysis of the particulate matter.

Analytical methods

The analytical scheme used here and described in greater detail elsewhere (13}, is depicted schematically in Fig. 1. Following extraction of the unfiltered and filtered wastewater samples with $CHCl_3$, the combined extracts were concentrated, dehydrated, treated for sulfur removal, analyzed gravimetrically and esterified. Exact portions of the extracts (in the range of 10-12 mg) were then quantitatively applied to thin layers of pre-activated silica gel and eluted with CH_2Cl_2. Upon development in iodine, five bands were isolated corresponding to: total hydrocarbons (THC), fatty acid, methyl esters (FA), ketones (KET), polar compounds (PLR) and non-elutable polar compounds (NEP). Chromatographic details have previously been described (13). Among other things, the polar fraction (PLR) contains hydroxy acids, sterols, alcohols and phenols--a" 1 common constituents of wastewaters (10,14). The FA fraction represents a combination of acid-hydrolyzable and free carboxylic acids.

The fractions were analyzed gravimetrically and, in the case of the THC, the resultant product was re-chromatographed on silica gel G by pentane elution to isolate aliphatic (Al) and aromatic (Ar) hydrocarbons. These subfractions were also analyzed. gravimetrically. The results presented here were achieved by triplicate weighings of solution residues at constant weight using a Mettler ME 22 electro-microbalance. Based upon replicate weighings of 40 µg residues, the instrumental precision is estimated at ±5%.

A study was conducted on two of the effluents, JWPCP and Hyp-7 (sludge), to estimate the extraction efficiency of this methodology. 'The results given in Table 2 show that removal of the non-polar, THC fraction was nearly complete ($\sim$ 97-99%). However, the polar NEP fraction was extracted with somewhat lower efficiency (86-94%), whereas other fractions gave intermediate results.

An effort was also made to quantify the recovery of extractable components after thin-layer chromatography. Table 3 lists data indicating that in most cases the recovery was > 90%. This is similar to results obtained by others using different techniques. The JWPCP samples gave consistently lower yields.

This is probably due to volatilization of phenolic compounds during rotary evaporation and volubility losses during solvent changes. Both of these phenomena were observed for the PLR fraction of JWPCP samples. Filtered samples a so generally showed lower recoveries than their unfiltered counterparts owing to the higher aqueous solubilities of more volatile (polar) components.

RESULTS AND DISCUSSION

Table 4 lists gravimetric data for the unfiltered samples of all effluents. Some general features are readily apparent. In terms of the TEO and THC content of treated wastewater, the order of predominance among southern California's dischargers is Hyp-7mi > JWPCP > CSD > OCSD > Hyp-5mi. This trend follows the mean annual oil and grease data obtained by treatment plant personnel (Table 1). Only minor rearrangements of the ranking are seen for NEP and PLR fractions. In contrast, the order does not appear to hold for FA and KET fractions.

The results for non-hydrocarbons are difficult to compare with other published data due to differences in the analytical strategies employed (15,16). Nevertheless, the hydrocarbon concentrations reported here do fall within the range of literature values (17, 18, 19). For this reason, we conclude that with regard to oil and grease content, southern California's wastewaters are probably typical of those found in other parts of the United States.

The coefficients of variation for the TEO measurements average around 12%, indicating that extractable organics are a fairly consistent component of these wastewaters. THC, FA, PLR and NEP fractions all showed mean coefficients of variation < 25%, whereas, the KET fraction was more than 37%. The higher variability in KET contents is due partly to imprecision in the chromatographic separation and isolation of this band, as well as the fact that the KET fraction represents only a small component of the total extractable. Gravimetric analysis of this fraction is, thus, subject to greater error. Considering collective measurements for individual effluents, the CSD data showed that lowest mean variation (∿ 16.6%). Hyp-7mi and JWPCP effluents had higher mean variations of ∿ 24%; whereas intermediate values were obtained for other effluents. These results suggest that variation in the concentration of major extractable organic constituents are relatively low, in the range of 12-22%. Furthermore, the variations appear to be similar for all the effluents examined. This is despite notable differences in the nature of their influents and treatment procedures (4).

Table 5 lists gravimetric data for the filtered samples. Excluding Hyp-7mi (sludge), all effluents contain comparable levels of "dissolved" organics. In general, however, the variations observed for any individual wastewater are much larger than for the bulk effluent. The data in Tables 4 and 5 can be used to calculate the percent extractable organic matter passing through the filter (Fig. 2). For non-sludge effluents, 31-49% of the TEO was found to be "dissolved". This is undoubtedly due to the abundance of water-soluble polar moieties such as phenols, hydroxy acids, and salts of fatty acids in the FA and PLR fractions. The majority of the hydrocarbons, fatty acids and keteones in non-sludge effluents are retained by the glass fiber filter; however, polar compounds represented by PLR and NEP fractions are, in most cases, distributed preferentially in the aqueous phase. The Hyp-7mi effluent has a rather low proportion of "dissolved" extractable substances because of its high solids levels (cf., Table 1) and the limited accommodation of oil and grease by water.

These features are demonstrated graphically in Figure 3 where calculated mean compositions of the total extractable organic matter in the "particulate" and "dissolved" phases are presented for each of the effluents. The former values were computed as the difference between measured concentrations in unfiltered and filtered samples. The "dissolved" phase simply represents data for the filtered samples. It should be recognized that colloidal material with diameters < 0.9μ may be a significant component in these samples (20,21). The difference in composition between "particulate" and "dissolved" phases clearly shows the influence of compound class polarity on phase distribution. Surprisingly, no fractionation were observed for the hydrocarbons, that is, the ratio of Al/Ar fractions was nearly identical for both phases. This may be due to presence in filtrates of substantial quantities of fine colloidal material in the form of emulsified hydrocarbons (22). If representative of the bulk hydrocarbon composition, these colloids would tend to mask fractionation due to molecular solution. Such an effect is further enhanced by the sparing solubility of hydrocarbons > C_{15}.

The dominant component in the "particulate" phase of non-sludge effluents appears to be the -fatty acids, in agreement with earlier findings (15,16). The CSD effluent maintained the highest proportion (∿ 59%), possibly reflecting the fact that it is the only plant treating strictly domestic wastes (4). It is well known that anaerobic digestion of sludge. solids leads to preferential removal of FA with respect to refractory, non-saponifiable constituents such as hydrocarbons (23). This accounts for the high THC and relatively lower FA contents of the Hyp-7mi sludge effluent. With the exception of the OCSD effluent, KET fractions comprised < 10% of the TEO. The proportion of extractable eluting in the PLR and NEP bands were similar in all effluents (∿ 9-19%), despite being highly variable in a temporal sense.

SUMMARY

The aim of this *work* was to document the compositional variation and phase partitioning of solvent-extractable organic substances in a number of wastewater effluents. In combination with molecular analysis (14) this provides new and revealing information on the nature of wastewater organics of possible use in evaluating the effects of waste discharges on the environment. Among the salient findings reported in this paper are the following:

1) Temporal variations in the concentration of extractable substances in a given effluent are smaller than variations between effluents. For the major components, mean coefficients of variation were from 12-22%.

2) Except in the case of digested sludge, fatty acids are the dominant compound class of sewage. Hydrocarbons, due to their biochemical stability, apparently survive treatment and are relatively enriched in sludge.

3) Most of the extractable material in non-sludge effluents (51 to 69%) is found in the "particulate" phase. In the case of digested sludge > 93% of the TEO were retained by filters.

4) The extractable organic composition of "particulate" and "dissolved" phases are markedly different, partitioning being governed by the aqueous accomodation of individual compound types.

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LIST OF FIGURES

REFERENCES

1. Giger, W., et al., "Analyses of Organic Constituents in Water by High-Resolution Gas Chromatography in Combination with Specific Detection and Computer-Assisted Mass Spectrometry." In Keith, L.H. (Ed.) Identification and Analysis of Organic Pollutants in Water (Ann Arbor: Ann Arbor Science), 433 (1976).

2. Burlingame, A.L. et al., "The Molecular Nature and Extreme Complexity of Trace Organic Constitutents in Southern California Municipal Wastewater Effluents". ibid., 557 (1976).

3. Loehr, R.C. and de Navarra, C.T., "Grease Removal at a Municipal Treatment Facility." Jour. Water Poll. Control Fed., 41, 142 (1969).

4. Eganhouse, R.P. and Kaplan, I.R., "Extractable Organic Matter in Municipal Wastewaters: 1. Petroleum Hydrocarbons--Temporal Variations and Mass Emission Rates to the Ocean. (Paper in this report).

5. Alexander, M., "Biodegradation of Chemicals of Environmental Concern." Science, 211, 132 (1981).

6. Borneff, J. and Kunte, H., "Carcinogenic Substances in Water and Soil--XVII: About the Origin and Evaluation of the PAH in Water." Arch. Hyg. Bakt., 149, 226 (1965).

7. Thorn, N.S., and Agg, A.R., "The Breakdown of Synthetic Organic Compounds in Biological Processes." Proc. R. Sot. Lend., 189, 347 (1975).

8. Saleh, F.Y. et al., "Selected Organic Pesticides, Occurrence, Transformation and Removal from Domestic Wastewater." Jour. Water Poll. Control Fed., 52, 19 (1980).

9. Sheldon, L.S. and Hites, R.A., "Sources and Movement of Organic Chemicals in Delaware River." Environ. Sci. Technol., 13, 574 (1979).

10. Garrison, A.W., et al., "GC/MS Analysis of Organic Compounds in Domestic Wastewaters." In Keith, L.H. (Ed.) Identification and Analysis of Organic Pollutants in Water (Ann Arbor: Ann Arbor Science), 517 (1976).

11. Eganhouse, R.P. and Kaplan, I.R., "Extractable Organic Matter in Municipal Wastewaters: 2. Petroleum Hydrocarbons--Molecular Characterization. (In preparation).

12. Schafer, H.A., "Characteristics of Municipal Wastewater." Southern Calif. Coastal Water Res. Proj. Ann. Rpt., 235 (1980).

13. Eganhouse, R.P. and Kaplan, I.R., "Extractable Organic Matter in Stormwater Runoff. 1. Transport Dynamics and Mass Emission Rates." Environ. Sci. Technol., 15, 310 (1981).

14. Eganhouse, R.P. and Kaplan, I.R., "Extractable Organic Matter in Municipal Wastewaters. 3. Polar Constituents--Molecular Characterization. " (In preparation). *

15. Hunter, J.V. and Heukelekian, H., "The Composition of Domestic Sewage Fractions." Jour. Water Poll. Control Fed., 37, 1142 (1965).

16. Viswanathan, C.V., et al., "Fatty Matter in Aerobic and Anaerobic Sewage Sludges." Jour. Water Poll. Control Fed., 34, 189 (1962).

17. Van Vleet, E.S. and Quinn, J.G., "Input and Fate of Petroleum Hydrocarbons Entering the Providence River and Upper Narragansett Bay from Wastewater Effluents." Environ. Sci. Technol., 11, 1086 (1977).

18. Tanacredi, J.T., "Petroleum Hydrocarbons from Effluents: Detection in the Marine Environment." Jour. Water Poll. Control Fed., 49, 216 (1977).

19. Barrington, J.W. and Quinn, J.G., "Petroleum Hydrocarbons and Fatty Acids on Wastewater Effluents." ibid., 45, 704 (1973).

20. Rickert, D.A., and Hunter, J.V., "Rapid Fractionation and Materials Balance of Solids Fractions in Wastewater and Wastewater Effluent." ibid., 39, 1475 (1967).

21. Sheldon, R.W., "Size Separation of Marine Seston by Membrane and Glass-Fiber Filters." Limnol. Oceanogr., 17, 494 (1972).

22. Tarras, M.J. and Blum, K.A., "Determination of Emulsifying Oil in Industrial Wastewater." Jour. Water Poll. Control Fed., 40, R404 (1968).

23. Heukelekian, H. and Mueller, P., "Transformation of Some Lipids. in Anaerobic Sludge Digestion." ibid., 30, 1108 (1958).

Table 1. Characteristics of Southern California Wastewater Treatment Plant Effluents Sampled during 1979.

Discharger	Municipality/ Agency	Frequency of Sampling	Nature of Effluent	General Characteristics[a]		
				Total Flow (1061 /day)	Total Suspended Solids (mg/l)	Oil and Grease (mg/l)
JWPCP	Los Angeles County Sanitation Districts	monthly	Primary + Digested sludge centrate	1390	195	39.9
Hyperion:	City of Los Angeles, Bureau of Sanitation					
Hyp-5mile		quarterly	Primary + Secondary	1336	7 5	19.0
Hyp-7mile		quarterly	Digested sludge + Secondary	18.1	7060	400.
OCSD	Orange County Sanitation Districts	quarterly	Primary + Secondary	712	140	26.0
CSD	City of San Diego	quarterly	Primary	484	143	36.7

[a] Data taken from reference (12).

Table 2. Extraction Efficiencies for Various Organic Fractions in JWPCP and Hyperion-7-mile effluents[a]

Effluent	Number of Extractions	% Recovered TEO	THC	FA	KET	PLR	NEP
JWPCP 3/14/79	Σ 1-3[b]	95.5	99.2	99.0	96.6	89.7	86.5
	4	1.3	0.3	0.4	1.1	3.8	3.5
	5	1.5	0.2	0.4	0.9	3.0	4.2
	6	1.1	0.2	0.2	0.8	3.0	4.5
	7	0.6	0.1	<0.1	0.6	0.5	1.3
Hyperion 7-mile 10/15/79	Σ 1-6[b]	95*4	96.6	92.8	95.8	96.1	93.8
	7	2.1	1.4	3.4	2.1	1.7	2.9
	8	1.6	1.3	2.6	1.6	1.4	2.3
	9	0.9	0.7	1.2	0.5	0.8	1.0

---

[a] Percentages given relative to total mass recovered for unfiltered samples.

[b] Represents number of extractions employed in this study.

Table 3. Recovery of Wastewater Organic Constituents following Thin Layer Chromatography[a]

Effluent	Number of Samples	Unfiltered Samples (%)	Unfiltered Samples (%)
JWPCP	9-11	88.0 ± 7.1	83.6 ± 9.6
Hyp-5mi	4	100.6 ± 1.1	96.8 ± 5.2
Hyp-7mi	4	95.1 ± 1.9	95.2 ± 1.0
OCSD	4	95.024.5	90.8 ± 3.4
CSD	4	102.0 ± 3.8	93.7 ± 2.9

[a] Recoveries are equivalent to: $\left\{\sum \text{Fraction weights/mg TEO applied} \cdot 100\right\}$ and are given as means ± 1 standard deviation,

Table 4. Concentrations (mg/l) of Extractable Organic Constituents in Municipal wastewater Effluents[a]

Effluent	Sampling Date	Total Extractable Organics	Total Hydrocarbons	Acids	Ketones	Polar Compounds	Non-elutable Polar Compounds
JWPCP:	1/15/79	59.8	10.6	18.0	2.51	13.2	9.99
	2/15/79	75.0	14.2	24.7	1.29	20.1	11.9
	3/14/79	71.2	14.3	26.2	3.38	8.61	5.98
	4/4/79	71.5	16.6	21.5	2.27	12.9	9.98
	5/15/79	67.5	13.0	23.6	4.27	12.8	11.7
	6/15/79	77.9	15.6	26.6	1.92	12.5	3.1
	7/16/79	79.8	15.9	28.5	1.89	10.1	3.9
	8/15/79	83.6	20.9	28.3	2.13	8.82	2.8
	9/13/79	69.0	18.2	22.7	1.92	4.51	3.1
	10/15/79	65.6	16.1	24.8	1.25	8.10	8.77
	11/15/79[b]	---	---	---	----	----	-----
	12/13/79	75.0	14.0	27.7	1.30	6.98	12.5
x + s		72.4±6.8	15.5±2.8	24.8±3.2	2.19± 0.93	10.8± 4.2	11.2± 2.4
Hyp-5mi:	1/15/79	47.3	5.09	22.2	2.41	8.33	9.31
	4/18/79	48.8	6.92	21.5	3.60	8.72	8.83
	7/16/79	43.8	5.70	20.5	1.18	7.92	8.25
	10/16/79	46.2	6.52	18.6	3.73	8.78	8.83
x + s		46.5±2.1	6.06±0.82	17.7± 5.2	2.73± 1.19	8.44± 0.40	8.80± 0.43
Hyp-7mi:	1/15/79	1088.	397.	239.	48.2	193.	157.
	4/18/79	994.	374.	176.	46.1	204.	142.
	7/16/79	796.	297.	160.	25.2	175.	120.
	10/15/79	717.	297.	127.	18.1	138.	87.9
x + s		899 ±172	341 ±52	176 ± 47	34.4± 15.0	177 ± 29	127 ± 30

continued on next page

Table 4. continued

Effluent	Sampling Date	Total Extractable Organics	Total Hydrocarbons	Fatty Acids	Ketones	Compounds	Non-elutable Polar Compounds
OCSD :	1/15/79	40.3	5.69	12.6	3.61	7.01	8.19
	4/12/79	63.2	10.9	20.3	4.28	9.17	12.5
	7/16/79	47.3	6.95	18.6	3.64	7.41	9.58
	10/16/79	50.1	7.75	15.8	6.30	9.48	10.7
x ± s		50.2±9.6	7.82±2.22	16.8±3.4	4.46±1.27	8.27±1.24	10.2±1.8
CSD :	1/16/79	56.3	11.8	24.8	1.18	8.78	9.41
	4/17/79	58.9	8.24	31.5	2.04	9.66	9.68
	7/17/79	65.3	10.4	34.3	1.33	8.15	9.76
	10/16/79	69.1	18.7	33.2	1.27	9.39	10.6
x + s		62.4±5.8	12.3±4.5	31.0±4.2	1.46±0.40	9.00±0.67	9.86±0.51

[a] Analytical results shown here are for unfiltered samples only.

[b] Sample lost.

Table 5. Concentrations (mg/ of Extractable Organic Constituents in Filtered Samples of Municipal Wastewater Effluents.

Effluent	Sampling Date	Total Extractable Organics	Total Hydrocarbons	Fatty Acids	Ketones	Polar Compounds	N[illegible] Polar Compounds
JWPCP:	1 15 79	28.0	2. 8	5.78	0.60	6.[illegible]6	7.17
	2/15/79	20.0	1.78	3.60	0.59	6.69	4.84
	3/14/79	27.2	2.36	4.68	0.65	7.[illegible]0	7.95
	4/4/79	22.6	1.53	4.2	0.32	2.71	5.27
	5/15/79	21.1	1.29	4.02	0.47	3.33	b
	6/15/79	25.8	2.13	3.26	2.01	7.42	7.67
	7/16/79	23.5	2. 8	4.78	1.28	7.11	6.26
	8/ 5 79	29.0	3.29	5.42	1.35	7.[illegible]6	7.64
	9/13/79	22.3	1.6	3. 9	0.90	7.[illegible]2	7.34
	10/15/79	23.6	2.19	5.12	1.47	6.04	7.13
	11/15/79[a]	----	----	----	----	----	----
	12/13/79[a]	----	----	----	-----	----	----
x ± s		24.3±3.0	2.05±0.56	4.41±0.90	0.96±0.54	6.12+1.73	6.81±1.11
Hyp-5mi:	1/15/79	17.2	1.92	5.57	0.45	3.32	4.64
	4/18/79	23.4	3.04	8.17	1.43	4.44	.69
	7/ 6/79	22.8	2.90	8.32	0.93	4.30	5.96
	10/16/70	21.4	3.10	8.80	0.58	4.54	5. 4
x ± s		2 .2±2.8	2.74±0.55	7.72±1.46	0.85±0.44	4.15±0.56	5.11±0.61

continued on next page

Table 5. Continued

Effluent	Sampling Date	Total Extractable Organics	Total Hydrocarbons	Fatty Acids	Ketones	Polar Compounds	Non-elutable Polar Compounds
Hyp-7mi:	1/15/79	81.0	17.6	11,0	13.1	21.6	14.2
	4/18/79	64.5	13.2	6.56	11.1	19.9	10.8
	7/16/79	50.3	9.42	5.05	8.19	18.5	7.11
	10/15/79	41.5	7.08	4*00	6.91	13.8	7.17
x + s		59.3±17.3	11.8±4.6	6.65±3.08	9.82±2.80	18.4±3.3	9.82$3.39
OCSD:	1/15/79	19.3	1.23	4.71	0.33	4.79	5,89
	4/12/79	20.2	1.63	6.51	0.42	4.56	5.35
	7/16/79	23.0	1.73	7.09	0.71	4.38	6.51
	10/16/79	33.3	4.80	13.5	1.67	6.31	5.42
x + s		23.8±6.2	2.35±1.65	7.95±3.80	0.78±0.61	5.01±0.88	5.79±0.54
CSD:	1/16/79	12.1	1.22	2.92	0.18	3.93	3.41
	4/17/79	21.1	1.78	5.52	2.45	4,25	6.08
	7/17/79	23.3	2.21	7.38	2.35	3.98	5.85
	10/16/79	22.2	2.66	7*37	0.67	3.51	5,72
x + s		19.7±5.1	1.97±0.61	5.80±2.11	1.41±1.16	3.92±0.31	5.27±1.25

[a] Sample lost.

[b] Questionable data obtained.

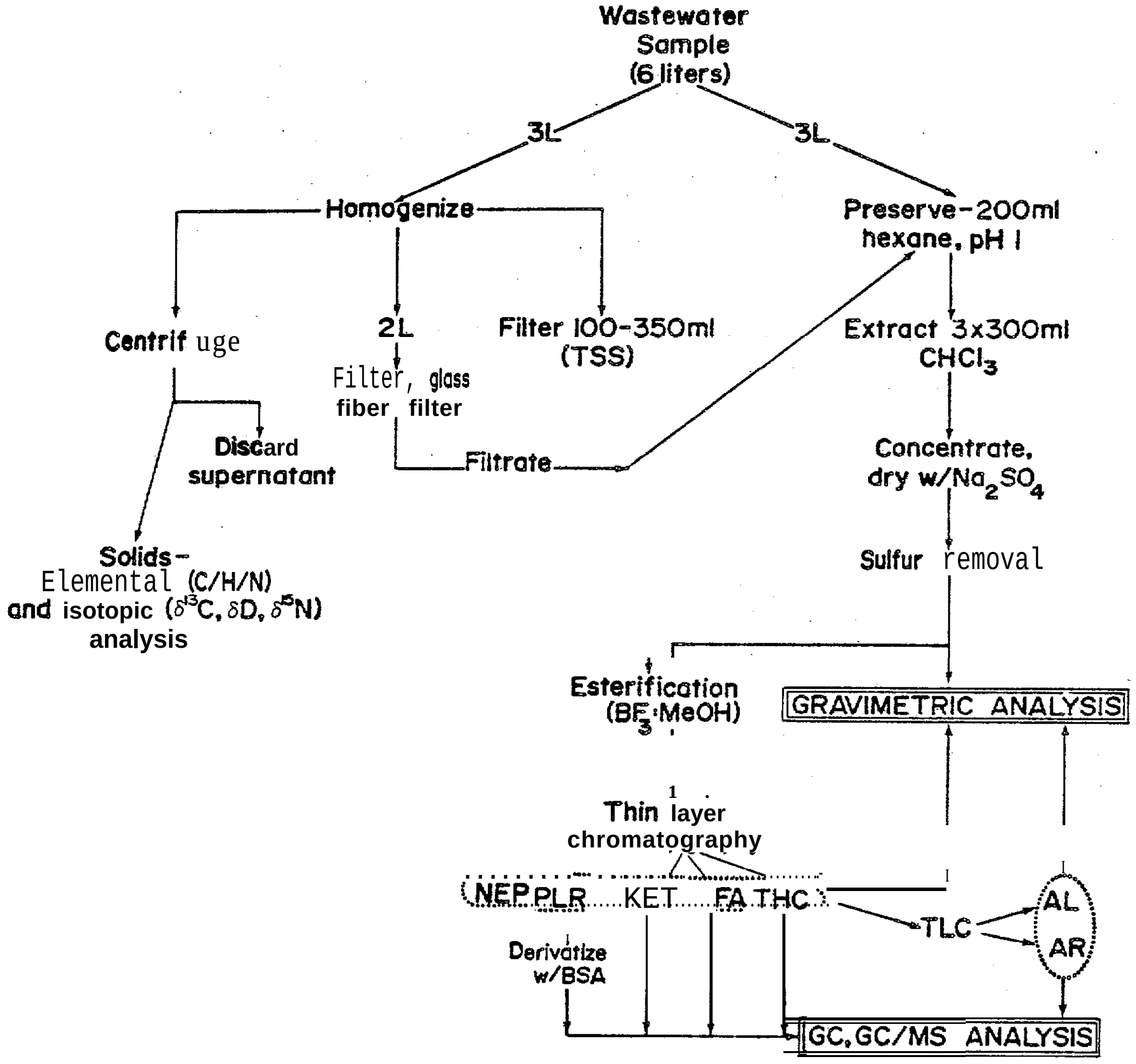
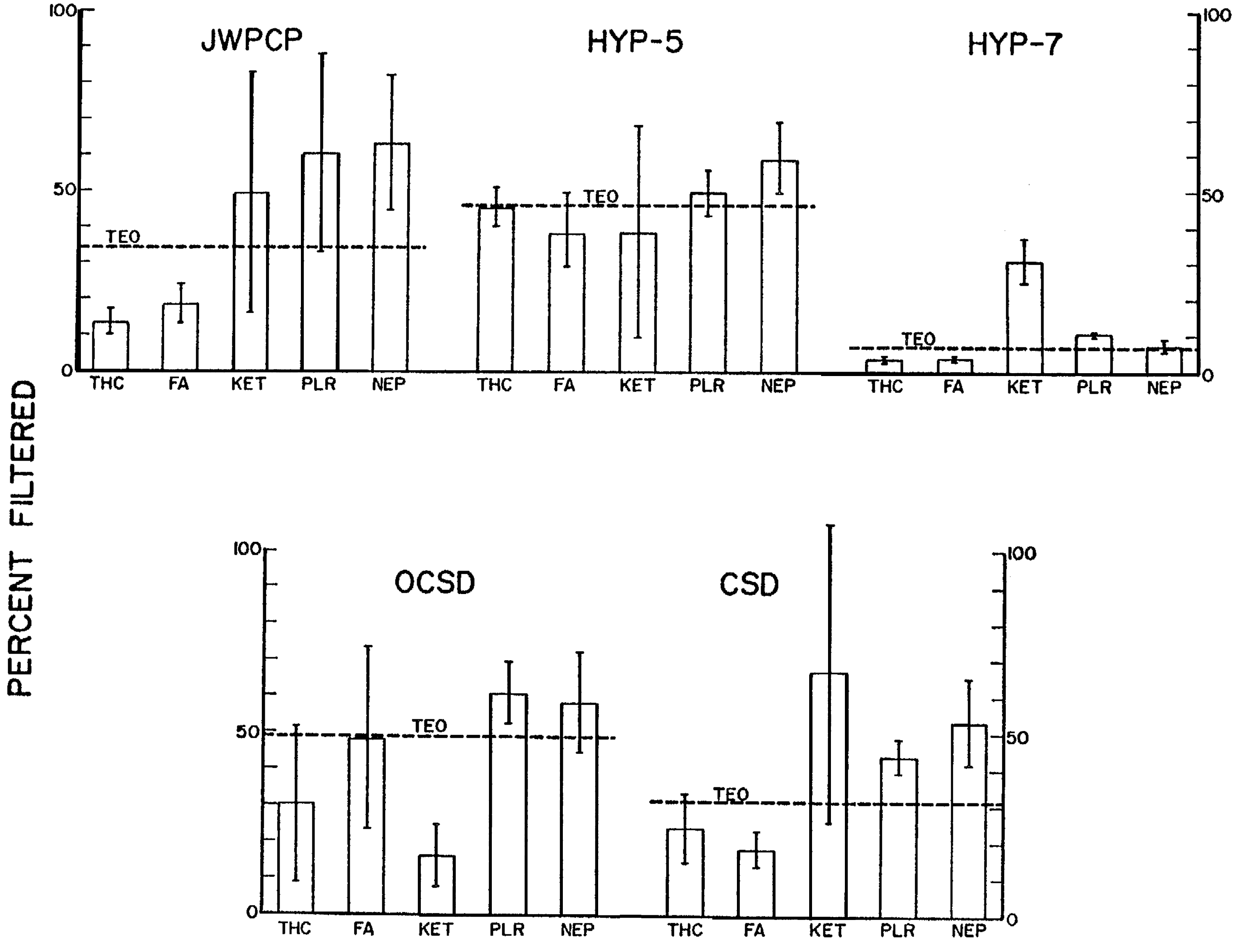

Wastewater Sample (6 liters)
3L
3L
Homogenize
Preserve-200ml hexane, pH 1
Centrifuge
2L
Filter, glass fiber filter
Filter 100-350ml (TSS)
Extract 3x300ml $CHCl_3$
Discard supernatant
Filtrate
Concentrate, dry w/Na_2SO_4
Solids- Elemental (C/H/N) and isotopic ($\delta^{13}C$, δD, $\delta^{15}N$) analysis
Sulfur removal
Esterification (BF_3:MeOH)
GRAVIMETRIC ANALYSIS
Thin layer chromatography
NEP PLR KET FA THC
TLC
AL
AR
Derivatize w/BSA
GC, GC/MS ANALYSIS

Figure 1


PERCENT FILTERED
100
50
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HYP-5
HYP-7
OCSD
CSD
TEO
THC
FA
KET
PLR
NEP

Figure 2

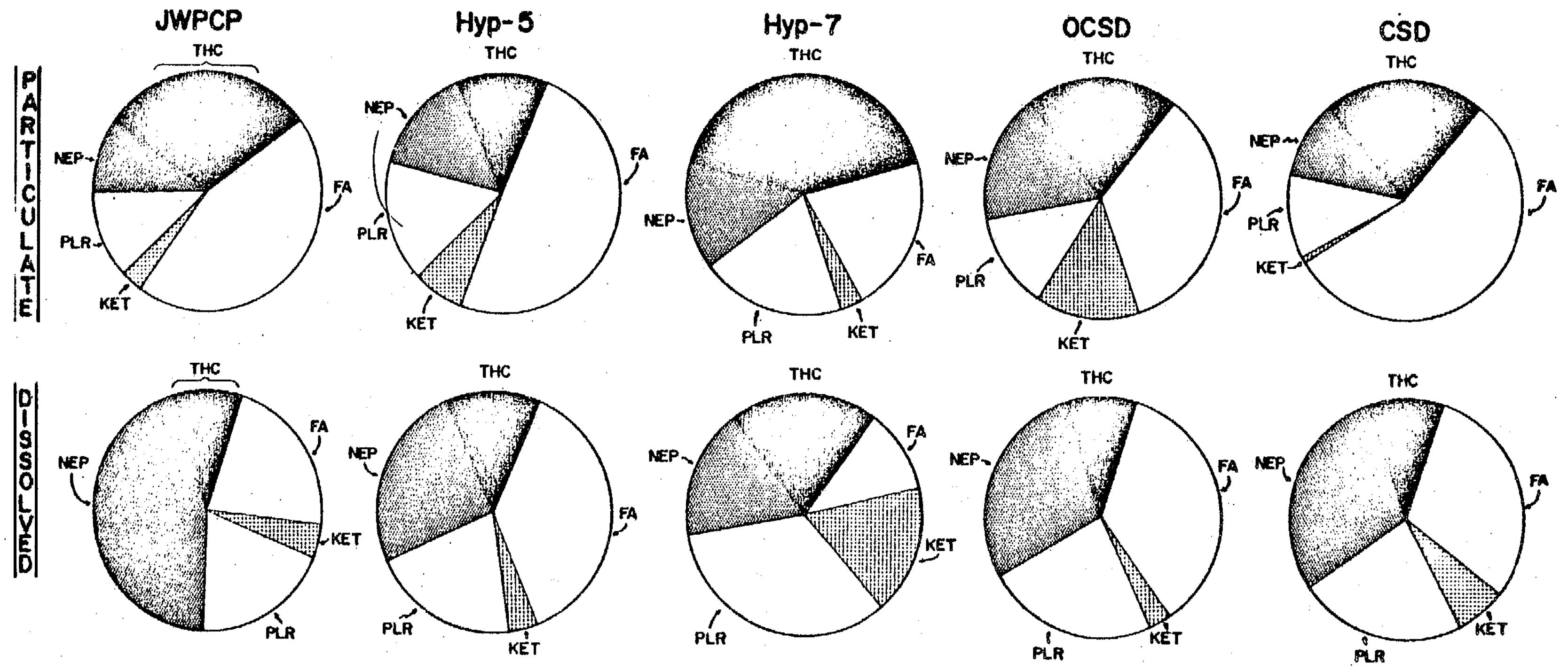
JWPCP
Hyp-5
Hyp-7
OCSD
CSD
PARTICULATE
DISSOLVED
THC
NEP
PLR
KET
FA

Figure 3