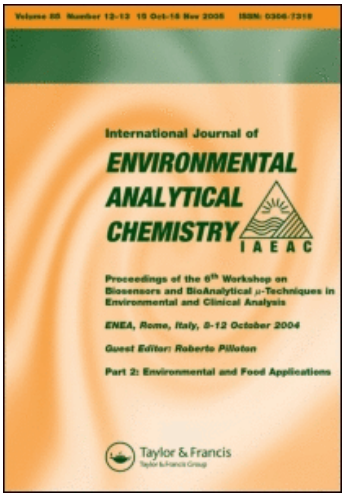

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Simoneit, Bernd R. T.(1982) 'Some Applications of Computerized GC-MS to the Determination of Biogenic and Anthropogenic Organic Matter in the Environmentt', International Journal of Environmental Analytical Chemistry, 12: 3, 177 — 193
To link to this Article: DOI: 10.1080/03067318208078326
URL: http://dx.doi.org/10.1080/03067318208078326

Intern. J. Environ. Anal. Chem. 1982, Vol. 12, pp. 177–193
0306-7319/82/1204-0177 $06.50/0

Printed in Great Britain

Some Applications of Computerized GC-MS to the Determination of Biogenic and Anthropogenic Organic Matter in the Environment†

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(*Received January 9, 1982*)

This is an overview of the application of organic mass spectrometry and ancillary techniques to the analysis of organic matter in environmental research. Such organic matter is usually analyzed in terms of gas, bitumen (lipids), and "kerogen", with asphaltenes and humic substances for some samples. This approach is illustrated with some examples and the origin, the environmental history and the nature of secondary products of this organic matter can be evaluated by using the data derived from both specific molecular and bulk chemical (also physical) analyses. Evaluations of production and fluxes and cross-correlations can thus be made by the application of the same separation and analytical procedures to samples from different environmental compartments (eg., biota, atmosphere, hydrosphere, lithosphere, etc.).

INTRODUCTION

Organic mass spectrometry (MS) has been a tool of analytical chemistry for about 20 years, and it has been applied to environmental research over the past decade, mainly in conjunction with gas chromatography (GC). New mass spectrometric techniques such as chemical ionization MS, high resolution GC-MS, high resolution mass spectrometry, field ionization and desorption MS, tandem mass spectrometry (MS-MS) and pyrolysis GC-

†Presented at the workshop on the chemistry analysis of Hydrocarbons in the Environment Barcelona, November 1981

MS, all with the associated online computers and processors are providing new ways to tackle the analytical problems associated with the analysis of complex organic mixtures. The overall field of mass spectrometry has been extensively reviewed.[1-9]

Here I illustrate the utility of some of these various instrumental methods in environnmental research with some examples of typical data and interpretations. The organic matter of environmental samples can be divided into the following categories:

Volatiles	Lipids (bitumen)	Fulvic/humic acids (asphaltenes)	Humin (kerogen)
C_1-C_{15}, CO_2 terpenes, etc.	C_8-C_{40+}	Macromolecular, M.W. $\sim 10^3 - > 10^6$	Macromolecular (>fulvic/humic acids)
Minor amt. of total org. C	Variable amount	Variable amount	Major amount

These categories are based upon the usual operational limits imposed by the organic chemical separation and identification procedures.

Mass spectrometric instrumentation

Low resolution mass spectrometric requirements for most organic compounds of ecochemical significance can be satisfied with either a magnetic or quadrupole mass spectrometer of current design and construction. The quality of the data from either are quite comparable.

Electron impact (EI) is by far the most common method used for sample ionization in mass spectrometry. The usual 70 eV energy causes extensive molecular fragmentation with a high yield of ions and to date the best sensitivity, whereas both EI at lower voltages ($\sim$15 eV or less) and chemical ionization are lower energy processes resulting in less fragmentation and thus stronger molecular ion signals, but overall lower sensitivity.

The most commonly utilized inlet system to the mass spectrometer is the gas chromatograph,[8] however, other methods as for example batch inlets, direct insertion probes, liquid chromatographs and pyro-probes have also been used. The application of the GC/MS technique to environmental research has been extensive and has been amply reviewed.[10-12]

High resolution mass spectrometry (HRMS) has been applied primarily to group type analyses to determine H to C and heteroatomic

composition (eg., 13, 14). GC-HRMS is beginning to be applied and has great potential in the use of accurate mass elemental composition chromatograms (vis a vis nominal mass chromatograms at low resolution) of characteristic fragment ions.[15]

Most MS techniques utilize dedicated computer systems and numerous such systems have been assembled for acquisition and processing of mass spectrometric data. They all basically consist of the same programs for data processing and searching of data files.[16,17] The commercial systems are also similar. Most systems have the capability of plotting mass spectra with optional background deletion, scale expansion and scan summing, plotting of total ion current traces and mass chromatograms for GC-MS analyses, listing of prominent ions and optionally, data file searching.

Applications

Analyses of volatile compounds are usually accomplished by GC and confirmed by GC-MS.[14,18–21]

The lipids of environmental samples are extracted with solvents and commonly separated by thin-layer or column chromatography after esterification of free fatty acids (Figure 1). The discrete fractions are then

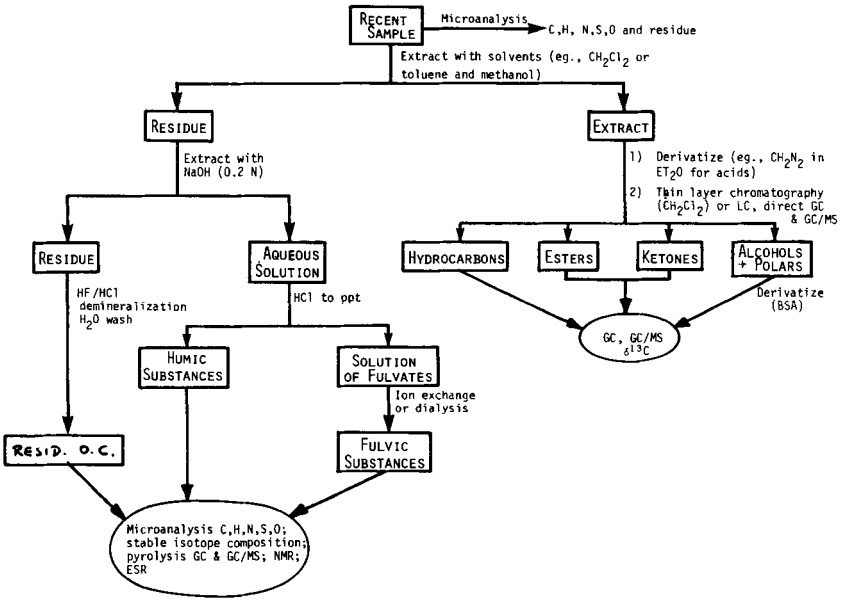


FIGURE 1 Schematic for fractionations and chemical separations of organic matter in environmental samples.

analyzed by GC and GC/MS (eg., 22). It should be noted that lipids of such recent samples compared to geologically ancient samples contain more labile and functionalized compounds (eg., olefins).

Argentation-TLC can be utilized to separate saturated from olefinic compounds and 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 chemical alteration (eg., hydrogenation), stable isotope ratios, UV-visible spectrophotometry, infrared spectrophotometry and nuclear magnetic resonance spectroscopy.

Humic and fulvic substances can be extracted from environmental samples with aqueous sodium hydroxide after lipid removal (eg., 23,24). The residual organic matter, the humin, is concentrated in samples with a high mineral content by treatment with hydrochloric and hydrofluoric acids (eg., 25,26). Humin (also humates) can be characterized mainly by bulk properties and to a limited extent by chemical degradation (cf., Figure 1). 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[24] and maceral description. Pyrolysis GC and pyrolysis GC-MS have also proven to be of utility for analysis of humin and humates, since they provide a fingerprint pattern and are rapid analytical methods.[27,28]

DISCUSSION

Lipid data

Three types of data are usually monitored in GC-MS analyses of lipid fractions: homologous compound series, molecular markers and the unresolvable complex mixture of branched and cyclic compounds (the hump). Both homologies and molecular markers originate from primary biological precursors with some diagenetic alteration (eg., 29) and some examples of the major classes of such hydrocarbon compounds are summarized in Figure 2. Examples of typical GC analyses of some environmental samples are shown in Figure 3. They are total hydrocarbons in oysters from the Arabian Gulf, illustrating a comparison of the natural biogenic components (resolved peaks in Figure 3a) with the degraded petroleum residues in a contaminated oyster (major hump in Figure 3b).[30] The major biogenic components in these examples are C_{21} and C_{25} polyolefins present in both fractions. The origin of the major hump from petroleum was confirmed by the composition of the minor molecular marker compounds.[30]

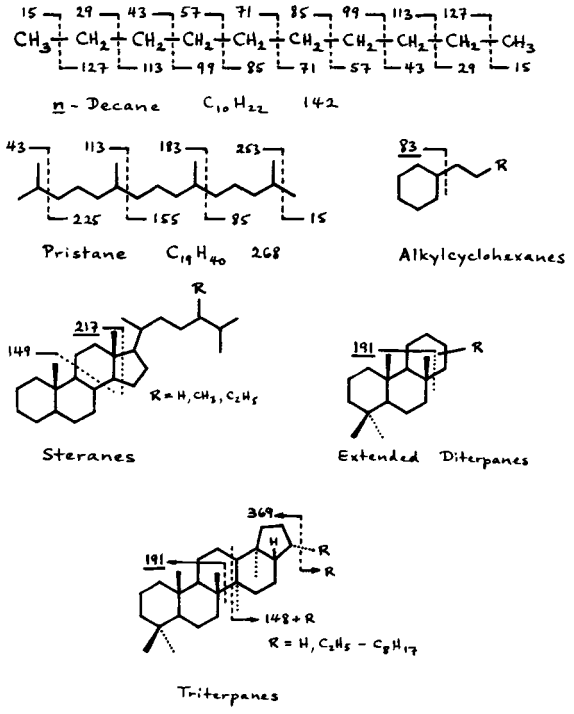


FIGURE 2 Chemical structures of some common hydrocarbon modecular markers with their major mass spectrometric fragmentation patterns.

Some salient features of the data of a typical GC-MS analysis are shown in Figure 4 (total hydrocarbons of a marine sediment of recent age, contaminated by petroleum seepage—Santa Barbara Basin).[31] The total ion current trace is shown in Figure 4a, where the dominant peaks are *n*-alkanes and a bimodal hump is evident above the base line. The molecular markers are distinguished by plotting key ions (eg., m/z 99 for *n*-alkanes, Figure 4b, m/z 191 for extended diterpanes and triterpenoids, Figure 4c, or m/z 217 for steranes, Figure 4d—cf., structures in Figure 2), then analyzing and interpreting the corresponding mass spectra of the various ion maxima. The basic procedures for the interpretation of mass spectra are found in the works by McLafferty,[32] Biemann[33] and Silverstein *et al.*[34]

Some examples of hydrocarbon distributions extracted from aerosol samples are shown in Figure 5.[35] Comparisons are made between rural and urban aerosols and natural plant wax.[35,36] The *n*-alkanes range from

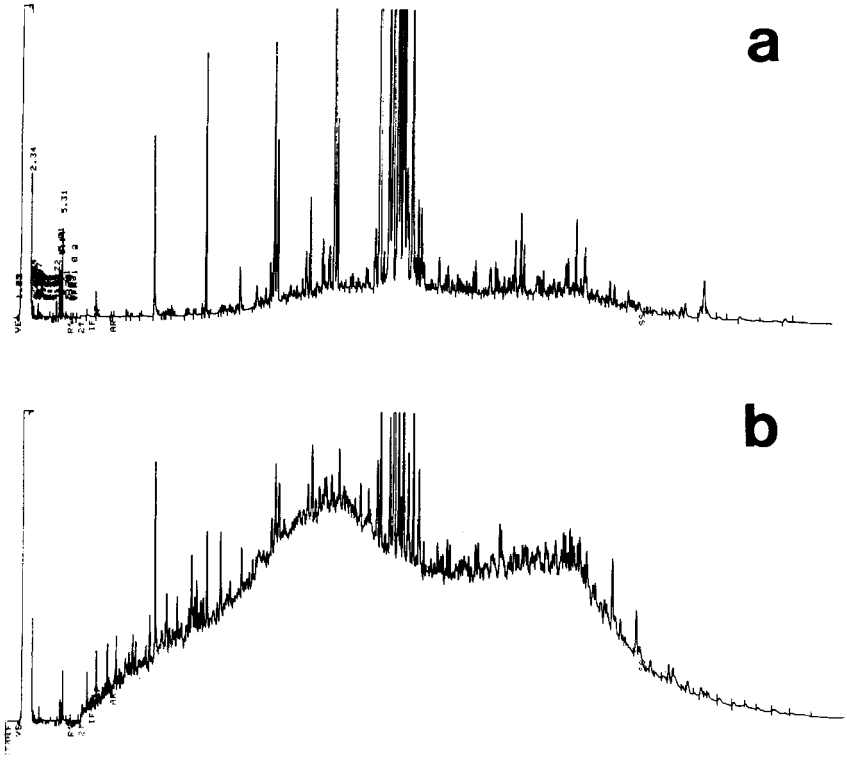


FIGURE 3 Gas chromatograms (FID) of fractions I (primarily hydrocarbons) of extracts of oysters: (a) from Ras az Zaur, (b) from Mina Abdullah[30].

about C_{15} to C_{34} with an odd carbon number predominance (CPI > 1.2[36]) for the rural samples from Lake Tahoe (during summer) and Mt. Lassen (Figure 5a–c). The homologs > n-C_{23} are believed to be derived chiefly from waxes of vascular plants.[36] These distributions compare quite favorably with the n-alkane distribution of the mixed grass wax (Figure 5d). The dominance of n-C_{29} and n-$C_{27} \simeq n$-C_{29} may indicate a mixed origin from forest and grassland.

The ratios of branched and cyclic hydrocarbons to the n-alkanes can be used as an approximate measure of the level of petroleum contamination (e.g. 31). Values of 10–200 have been observed for sediment lipids contaminated with petroleum seepage, whereas the natural hydrocarbons derived from vascular plants exhibit no hump and this ratio is < 1.0 for aerosols over oceanic areas.[36] For these samples the hump: n-alkane ratio ranges from 1.4 to 3.4, indicating some contamination by petroleum

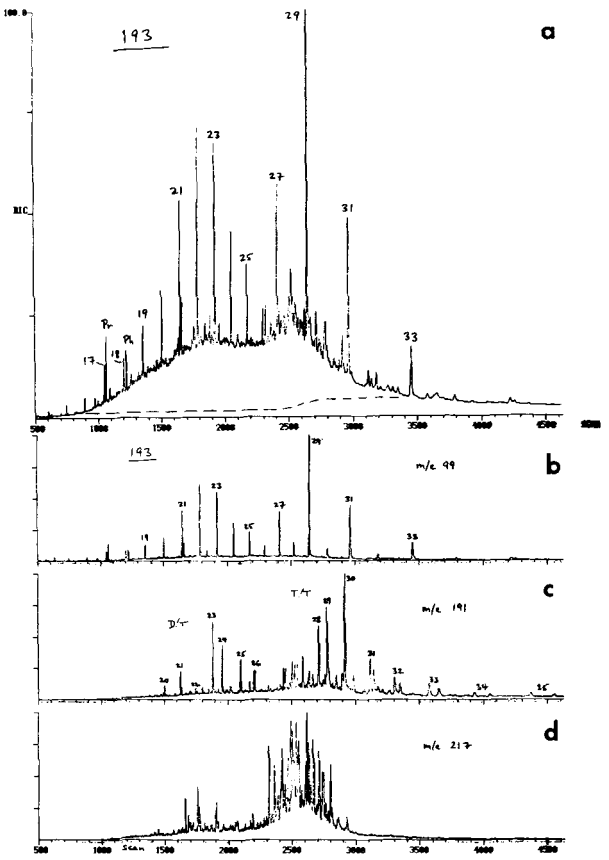


FIGURE 4 Salient features of a GC/MS analysis showing: (a) Total ion current trace and mass chromatograms: (b) m/z 99; (c) m/z 191; and (d) m/z 217. (The carbon numbers of the homologs are indicated in the plots).

residues. The hydrocarbons of the sample from Mt. Lassen consist essentially of *n*-alkanes from only natural sources.

Most petroleums contain *n*-alkanes ranging from C_1 to about C_{35} with no carbon number predominance (CPI $\simeq$ 1.0) and isoprenoid hydrocarbons (e.g. phytane and pristane). The C_1-C_{20} homologs are usually lost due to evaporation (according to their boiling points) in the environment and/or in the experimental procedure, or were separated by distillation in the refining processes. Thus, absolute concentrations of the homologs $< C_{20}$ (Figure 5) are not accurate, but qualitative comparisons can be made.

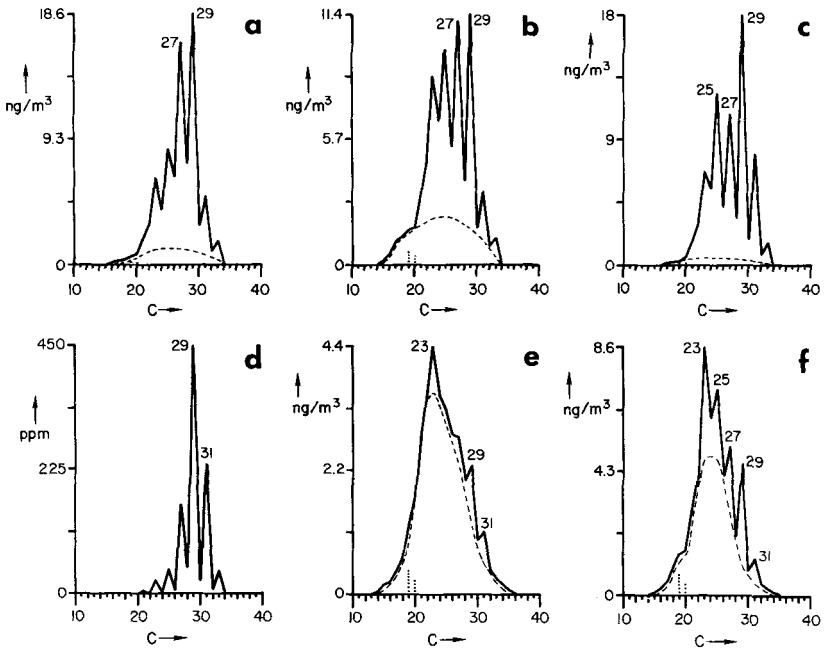


FIGURE 5 Distribution diagrams for *n*-alkanes extracted from various aerosol and plant wax samples[35] (height of dotted lines indicates isoprenoid hydrocarbons and the dashed line envelope indicates the approximate contribution of *n*-alkanes from petroleum residues): (a) Sugarpine Point State Park, Lake Tahoe, night, summer; (b) Sugarpine Point State Park, day, summer; (c) Battle Creek Meadow Ranch, Mt. Lassen, summer; (d) grass epicuticular wax; (e) Sugarpine Point State Park, winter; (f) Sierra Ski Ranch, Lake Tahoe, summer.

Pristane and phytane are diagenetic products of phytol and are not primary consistuents of most terrestrial organisms. Their presence in these hydrocarbon fractions, coupled with the presence of a broad hump, indicate petroleum contamination. An estimate of the *n*-alkane component derived from petroleum can be made from these data (smooth envelopes in Figure 5 indicated by the dashed lines).[35] At Sugarpine Point State Park and the Mt. Lassen area, a diurnal variation is evident: the contribution from petroleum residues is less during the night (Figure 5a) than during the day (Figure 5b). The sample from the Mt. Lassen area (Figure 5c) exhibits the lowest level of such contamination. The influence of heavy vehicular traffic is illustrated with the sample from Sierra Ski Ranch (Figure 5f) collected during summer, and can be compared with the distribution in Figure 5a. The level of contamination at Sierra Ski Ranch is significantly higher. Seasonal variation is illustrated with the samples

from Sugarpine Point State Park collected during winter (Figure 5e) and summer (Figure 5a). The contamination by petroleum residues is greater during winter. It should also be noted that the amount of natural plant wax is lower in the winter. The presence of petroleum contamination is also confirmed by the molecular markers (triterpanes, steranes and extended tricyclic diterpanes) in the hydrocarbon fractions.[35,36]

Some typical examples of homologous compounds in lipid fractions from sediments, geologically recent and ancient, are shown in Figure 6 to illustrate patterns of their distributions. Sample 36-330-10-1, 95–102 cm, which is of Jurrasic age from the South Atlantic, exhibits *n*-alkanes maximizing at *n*-C_{17} and *n*-C_{19} (Figure 6a) and even carbon numbered *n*-fatty acids with a maximum at *n*-C_{16} (Figure 6e). Both of 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.[22,29,37]

Sample ML71-2-23, 8.0 m is from Mangrove Lake, Bermuda, of recent origin in a highly productive sapropelic environment.[29] The *n*-alkanes (Figure 6b) 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

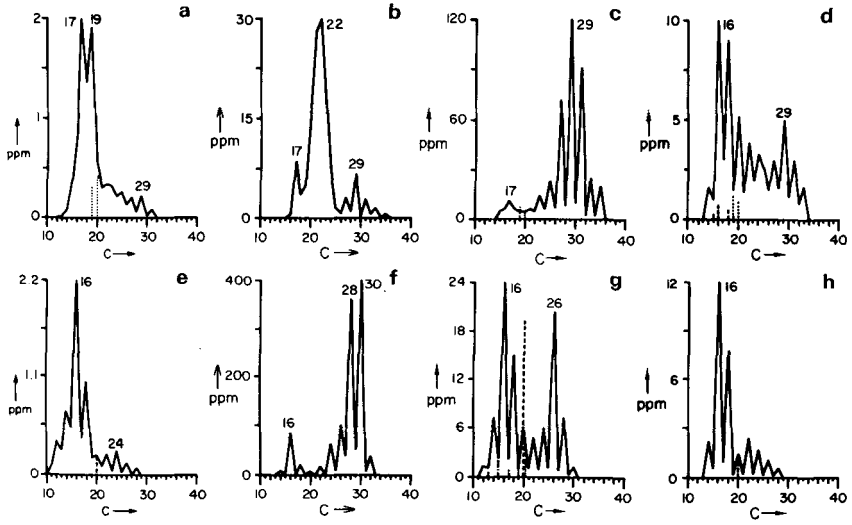


FIGURE 6 Distribution diagrams of *n*-alkanes (a–d) and *n*-fatty acids (e–h) extracted from various sediments (...indicates isoprenoids, ---diterpenoids): (a, e) Sample 36-330-10-1, 95-102 cm, S. Atlantic[60]; (b, f) Sample ML71-2-23, 8.0 m, Mangrove Lake, Bermuda[61]; (c, g) Sample AII49-1462K, 5.0 m, Black Sea[56]; (d, h) Sample 18-175-2-2, 45-47 cm, N.E. Pacific[40].

higher plant wax.[22,31,38] The *n*-fatty acids (Figure 6f) 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 (Figure 6c, 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.[22,29] 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.[22,29]

Sample 18-175-2-2, 45–47 cm is an example of a reducing microenvironment in the northeastern Pacific Ocean, where the *n*-alkanes (Figure 6d) exhibit a strong even-to-odd carbon number predominance for the homologs $< C_{24}$ and the distribution follows that of the *n*-fatty acids $< C_{24}$ (Figure 6h). These even *n*-alkanes ($< C_{24}$) may be derived from reduction of fatty acids or of olefins from fatty alcohols.[39,40] The *n*-alkanes $> C_{24}$ with the odd carbon number predominance and maximum at *n*-C_{29} are derived from vascular plant wax.

It should be emphasized that these distributions are found only under ideal environmental conditions, precluding the occurrence of extensive biodegradation. Biodegradative and oxidative alterations first remove the labile compounds, followed by the other metabolizable lipid components, which in turn leads to changes in the relative distributions of the homologous compounds such as for example *n*-alkanes or fatty acids. Therefore, homolog distributions in environmental samples should be interpreted with caution and such data coupled with supportive evidence from molecular indicators and other available parameters.

Petroleum products and coal extracts exhibit hydrocarbon distributions where, for example, the *n*-alkanes exhibit essentially no carbon number predominance and range from $< C_{10}$ to C_{35+} (eg., 39, 41). The contents of fatty acids, ketones and alcohols are usually low in petroleums.

Molecular markers or indicators are organic compounds with specific chemical structures, which can be correlated with an origin from biogenic precursors and which cannot be synthesized by abiogenic processes. Such markers can thus be utilized as indicators, for example of sources, environmental conditions and alteration, diagenetic and catagenetic alteration, geologic maturity and product-precursor relationships. The markers that are most often utilized in source correlations are the triterpenoids and the steroids, however, other cyclic molecules can also be used (e.g., 22, 29, 31, 39, 41, 42, 43).

The sesquiterpenoids that have been identified in environmental samples

(mainly sediments) are primarily cadalene, with various tetrahydro analogs, and they are of both a marine (algal) and terrigenous origin.[31]

The diterpenoids that have been characterized fit into two classes, those derived from terrigenous sources[40,44] and extended tricyclic diterpanes of a probable marine origin. The terrigenous diterpenoids consist of a large number of compounds and the most abundant analogs are dehydroabietic acid; dehydroabietin; dehydroabietane; simonellite; retene; tetrahydroretene; fichtelite; pimanthrene; 17-nordehydroabietane; iosene; 13-methylpodocarpa-8,11,13-triene; and norsimonellite.[40] The extended tricyclic diterpanes are found in shales, petroleum, and 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.[31,45,46] 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. Some distributions are shown as examples in Figure 7. The samples from the Southern California Bight (Figure 7c, d) are contaminated by petroleum seepage, indicating that the extended tricyclic diterpanes are syngenetic with the 17α(H)-hopane series. However, the same extended tricyclic diterpanes in a recent sample from Walvis Bay (Figure 7b) must be derived from a marine source since no petroleum contamination is evident.

The triterpenoids found in many environmental samples are of a microbial origin and are usually comprised of the hopane and to a lesser extent the moretane series. Some sedimentary sinks can also receive triterpenoid residues from terrigenous sources. The common homologs consist of trisnorhopane (I†, R=H), norhopane (I, R=C_2H_5), hopane (I, R=C_3H_7) and extended hopanes ranging from C_{31} to C_{35} (II) with minor amounts of the corresponding moretanes (III). The 17β(H) stereochemistry predominates in viable and recent, immature samples[49,50] and various triterpenes such as diploptene (IV), 17β(H)-hop-21(22)-ene (V) hop-17(21)-ene (VI) are also present.[51] The examples of recent sediments from the Gulf of California and Walvis Bay (Figure 7a and b, also cf. Figure 4c with 7a) illustrate this point in that only 17β(H)-hopanes and hopenes are present in the latter. The extended 17β(H)-hopanes occur as only the 22S diastereomer in recent samples 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 diastereomeric pairs, where full maturity is indicated by an S/R ratio of about one.[31,49,51] The samples from the Southern California Bight (Figure 7c and d) show this type of distribution, where in sample 193 only petroleum residues and matured 17α(H)-hopanes are found and in sample

†These chemical structures are given in Appendix I.

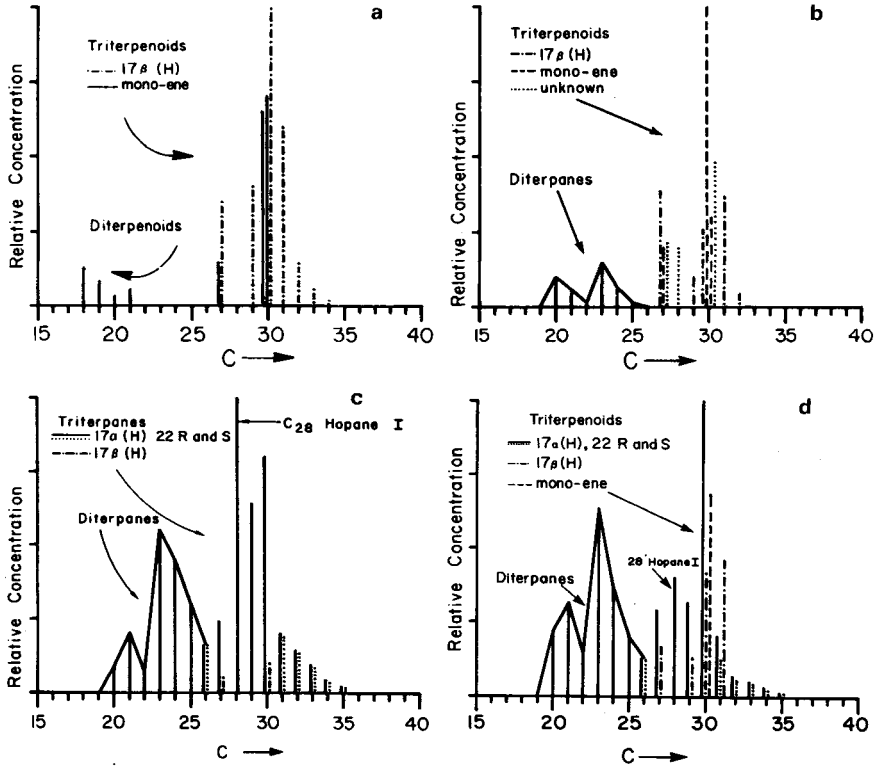


FIGURE 7 Relative distribution histograms for diterpenoids and triterpenoids (based on the m/z 191 mass chromatograms or gas chromatographic response) of some examples. The R and S diastereomers are also indicated and C_{28} Hopane I is 17α(H), 18α(H), 21β(H)-28, 30-bisnorhopane. (a) Sample 30G-I (102-105 cm), Guaymas Basin, Gulf of California[37]; (b) Sample AII 93/3-18 (197-201 cm), Walvis Bay, SW Africa[31]; (c) Sample 193 (25–31 cm), Santa Barbara Coastal Area, Southern California Bight[31]. (d) Sample 575 (25–31 cm), Tanner Basin, Southern California Bight[31].

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 (VIII).[31,52] This compound appears to be a specific marker for Southern California peteroliferous residues, as it is not commonly found in most other areas.[31,35]

Steroidal compounds are common in environmental and geological samples and they undergo complex diagenetic reactions yielding various series of hydrocarbons, alcohols and ketones (VIII).[43,47,48,53,54] The saturated hydrocarbons are comprised of the steranes [VIII, R,R′,R″=H,

eg., cholestane, 5α(H) *vs.* coprostane, 5β(H)], diasteranes (IX) and traces of other isomers, and the 5α stereomers usually predominate over the 5β. Various series of 4-methylsteroids have also been identified in some samples.[55,56] Recently, more detailed analyses of steroid products from environmental samples have revealed a more complex diagentic pattern and a miriad of compounds (eg. 43,47,48). The general concensus is that the steroid nucleus is limited in defining the biological source organisms since the steroid skeletal structures are ubiquitous in the biosphere. It is the constitution of the steroid side chain that may prove to be more characteristic for genetic correlations.

Other minor components that can also be utilized as molecular markers are for example tetraterpenoids, *iso*- and *anteiso*-alkanes or fatty acids, hydroxy fatty acids, tetrapyrrole pigments and aromatic hydrocarbons.

Humin or protokerogen data

Humin (protokerogen) and to some extent humic and fulvic substances are complex mixtures of high molecular weight moieties of various, essentially undefined structures and compositions.[22,29,67] The end member products of humin are coals for terrigenous and alginites for marine origins. Most protokerogens of the aquatic realm are admixtures of all input sources (eg., 37,58).

Since protokerogen (also humic substances) is an invaluable endogenous environmental marker for the origin and nature of the bulk of the organic matter, it is important to know its constitution. Protokerogen and to some extent humic and fulvic substances are commonly characterized by their bulk chemical and physical properties. Some of these are the elemental composition, stable isotopic compositions, electron spin resonance and nuclear magnetic resonance spectroscopy, pyrolysis GC and pyrolysis GC/MS fingerprinting (Figure 1).[25,36,39,58,59] Some protokerogens have also been chemically degraded for analysis of the resultant components.[58] Bulk chemical parameters can then be correlated to indicate trends.

Protokerogen is also sensitive to thermal stress (eg. the normal geothermal gradient due to depth of burial[37,58] or from transients such as intrusives[25,29] or combustion).[36] This catagenesis results in the generation of bitumen (also gases) from the protokerogen, which in turn becomes more aromatized. This phenomenon can be followed by monitoring various bulk properties as decribed above. Catagenesis can also be simulated by subjecting organic matter to pyrolysis and analyzing the bitumen that forms by GC and GC/MS (eg., 28). Such bitumen can be characterized in terms of homologous and marker compounds as

described above. Carbonaceous detritus that has been under severe thermal stress does not yield liquid products on pyrolysis.[28]

CONCLUSIONS

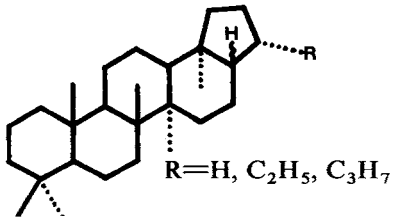
The applications of mass spectrometry with its ancillary techniques and the other methods of organic geochemistry are of great utility for the investigation of organic matter in environmental research. The characterization of gas, lipids and protokerogen (also humic and asphaltic substances) of environmental samples and of secondary products can provide information about the origin, environmental history, toxicity potential and results of degradation of the organic matter. Thus it is recommended to carry out detailed analyses of all the fractions of organic matter in the same manner in order to facilitate the interpretation and intercorrelation of data from various types of environmental samples.

Acknowledgements

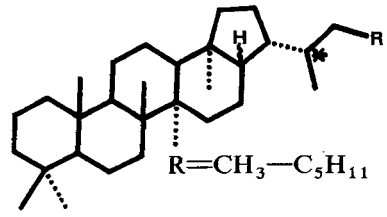
I thank the National Science Foundation (Grant ATM81-18101) for partial financial assistance.

Appendix I

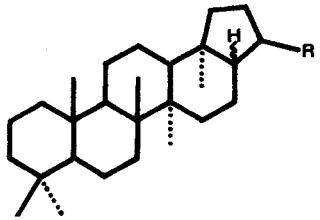
Chemical Structures Cited



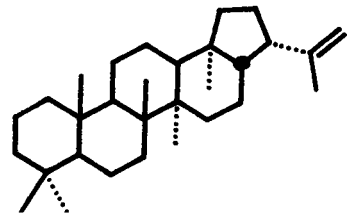
I. Hopanes



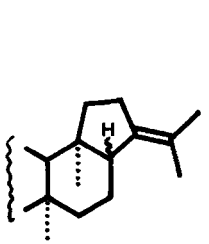
II. Extended Hopanes



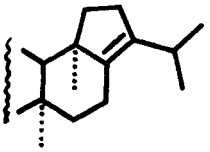
III. Moretanes



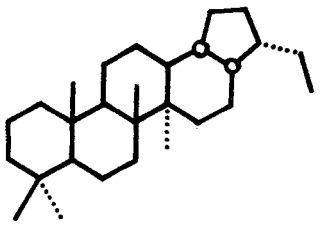
IV. Diploptene



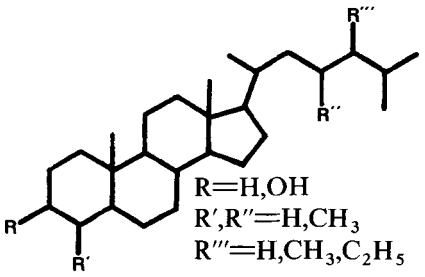
V. Hop-21(22)-ene



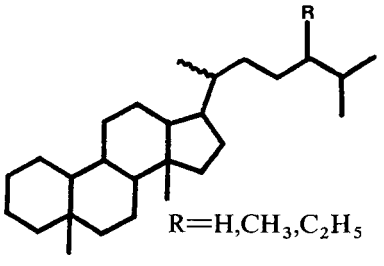
VI. Hop-17(21)-ene



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



VIII. Steroidal derivatives



IX. Diasteranes

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