AN ABSTRACT OF THE THESIS OF

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Redacted for privacy

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Bernd R.T. Simoneit

A comprehensive chemotaxonomic study of different environmental samples (sewage, sediment, water, fallout) from different sites along the Alexandria coast (Egypt) was carried out to characterize their contents of both biogenic and anthropogenic hydrocarbon molecular markers. By means of multivariate statistical analyses, the biomarkers were grouped according to the probable input sources and the sampling stations according to the relative importance of source contribution.

Homologous long chain *n*-alkanes (C_{15}-C_{40}), CPI, UCM, pristane and phytane, tricyclic and tetracyclic terpanes, as well as suites of mature sterane (C_{27}-C_{29}), diasterane and hopane (C_{27}-C_{35}) biomarkers were found to be the most suitable indicators to differentiate between anthropogenic pollution and background from natural vegetation. Several ratios of the terrigenous and anthropogenic markers were calculated for each station. These ratios and the statistical analyses point toward a strong signal of petrochemical and vascular plant hydrocarbons in the Alexandria environment.

MOLECULAR BIOMARKER HYDROCARBONS AS DISCRIMINANT INDICATORS OF ENVIRONMENTAL POLLUTION - CHARACTERIZATION AND SOURCES

by

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Redacted for privacy

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Date thesis is presented May 10, 1994

Typed by Tarek A.T. Aboul-Kassim

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CHAPTER I

INTRODUCTION

The need for environmental protection, particularly from various forms of pollution, which man creates, becomes an everyday agenda and demand. Nevertheless, man continues to expand his activities, unaware of the severe consequences and stresses which will eventually affect his existence.

In recent years, the problem of environmental pollution of most of the Mediterranean cities has become a point of national and multinational concern. Alexandria (Egypt), a southeastern Mediterranean city, is one of the most densely populated regions of the Eastern Mediterranean. The problem of organic pollution of the Alexandria environment is proposed as industrial with agricultural pollution on one hand and sewage pollution on the other. The dominance of either depends mainly on the dispersal location.

The overall goals of this study were to determine the extractable organic matter composition in different environmental compartments and to use the aliphatic hydrocarbon fractions for tracing anthropogenic and biogenic molecular biomarkers. The aliphatic hydrocarbon fractions were analyzed by capillary gas chromatography and gas chromatography/mass spectrometry and characterized for homologous series of *n*-alkanes, isoprenoid hydrocarbons (nor-pristane, pristane, phytane), UCM, tricyclic (C_{19}-C_{29}) and tetracyclic terpanes, as well as mature suites of hopanes (C_{27}-C_{25}) and diasteranes/steranes (C_{27}-C_{29}).

Each of the chapters (presented as papers) of this thesis contributes to the accomplishment of the objectives. The first (Chapter II) is a general study of the different extractable lipid fractions from environmental samples and their emission rates to the Alexandria environment. In addition, statistical analysis techniques were used to test the

hypothesis that certain lipid components represent the same population and to determine the number of end members in the study area.

The second paper (Chapter III) is a more detailed characterization of particulate fallout samples over Alexandria in terms of their hydrocarbon compositions and their original sources.

The third paper (Chapter IV) describes petroleum hydrocarbon fingerprinting in a heavily polluted area, the Eastern Harbor of Alexandria. It discusses some possible ways to differentiate between the petroleum hydrocarbon end member using its biodegradation indices as well as the use of these indices to study the possible sediment transport in the area.

The final paper (Chapter V) characterizes samples of the surficial bottom sediments collected off the Alexandria coast in terms of their contents of biogenic and anthropogenic aliphatic hydrocarbon biomarkers. By means of multivariate statistical analyses, the molecular biomarkers were grouped according to their probable input sources and the sampling stations according the relative importance of each source contribution.

Chapters II and III will be submitted, after revision, to *Environmental Science and Technology*, Chapter IV to *Marine Pollution Bulletin,* and Chapter V to *Marine Chemistry*. Some parts of this research were presented in International Conferences: the 33rd Congress and Plenary Assembly of the International Commission for the Scientific Exploration of the Mediterranean Sea (ICSEM) held in Trieste, Italy in November 1992 (Aboul-Kassim and Simoneit, 1992), the 11th International Symposium on Environmental Biogeochemistry (ISEB) held in Salamanca, Spain in September 1993 (Aboul-Kassim and Simoneit, 1993a), and the 16th International Meeting of the European Association of Organic Geochemistry (EAOG) held in Stavanger, Norway in September 1993 (Aboul-Kassim and Simoneit, 1993b).

CHAPTER II

STATISTICAL INTERPRETATION OF EXTRACTABLE LIPID DATA FROM SAMPLES IN THE COASTAL ENVIRONMENT OF ALEXANDRIA, EGYPT.

ABSTRACT

The lack of information about the environmental quality of the coastal environment of Alexandria, Egypt and the impact of anthropogenic sources of pollution in the area initiated an extensive study of the different extractable lipid classes. Samples collected from various compartments of the Alexandria environment were analyzed for quantitative lipid data. A statistical approach for interpretation of lipid data is presented here. Analysis of variance (ANOVA) was used in order to compare the relative magnitudes of sample site and type variances. Q-mode factor analysis and linear programming technique were applied to reduce the data set and determine statistically and experimentally significant end members specific for the area, as well as their contributions to each sample. In addition, fossil fuel biomarkers were used in order to confirm the statistical findings.

INTRODUCTION

Lipids from biogenic sources are a diverse group of compounds, classified as extractable and bound, and include hydrocarbons (aliphatic and aromatic), fatty acids, ketones, aldehydes, esters and alcohols. Most lipid components are composed of C, H and O, but some may contain N and P. They have neither a common structure nor functional group, although the majority are esters of long chain carboxylic acids (fatty acids).

The study of the lipid geochemistry in environmental samples is important since the wide-spread accumulations of these molecular fractions in the aquatic environment (especially on the sea floor), as well as the interactions between air-water and water-sediment interfaces, play an important role in the cycling of organic matter. So, both the qualitative and quantitative aspects of lipid characterizations are necessary in order to define the bulk organic geochemical composition and biomarkers; to study their fluxes, sources, transport, fate and chemotaxonomy in the environment; and to evaluate changes in their composition relative to input sources, especially in coastal areas.

Assessment of lipids in contaminated compartments of coastal environments (e.g., atmospheric particulate fallout, untreated sewage and waste water discharge, surficial bottom sediments) is generally conclusive, recording any changes in the rate of anthropogenic pollution inputs and variations in the predominance of certain sources and/or irregular local emissions. Since information is limited on the composition and variability of lipids in coastal areas impacted by municipal waste, substantial descriptive and statistical data bases are urgently needed. In order to evaluate the role of anthropogenic inputs versus natural biogenic sources, the lipid composition of environmental samples from various sources must be determined and the proportion of each must be identified in the samples. The direct approach for source characterization and partitioning would be to isolate lipid fractions from pure individual sources and to determine their composition analytically (qualitatively and quantitatively) and then to determine their relative importance in each sample. In environmental organic geochemical studies, the widely used approach is to determine the chemical composition directly by analysis of samples presumed to be end members (Simoneit, 1984, 1985, 1989; Simoneit *et al.*, 1991; Rapp, 1991). Other studies have used multivariate analysis (statistical

approach) to determine quantitatively the contribution of each element from various sources. These include partitioning based on inter-element ratios to determine the importance of each end member in bulk sediments, normative analysis, and linear programming (Dymond, 1981; Heath and Dymond, 1981; Leinen and Pisias, 1984).

In this paper, we present quantitative lipid data representing the environment of Alexandria, a heavily polluted south-eastern Mediterranean urban region and use both molecular biomarker and statistical approaches for data interpretation.

STUDY AREA

Alexandria is the second largest city and the principal summer resort of Egypt. It is one of the densely populated regions of the eastern Mediterranean (about 3.5 million inhabitants), receiving about 1 million tourists in summer who come to use its beaches for recreation. Alexandria encompasses 40% of the nations industry and hosts the main commercial and yachting harbors. Its coastal waters are highly polluted with untreated domestic sewage and industrial waste waters, discharged into the sea through several outfalls along the coast. The problem of organic pollution of Alexandria has been and is still being discussed on a national and multinational scale. The Alexandria coastal area, when considered in general, is one of the major pollution-stressed areas of the Mediterranean region. The problem has been attributed to industrial versus agricultural derived pollutants on one hand and sewage derived pollutants on the other. The domination of either depends mainly on the dispersal location.

The study area (Figure II.1) lies off Alexandria between 31° 08' to 31° 26'N and 29° 47 to 30° 04'E, extending for about 38 km from Agami to Abo-Qir headland. According to the type of regional impact, the coastal waters can be divided into six main zones (Table II.1). Zone I (beaches) receives a significant amount of untreated sewage; zones II (Eastern Harbor) and III (Western Harbor), the main trading and fishing harbors of the city, receive waste water and untreated sewage; zone IV (Kayet Bey) receives domestic sewage from the main metropolitan pumping station; zone V (Mex Bay)

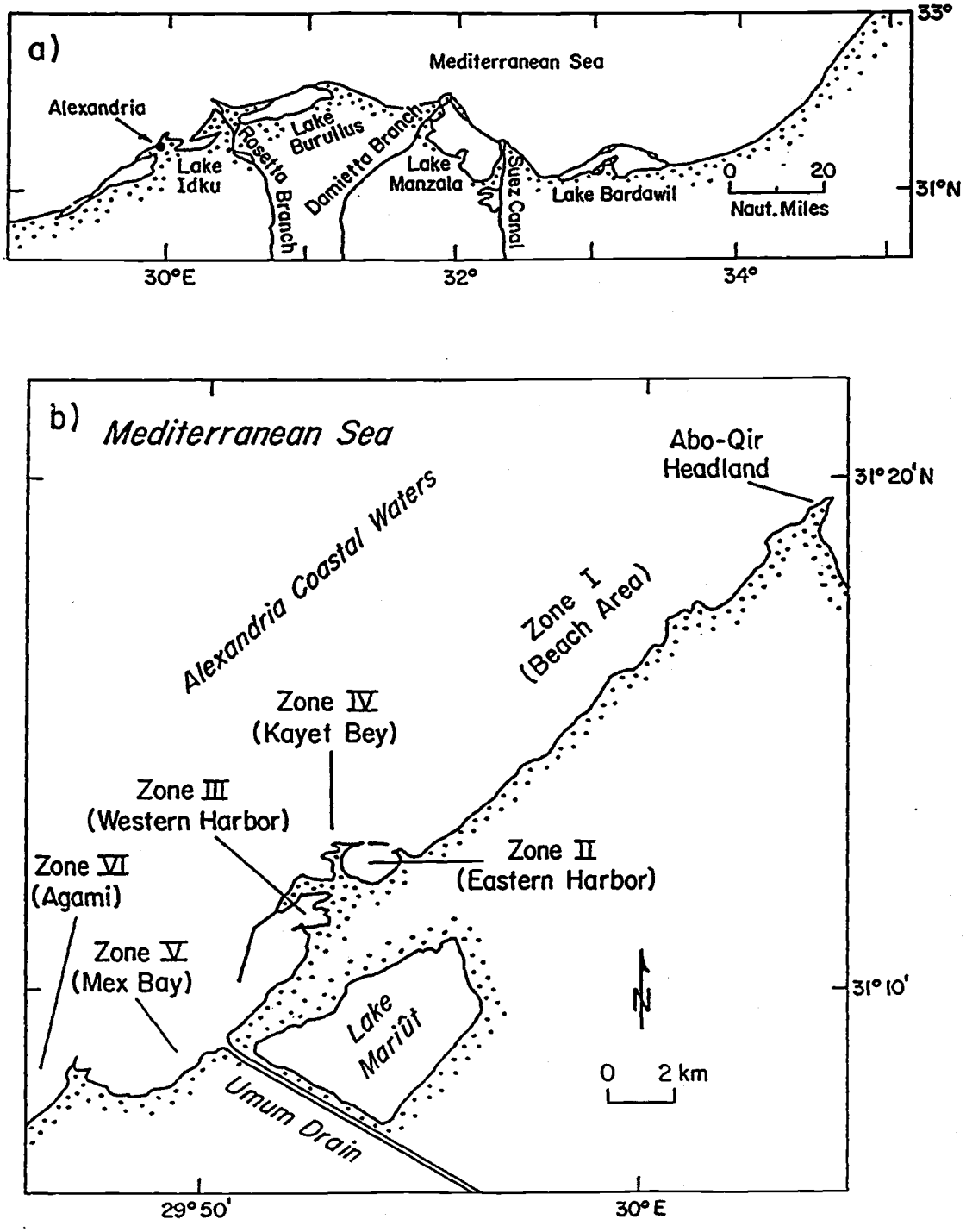


Figure II.1: The study area: a) Egypt in the Southeastern Mediterranean, b) Alexandria region.

Table II.1: General characteristics of the land runoff in the Alexandria coastal environment.

Table II.1

Zone	Name	Type of anthropogenic input	Flow rate (10^6 m^3/yr)	Area (km^2)	Mean depth (m)
I	Beach area	- untreated sewage and waste waters (18 outfalls)	34.0	30.0	12.0
II	Eastern Harbor	- untreated sewage and waste waters (11 outfalls)	36.0	2.5	6.0
III	Western Harbor	- brackish water (from NubariaCanal) - waste water (from 16 tanning factories)	33.0 0.5	7.5	10.0
IV	Kayet Bey pumping station	- sewage and waste waters (the main metropolitan outfall)	112.0	4.5	11.0
V	Mex Bay	- agricultural - chlor-alkali waste water	2200.0 12.8	19.4	9.8
VI	Agami (The control zone)	- minute local emissions		12.5	15.0

receives various industrial waters from several outfalls: agricultural and chlor-alkali plant; and zone VI (Agami) is regarded as the reference area receiving little local discharge.

PREVIOUS WORK AND OBJECTIVES

Most of the environmental research on the Alexandria area was concerned with its biological (El-Nady, 1986; Halim *et al.*, 1986), hydrobiological (Said and Karam, 1990), and inorganic marine chemistry features (Aboul-Kassim, 1987; Aboul-Dahab *et al.*,1986; 1990; Abdel-Moati, 1990; Gabrielides *et al.*, 1990; Abdel-Moati and Atta, 1991; Abdel-Moati *et al.*, 1991; Aboul-Kassim, 1992; Aboul-Kassim *et al.*, 1992a).

The lack of information about the organic geochemistry of the Alexandria coastal environment initiated this study of extractable lipid fractions in samples from this area. In this paper, our objectives are to:

(1) Report the impact of land runoff on the amounts and compositions of extractable lipid fractions (aliphatic and aromatic hydrocarbons, fatty acids, ketones, aldehydes and alcohols) in atmospheric particle deposition, untreated sewage and waste waters, and surficial sediments.

(2) Calculate the extractable lipid loading rates (ELLRs) to the Alexandria environment as well as their fluxes to sediments.

(3) Statistically confirm the significant differences among the various zones in the Alexandria region or the lipids from different environmental compartments by using the analysis of variance (ANOVA) technique. Identify significant end members (using both statistical and biomarker approaches) representative of the study area by using multivariate Q-mode factor analysis and linear programming techniques. This will help to evaluate the regions of concentration and to conceptually model the lipid composition of Alexandria environment.

MATERIALS AND METHODS

As a general precaution to minimize contamination, all glassware was cleaned with soap and water, rinsed with distilled water, heated in an oven at 550°C for 8 hrs to combust any traces of surficial organic matter, and finally rinsed twice with ultra-pure

methanol and methylene chloride. The KOH used for saponification was extracted 3 times with *n*-hexane and once with methylene chloride in a separatory funnel to remove organic interferences.

Sampling and Pretreatment

Atmospheric particle deposits (fallout) were collected from different sites along the Alexandria coast for a period of 30-55 days using plastic trays covered with solvent precleaned aluminum foil. Surficial bottom sediments were collected using a modified Ekman grab sampler and frozen until analysis. Prior to lipid analysis, sediment samples were air dried, sieved and homogenized. Untreated sewage and waste water samples were obtained from 10 outfalls (representative of the waste water disposal of Alexandria) using 5 L glass bottles previously cleaned with methylene chloride/methanol (3:1). Samples were filtered within 5 hrs after sampling using precombusted (450^{0}C/8 hrs) Whatman 0.7 µm glass fiber filters (GF/A). Both dissolved and particulate fractions were kept frozen at -20°C to prevent organic matter degradation until lipid analysis.

Extraction and analysis

All the extraction and analytical steps are shown in Figure II.2. In the case of waste water filtrates, liquid/liquid extractions were performed in separatory funnels using *n*-hexane followed by chloroform ($CHCl_3$), while the filters containing the particulate fractions were sonicated several times with methylene chloride/methanol (2:1). The atmospheric particle fallout and the surficial sediments were extracted in a Soxhlet apparatus with methylene chloride-methanol (2:1). This extract after water washing is a measure of the amount of extractable organic matter (EOM) in a sample. All the extracts (EOM) were concentrated to 2 ml, desulfurized with activated copper and hydrolyzed overnight with 35 ml of 6% KOH/methanol. The corresponding neutral and acidic fractions were successively recovered with *n*-hexane (4 x 30 ml), the latter after acidification (pH 2) with 6*N* HCl. The acidic fractions, previously reduced to 0.5 ml, were esterified overnight with 15 ml of 10% BF_3/methanol. The BF_3/methanol complex was

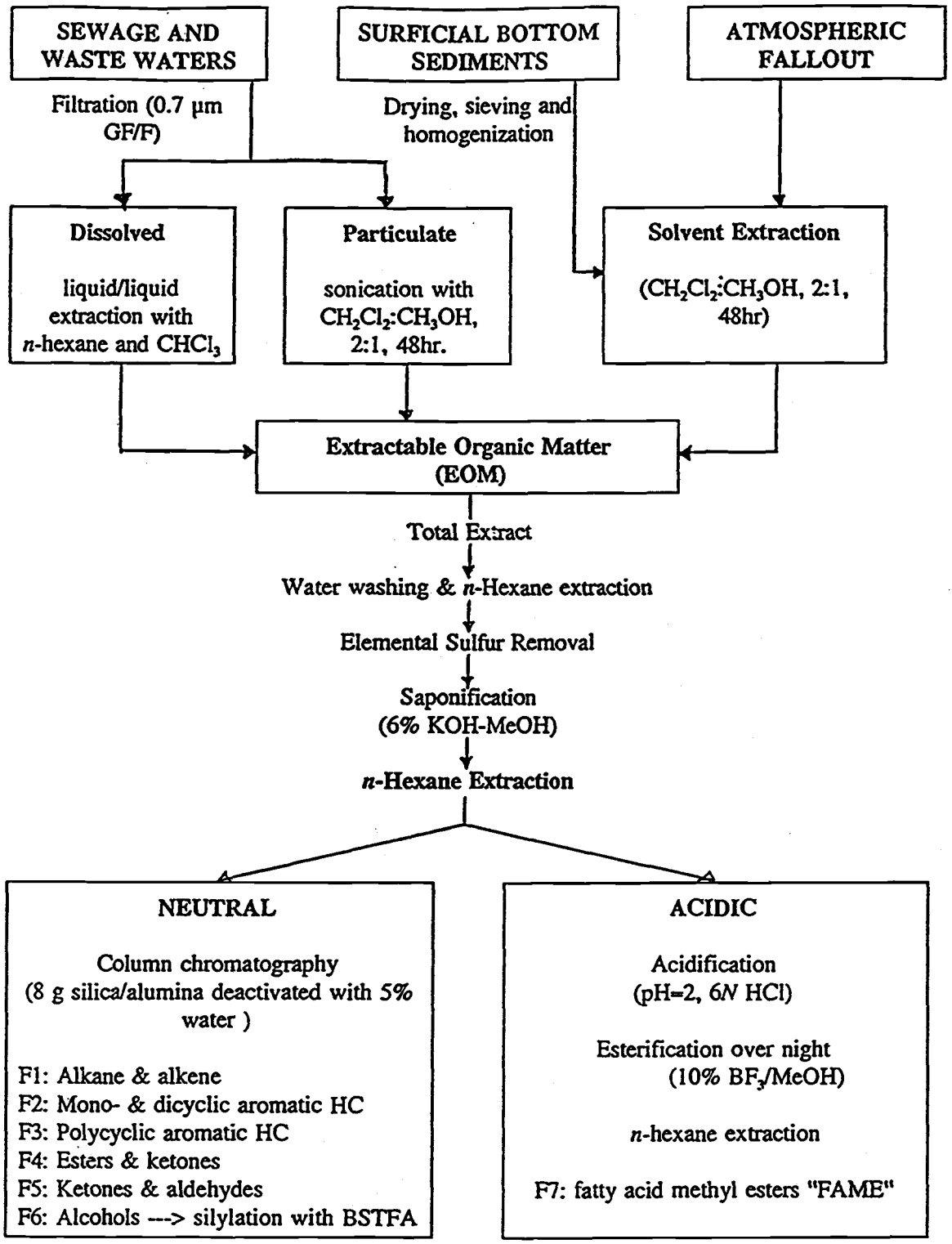


Figure II.2: Schematic diagram showing the extractable lipid analysis procedure.

destroyed with 15 ml of water, and the methyl esters were recovered by extraction with 4 x 30 ml of *n*-hexane. The neutrals were fractionated by column chromatography. A column (50 x 1.2 cm) filled with 8 g each of alumina (top) and silica (bottom), both deactivated with 5% water, was used. The following fractions were collected: (I) 45 ml of *n*-hexane (aliphatic hydrocarbons, F1), (II) 25 ml of 10% methylene chloride in *n*-hexane (monoaromatic hydrocarbons "MAHs", F2), (III) 40 ml of 20% methylene chloride in *n*-hexane (polycyclic aromatic hydrocarbons "PAHs", F3), (IV) 25 ml of 50% methylene chloride in *n*-hexane (esters and ketones, F4), (V) 25 ml of methylene chloride (ketones and aldehydes, F5), and (VI) 50 ml of 10% methanol in methylene chloride (alcohols, F6). The last fraction was derivatized prior to gas chromatographic (GC) analysis for further qualitative molecular examination by silylation with bis(trimethylsilyl)trifluoroacetamide.

Data presented here include quantitative results for the different lipid fractions. Measurements are based on duplicate weighings of fraction residues using a Mettler electromicrobalance. Replicate determinations showed the precision to be (coefficient of variation) $\pm$4.71%. Gravimetric yields of blanks treated by the same procedure gave results below the detection limit. As a check on the efficiency of Soxhlet extraction time, two different extraction periods gave maximum yields, i.e. 48 hr for surficial sediment samples close to sewage outfalls and 60 hr for samples away from direct impact or in the reference zone. A recovery experiment for column chromatography was carried out using $C_{32}D_{66}$ and a series of 35 *n*-alkane standards for the aliphatic fraction; d_{10}-pyrene, d_{10}-chrysene and a series of 37 PAH compounds for the aromatic fractions; coprostanone for the ketone fraction; coprostanol, epi-coprostanol, cholesterol and β-sitosterol for the alcohol fraction as well as a series of fatty acid methyl esters for the ester fraction. The recoveries obtained were 89%, 85%, 86%, 87% and 91%, respectively.

Selected fractions were analyzed by GC and gas chromatography-mass spectrometry (GC-MS). GC analyses were carried out using a Hewlett-Packard Model 5890A instrument, equipped with a 30 m x 0.25 mm i.d. DB-5 capillary column. Analyses by GC-MS were carried out with a Finnigan Model 4021 quadrupole mass spectrometer

operated at 70 eV over the mass range 50-650. The GC was fitted with an identical column as in the GC system used above for analyses of the lipid fractions. The GC-MS data was acquired and processed with an on-line Incos Model 2300 computer data system. Detailed molecular analyses of the different lipid fractions will be presented and discussed separately in another report.

All statistical analyses were performed using the SAS (1991) statistical package as well as the statistical package provided on the SUN SYSTEM of College of Oceanic and Atmospheric Sciences at OSU. These analyses include the measure of dispersion, correlation between variables, analysis of variance (ANOVA), regression analysis, extended Q-mode factor analysis and linear programming technique (LPT).

RESULTS AND DISCUSSION

General Trend of Lipid Classes

The average concentrations of the total EOM and its different fractions (hydrocarbons, alcohols, esters, aldehydes, ketones and fatty acids) are listed in Table II.2. During the extraction step most of these surficial sediment and particulate waste water samples had a significant fraction (20%) of inorganic salts in the total solvent extractable organic matter (EOM), which should be taken into consideration in the quantitation of free lipids.

In most cases, the EOM content of surficial sediments was high with an average of 67.3 mg/g $\pm$ 57.1 mg/g). The high standard deviation most likely reflects variations in the sediment grain size and the quantity and quality of both biogenic and anthropogenic organic matter sources. The surprisingly high percentage of EOM found in the waste water filtrate (i.e. 40%) is due to the presence of high concentrations of water soluble polar materials such as fatty acids and alcohols (Table II.2). The high concentrations of EOM in the atmospheric particulate fallout (Table II.2) are characteristic for Alexandria (a south-eastern Mediterranean city) when compared with the western Mediterranean aerosols (i.e., 140 µg/g; Simo *et al.*, 1991) or even the eastern Mediterranean on Crete (82 µg/g; Stephanou, 1992).

Table II.2: Average concentrations of extractable lipid fractions in the Alexandria environment.

Table II.2

Sampling Alexandria Environment		N*	EOM	Extractable lipid classes					
				Aliphatic	Aromatic	ΣHCs	Fatty acids	Esters + Aldehydes + Ketones	Alcohols
Coastal Sediments (zones) (mg/g)	I	8	41	3.6	2.1	5.7	29.9	4.1	1.6
	II	4	53	9.5	3.7	13.3	29.7	5.3	4.8
	III	2	25	14.0	1.2	15.2	4.1	4.6	1.4
	IV	3	191	22.9	3.8	26.8	149.0	7.6	7.7
	V	3	66	36.6	3.0	39.6	10.8	12.0	3.6
	VI	3	27	1.4	0.8	3.0	20.3	1.9	2.7
Atmospheric fallout deposition (mg/g)	Beach area	4	6	1.5	1.1	2.7	1.2	1.7	0.5
Untreated sewage and waste water (mg/l)	dissolved	10	165	26.3	19.8	46.1	49.4	11.5	57.9
	particulate	10	413	185.9	37.2	223.0	62.0	24.8	103.3
	total		578	212.2	56.9	269.1	111.3	36.3	160.8

** Number of samples*

Generally, aliphatic hydrocarbons represented greater than half of the total hydrocarbons (THCs) in Alexandria environmental samples (Table II.2, Figure II.3). The similarity in the aliphatic hydrocarbon contents of zones III, IV & V (Figure II.3) may suggest that sewage and waste water outfalls of Alexandria in these zones are receiving THC mixtures from similar sources, with each zone differing only in the amounts that they ultimately discharge. The general average THC concentration is 17.2 mg/g. The THC content of the waste water, i.e. 27 and 54% for dissolved and particulate fractions, respectively (Table II.2), is higher than that of outfalls in southern California (13-37%; Eganhouse and Kaplan, 1982). The combined concentrations of ketone, aldehyde and ester fractions never exceed 30% of the EOM in all these environmental samples, while the alcohol fraction amounted to about 35 and 25% of the dissolved and particulate fractions, respectively of the waste waters (Table II.2). The ratios of both the alcohol and fatty acid fractions between dissolved and particulate forms for the waste waters may reflect their water soluble nature.

Extractable lipid class inputs

In order to evaluate the input of the different lipid fractions to the Alexandria environment we calculated their emission rates (loadings) as follows:

- ***Atmospheric particle deposition:*** Using the atmospheric particle deposition rate of 66.1 mg/m^2/d (Aboul-Kassim and Simoneit, 1994) and the different lipid class concentrations in the fallout, the estimated rate of deposition of total extractable lipids is 144.8 mg/m^2/yr (Table II.3).

Terrestrial runoff: Terrestrial input is mainly from untreated sewage and waste waters disposed into the environment through several outfalls (Table II.1). Using the total annual flow rate from these outfalls (195.2 x 10^6 m^3/yr; Aboul-Kassim, 1992), the extractable lipid loading rates were computed according to the following equation (Table II.3):

$$\textbf{ELLRs (tons/yr)} = (C_A \cdot Q_A)/10^6$$

where: ELLRs = extractable lipid loading rates,

Figure II.3: Relative composition of the total hydrocarbon fractions in the environment of Alexandria, Egypt.

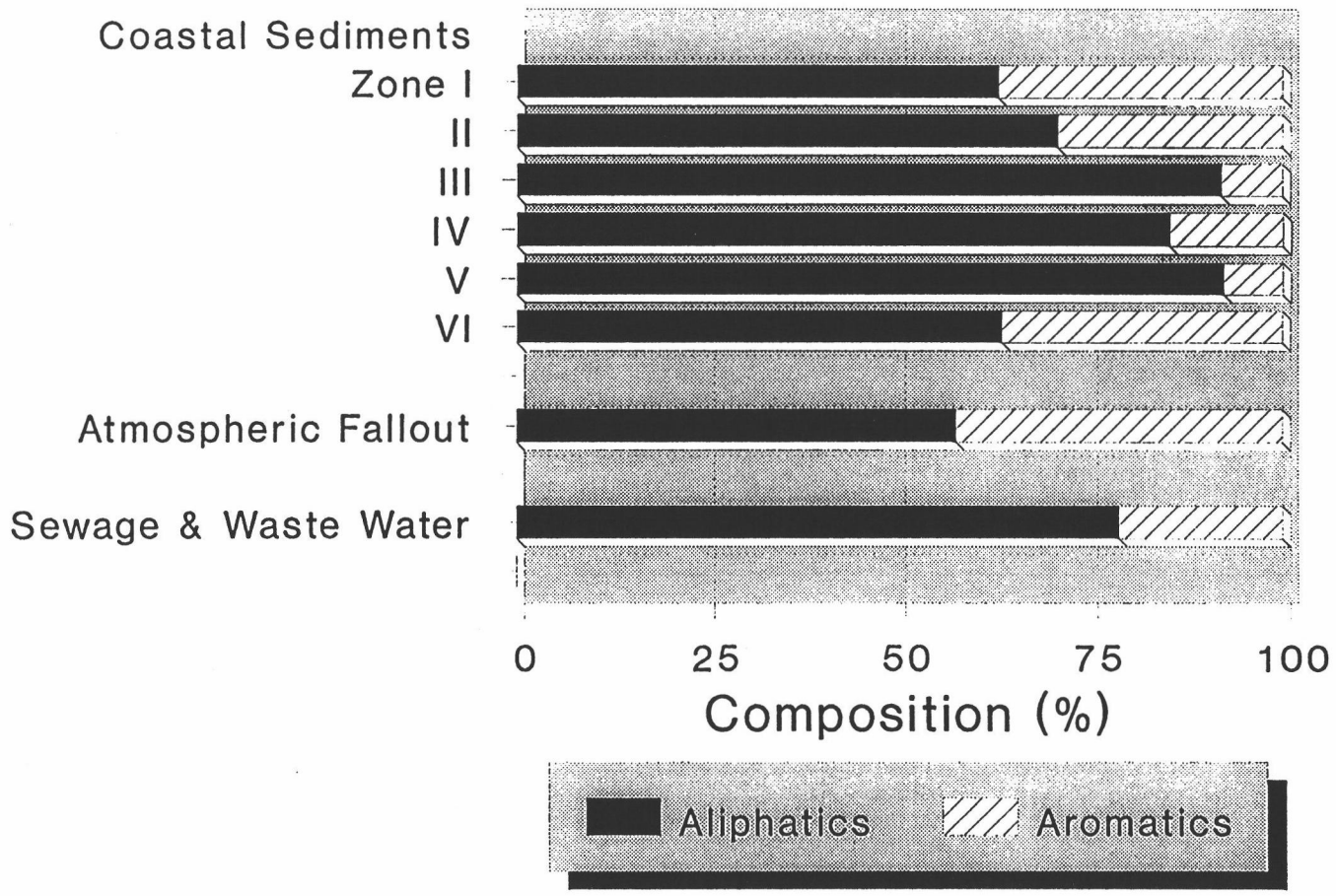

Coastal Sediments
Zone I
II
III
IV
V
VI
Atmospheric Fallout
Sewage & Waste Water
0
25
50
75
100
Composition (%)
Aliphatics
Aromatics

Table II.3: Extractable lipid loading rates (ELLRs) in the Alexandria environment.

Sample Type	EOM	Aliphatic	Aromatic	ΣHCs	Fatty acids	Esters + Ketones + Aldehydes	Alcohols
Fallout*1	144.8	36.2	26.5	62.7	29.0	40.0	12.1
Waste Water*2	113×10^3	41×10^3	11×10^3	53×10^3	22×10^3	7×10^3	31×10^3
Surficial Sediments*3							
- zone I	18.6	1.6	0.9	2.6	13.4	1.9	0.7
- zone II	3.0	0.5	0.2	0.8	1.7	0.3	0.3
- zone III	4.3	2.4	0.2	2.6	0.7	0.8	0.2
- zone IV	13.0	1.6	0.3	1.8	10.1	0.5	0.5
- zone V	19.3	10.7	0.9	11.6	3.2	3.5	1.1

*1: $mg/m^2/yr$, *2: tons/yr, *3: tons/d.

C_A = annual mean of lipid fraction (mg/l)

Q_A = annual flow rate (m^3/yr).

Farrington and Quinn (1973) estimated the total input of hydrocarbons from treatment plants in Rhode Island, USA to the ocean to be from 28,000-140,000 tons/yr. Van Vleet and Quinn (1978) calculated an annual hydrocarbon loading rate of 200,000 tons/yr for the USA (based on a coastal population of 68 million). Eganhouse and Kaplan (1982) calculated the aliphatic and aromatic hydrocarbon loadings to be 7840 and 9560 tons/yr, respectively for the greater Los Angeles region. From the present study, it appears that the annual hydrocarbon loading rate of 53,000 tons/yr for the Alexandria waters is high (Table II.3) compared to that of the greater Los Angeles region.

An interesting way to illustrate the magnitude of the ELLRs is to equate the lipids of wastes from specific sources to the number of people required to produce the waste on a daily basis. Using an average population for Alexandria of 4 million, the per capita emission rate of total lipids would be 77 g/day, and the ELLRs of THCs, alcohols and fatty acids would be about 36, 21, and 15 g/day, respectively. The per capita THC output for Alexandria is 9 times higher than that of the greater Los Angeles region (4 g/day/capita; population 12 million) and 16% of the Rhode Island region (230 g/day/capita; population 1 million; Farrington and Quinn, 1973).

In order to develop a simple, indirect and rapid method for estimating the different lipid fractions contained in untreated sewage and waste water, we investigated the possibility of correlating the EOM with the different lipid fractions using simple regression equations (Figure II.4) as follows:

"THCs" (mg/l) = 27.316 + 0.4193 "EOM (mg/l)"

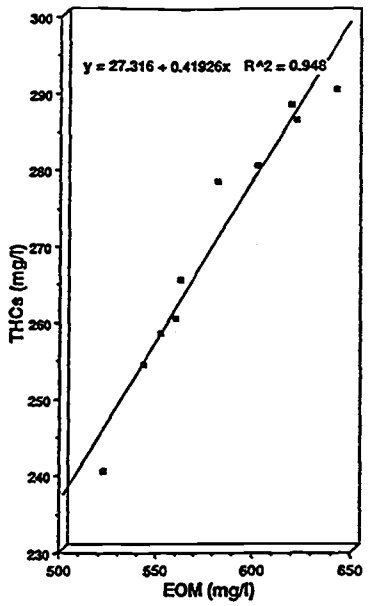
"Ketones+Aldehydes+Esters (mg/l)" = -6.7612 + 7.3991x0^{-2} "EOM (mg/l)"

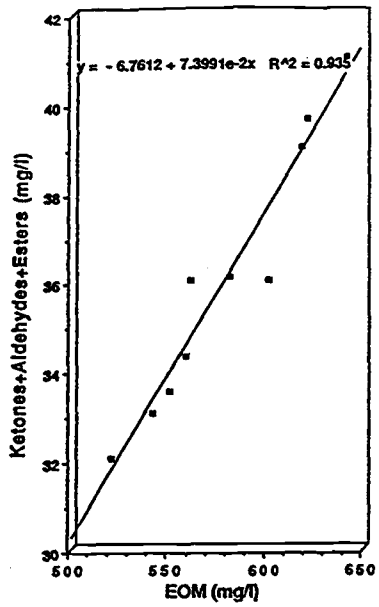
"Alcohols (mg/l)" = -14.490 + 0.3047 "EOM (mg/l)"

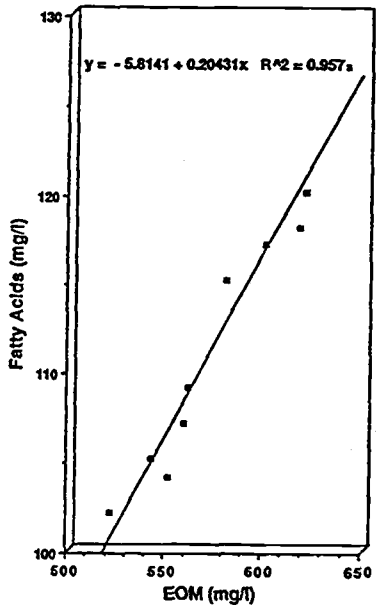
"Fatty acids (mg/l)" = -5.8141 + 0.2043 "EOM (mg/l)"

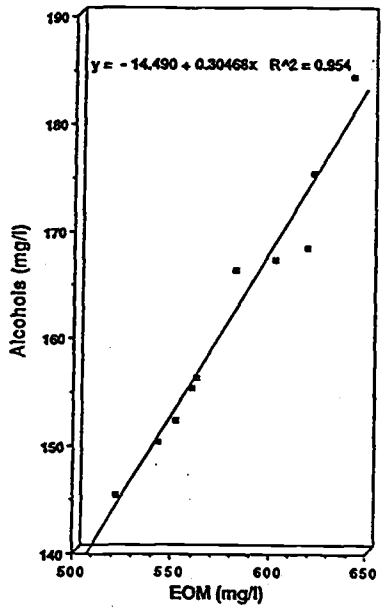
Despite the simplicity of this test, it demonstrates the self consistency of the method. A time series analysis data set of lipid fractions of the waste waters would evaluate whether the correlations (Figure II.4) found here are generally applicable and characteristic for

Figure II.4: Scatter plots showing the relation between EOM (mg/l) with a)- THCs, b)- esters+aldehydes+ketones, c)-alcohols and d)- fatty acids.


y = 27.316 + 0.41926x R^2 = 0.948
THCs (mg/l)
EOM (mg/l)
300
290
280
270
260
250
240
230
500
550
600
650


y = - 6.7612 + 7.3991e-2x R^2 = 0.935
Ketones+Aldehydes+Esters (mg/l)
EOM (mg/l)
42
40
38
36
34
32
30
500
550
600
650


y = - 5.8141 + 0.20431x R^2 = 0.957
Fatty Acids (mg/l)
EOM (mg/l)
130
120
110
100
500
550
600
650


y = - 14.490 + 0.30468x R^2 = 0.954
Alcohols (mg/l)
EOM (mg/l)
190
180
170
160
150
140
500
550
600
650

Alexandria waste waters and/or subject to change with time. This statistical tool is useful in estimating the waste water inputs of extractable lipids because of its simplicity.

Sedimentary flux: According to Hamilton-Taylor (1979), a way to convert the sedimentation rate to a weight basis is to use the following equations:

$$\mathbf{SF = C \times S \times R\ (1\text{-}p)\ d}$$

where **SF** = sedimentary flux (kg/d), **C** = lipid fraction concentration (mg/g), **S** = surface area (m^2), **R** = sedimentation rate, **p** = porosity and **d** = density.

According to Aboul-Dahab *et al.* (1990), the sedimentation rate, average density and porosity of sediments in Mex Bay are 0.85 cm/yr, 2.6 g/cm^3 and 75%, respectively (i.e. **R(1-p)d** = 0.55 $g/cm^2/yr$ = 15.1 $g/m^2/d$). Using the average lipid class concentrations in the sediments of Mex Bay, and given the surface area of the bay (19.4×10^6 m^2), the fatty acid sedimentary flux for the whole bay (**SF**) is: (10.8 mg/g) x (19×10^6 m^2) x (15.07 $g/m^2/d$) = 3.1×10^9 mg/d = 3.1 tons/d. Using the same (**SF**) equation for the various zones in the Alexandria region, the sedimentary fluxes of the different free lipid fractions are presented in Table II.3.

Statistical analysis

In using statistical analysis for interpreting environmental organic geochemical data, the main goals for assessing the impact of anthropogenic pollution on the levels of extractable lipid fractions in any impacted coastal environment are: (1) to determine any statistical differences between the various zones (environmental compartments) relative to the change in pollution stress, and (2) to determine the number of significant systems. A system is a source of the group of compounds studied, in this case the different extractable lipid fractions, which are contributing to the observed sample compositions. The first goal can be achieved by using univariate statistical analysis called analysis of variance (ANOVA), and the second by applying multivariate Q-mode factor analysis and linear programming techniques.

1- Analysis of Variance: ANOVA was applied to the data set to compare the relative magnitude of sample site and sample type variances, which were then tested for significance by means of an F-test. This test is a way of determining whether sets of samples could have been drawn randomly from the same normal population (i.e. there is no significant statistical difference between them). The F-values arising from the ANOVA (Table II.4) are compared with critical F-values given in statistical tables (Davis, 1987) in order to assess their significance. Critical F-values are tabulated for different degrees of freedom (dependent on the number of variables being considered) and levels of confidence. Thus, if the F-value from the ANOVA exceeds the tabulated critical value, the hypothesis that two sets of results come from the same normal population might be rejected at the 5% level (i.e. the calculated F-values would arise <5 out of 100 times if the samples belonged to the same population) or the 1% level (<1 out of 100 times). Generally, the results of the samples collected from the different zones and various compartments of the Alexandria environment were used for this analysis (Table II.2).

Single factor fixed ANOVA was used in this investigation to test the following specific hypotheses:

(1) For each environmental sample type (atmospheric fallout, waste waters, surficial sediments), the different lipid fractions collected from all individual sites of the Alexandria region form part of a single normal population. Rejection of the hypothesis would indicates that there are genuine differences in lipid concentrations between some of the sample types.

(2) Surficial sediment samples collected from each sampling zone along Alexandria coast form a single normal population. Rejection of the hypothesis indicates that there are significant differences in lipid levels between the various sampling zones probably reflecting differences in sources of pollutants to the zones. The rejection of the ANOVA hypothesis, however, does not mean that the samples from every zone necessarily show significant differences in sediment organic composition, only that those from at least one location (zone) are different.

Table II.4: General form of single factor fixed ANOVA (modified from Davis, 1987).

Source of variation	Degree of freedom (DF)	Sum of squares	Mean squares	F test
Among groups	m-1	$SS_A = \sum_{J=1}^{m}\left[\frac{\left(\sum_{I=1}^{m} X_{IJ}\right)^2}{n}\right] - \left[\frac{\left(\sum_{J=1}^{m}\sum_{I=1}^{n} X_{IJ}\right)^2}{N}\right]$	MS_A	MS_A/MS_W
Within groups	N-m	$SS_W = \sum_{J=1}^{m}\sum_{I=1}^{n} X_{IJ}^2 - \sum_{J=1}^{m}\frac{\left(\sum_{I=1}^{n} X_{IJ}\right)^2}{n}$	MS_W	
Total	N-1	$SS_T = \sum_{J=1}^{m}\sum_{I=1}^{n} X_{IJ}^2 - \frac{\left(\sum_{J=1}^{m}\sum_{I=1}^{n} X_{IJ}\right)^2}{N}$	MS_T	

DF (number of observations in a sample - number of parameters estimated from the sample)

These hypotheses assume a high degree of precision in the analytical program in order to be certain that any changes in concentration are not merely related to laboratory error. This concern has been addressed in the section on analytical methods.

Table II.4 summarizes the single factor ANOVA showing the derivation of the F-test ratio. The results of applying the F-test for the two hypotheses are given in Tables II.5 and II.6, respectively. In these tables, r represents rejection of the hypotheses at the 1% level, R is rejection at the 5% (but not 1%) level, and A is acceptance. Detailed ANOVA tables and calculated F-values are given in Davis (1987).

Table II.5 summarizes the ANOVA results for the test of hypothesis 1. There are statistically significant differences in lipid concentrations for all environmental samples. Exceptions to this general conclusion are the Σketone+aldehyde+ester fractions for both the atmospheric fallout and waste water samples.

The ANOVA results for the test of hypothesis 2 (between lipid concentrations vs. within site variation) are summarized in Table II.6. In the majority of the cases, the hypothesis would be rejected at the 5% level indicating that there is significant temporal variation in lipid composition of the sediment samples. Zone VI (Agami, the control zone) shows less variation in the lipid composition overall than the other stations. The data and ANOVA results demonstrate the existence of significant variations in lipid compositions between sample sites and temporal variations in lipid compounds in the sediments. These variations can be examined further by molecular characterization of each fraction.

2- Q-mode factor analysis and linear programming: Factor analysis has recently been used in Environmental Chemistry (e.g. Thurston and Spengler, 1985; Massart *et al.*, 1988; Irwin and Meyer, 1989; Grant, 1990; Malinowski, 1991; Rapp, 1991; Tysklind *et al.*, 1992), but few studies have been reported for the Mediterranean region (El-Sayed *et al.*, 1988; Grimalt *et al.*, 1990, Aboul-Kassim *et al.,* 1992b). Q-mode factor analysis is based on grouping a multivariate data set based on the data structure defined by the similarity between samples. It is devoted exclusively to the interpretation of the inter-object relationships in a data set, rather than to the inter-variable (or covariance)

Table II.5: Summary of ANOVA for hypothesis 1 for sample collection type (atmospheric fallout, surficial sediments, waste waters), samples from all sites are part of a single normal distribution.

Lipid fraction	Atmospheric fallout	Waste Water	Surficial sediment
Aliphatics	r	r	r
Monoaromatics	R	R	R
PAHs	r	r	r
Fatty acids	r	r	r
Esters+Ketones+ Aldehydes	A	A	R
Alcohols	r	r	r

Letters refer to probabilities for rejection of hypothesis (r = <1%, R = <5% but > 1%, A= ≥ 5%, i.e. acceptance at the 5% confidence level)

Table II.6: Summary of ANOVA for hypothesis 2 for surficial sediment samples from each zone form a single normal population.

Lipid fraction	Zones					
	I	II	III	IV	V	VI
Aliphatics	A	r	r	A	r	A
Monoaromatics	R	r	r	R	r	r
PAHs	r	r	R	R	r	r
Fatty acids	r	R	r	A	r	A
Esters+Ketones + Aldehydes	r	R	r	R	R	A
Alcohols	r	r	r	R	R	A

Letters refer to probabilities for rejection of hypothesis (r = <1%, R = <5% but > 1%, A = >5%, i.e. acceptance at the 5% confidence level)

relationships explored with R-mode factor analysis. The measure of similarity used is the cosine theta matrix, i.e. the matrix whose elements are the cosine of the angles between all sample pairs (Imbrie and Purdy, 1962).

The goal of Q-mode factor analysis is analogus to geochemical partitioning models which seek to determine the absolute abundance of the dominant components in a sediment sample (Imbrie and Van Andel, 1964). Factor analysis provides a description of the multivariate data set in terms of a few end members (factors), which account for the variance within the data set. These factors are usually orthogonal factors which are described in terms of the original data variables. The importance of each variable in each end member is represented by a factor score, which is a unit vector in n (number of variables) dimensional space, with each element having a value between -1 and 1 and the sum of the squared elements equal to 1.00. The set of scores for all factors makes up the factor score matrix (Klovan and Imbrie, 1971). The relative importance of each end member factor in each sample is its factor loading value. The complete set of factor loadings describing each sample in terms of its end members is the factor loading matrix.

Factor analysis has not often been used to determine the actual composition of end member sources in geologic mixtures (Figure II.5, Leinen and Pisias, 1984), because transformations of the original data variables during the analysis result in negative factor scores for some variables and negative concentrations of some variables in the end member. In this paper, we use the technique proposed by Leinen and Pisias (1984) to determine the number of end members in the data set with an extended Q-mode factor analysis (Miesch, 1976) to identify the principal sources of variations in the data set (i.e. end members within the data set). To determine the composition of end members, the extended Q-mode factor analysis was combined with the Leinen and Pisias (1984) new vector rotation scheme to obtain reasonable compositions for the end members and the relative importance or concentrations of each end member in each sample (Figure II.5). The compositions derived by this technique are used as inputs to a partitioning technique such as the linear programming technique (LPT) to determine the importance or concentration of each end member within each sample (Leinen and Pisias, 1984). Since surficial bottom sediments from the Alexandria coast provide an integrated picture of the

Figure II.5: Examples of a) principal components determined for a hypothetical two variable system with P (PAH), AL (Alcohol) and its varimax rotation, b) an oblique vector rotation for a hypothetical three variable system with P, AL and K (Ketone) and c) the new rotation developed by Leinen and Pisias (modified from Leinen and Pisias, 1984).

FAILURE OF SIMPLE Q-MODE FACTOR ANALYSIS (FA) TO PARTITIONING PROBLEM:

I- Problems associated with the absolute composition of end member:

- Vectors generated by FA are not composition vectors, so cannot be used to indicate the absolute end member composition.
- Factor scores only give a relative measure of the importance of each variable in each end member, also reflect any scaling done on the data set prior to the analysis.
- Factor loading matrix indicates only the relative importance of each end member and not an absolute abundance.

The solution is to use an extension of Q-mode factor analysis, which will help obtain an absolute composition of end members.

II- Problems associated with negative values in:

- Factor score matrix.
- Factor loading matrix.

The solution is to use:

1- Varimax rotation (orthogonal):

- It rotates the principal component axes so that the variability within the data set explained by each axis is maximized (Solid vectors with arrowhead represent P & Al data points). P_1 is the first principal component (PC, mean vector), P_2 is the second and is constrained to be orthogonal to P_1.
- The rotation brings the end member axis closer to real sample compositions.
- The composition of the varimax end members can and usually contain large negative values for some variables, thus cannot represent real geological end member composition.

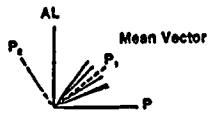
2- Oblique rotation (non-orthogonal):

- It involves the rotation of each varimax end member (PC vectors) to the sample vector (dotted lines with data points) nearest to it in composition, resulting in positive values for all variables. Since each varimax axis is rotated to a sample contained in the data set, the end member factors are constrained to have realistic compositions.
- Some samples in the data must be pure end members.
- The dotted lines indicate and represent a set of principal component vectors; V_1, V_2, V_3. V_3 has a negative value for Al, an unreasonable organic geochemical composition.

3- Leinen and Pisias's new rotation):

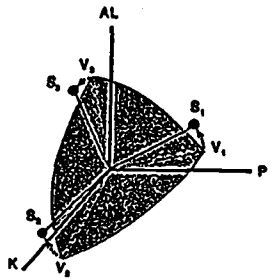
- No need for having sampled pure end members.
- The end members lie between the mean concentration and varimax axes which contain negative values, because the best known statistical parameter within a data set is the vector of mean composition.
- The end member composition is found by rotating one at a time, each varimax axis toward the mean vectors until the composition of the rotated axis is reasonable, i.e. variable concentrations $\geq$ zero.
- open dots labeled V_1-V_3 represent the original PC vectors. Light dotted lines with arrows show the path of rotation of the PC axes which are rotated toward the mean until they intersect the positive vector space. Solid lines with black dots labeled E_2 and E_3 show the resulting end member vectors. V_1 is not rotated since it is already in the positive vector space.

Principal Components

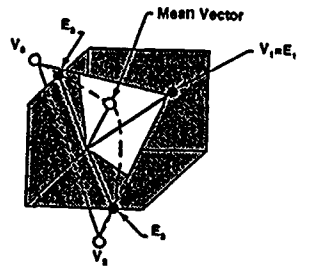


Varimax Rotation

Oblique Rotation



The New Rotation



P= PAH, K= ketone, AL=alcohol.

events taking place in the water column, we only applied Q-mode factor analysis and LPT to the lipid data set of these samples.

The first result from Q-mode factor analysis of this data yields two significant principal factor loading scores, providing information about sample variation of about 93.2 and 4.96%, respectively (maximum cumulative information 98.2%). When individual elements of this factor loading matrix are squared, the sum of the squared loadings for all factors of a particular sample equals 1.00 (i.e. communality; which is the proportion of the total variance in a particular sample that is explained by those factors). The individual squared loading of one factor represents the fraction of the sample which that factor contributes to the sample (e.g., if a sample has a factor 1 loading of 0.4 then $(0.4)^2$ = 0.16 or 16% of the sample is from factor 1). Thus the distribution of the various factors in each sample was obtained. A plot is used to observe associations (SAS, 1991, Rapp, 1991) between samples (groupings)(Figure II.6). All the samples plot near the binary mixing line (a line from factor 1=1.00, factor 2=0 to factor 1=0, factor 2=1.00), indicating that only two factors are needed to explain the majority of the composition of the samples. The second result is from squaring individual elements of the factor score matrix yielding the sum for a particular factor equal to 1.00. The proportion which an individual lipid class contributes to the total composition of an end member is determined by dividing the absolute values of all lipid fraction scores for that factor by the sum of the absolute values of all the scores for that factor.

After varimax rotation (Figure II.5a) of the composition scores, the principal component axes were rotated so that the variability within the data set explained by each axis is maximized (orthogonal axes) and the end member axis is brought closer to real sample compositions (Imbrie and Van Andel, 1964). Because factor analysis uses orthogonal axes to describe the original data set, the analysis usually results in negative factor scores and negative concentrations of some variables (Imbrie and Van Andel, 1964; Klovan and Miesch, 1976, Klovan, 1981) in the end members (which are unrealistic in organic geochemical studies), a non-orthogonal (oblique) rotation of end member vectors is necessary (Figure II.5b). One strategy is to rotate each varimax end member to the sample nearest to it in composition. Since each varimax axis is rotated to a sample

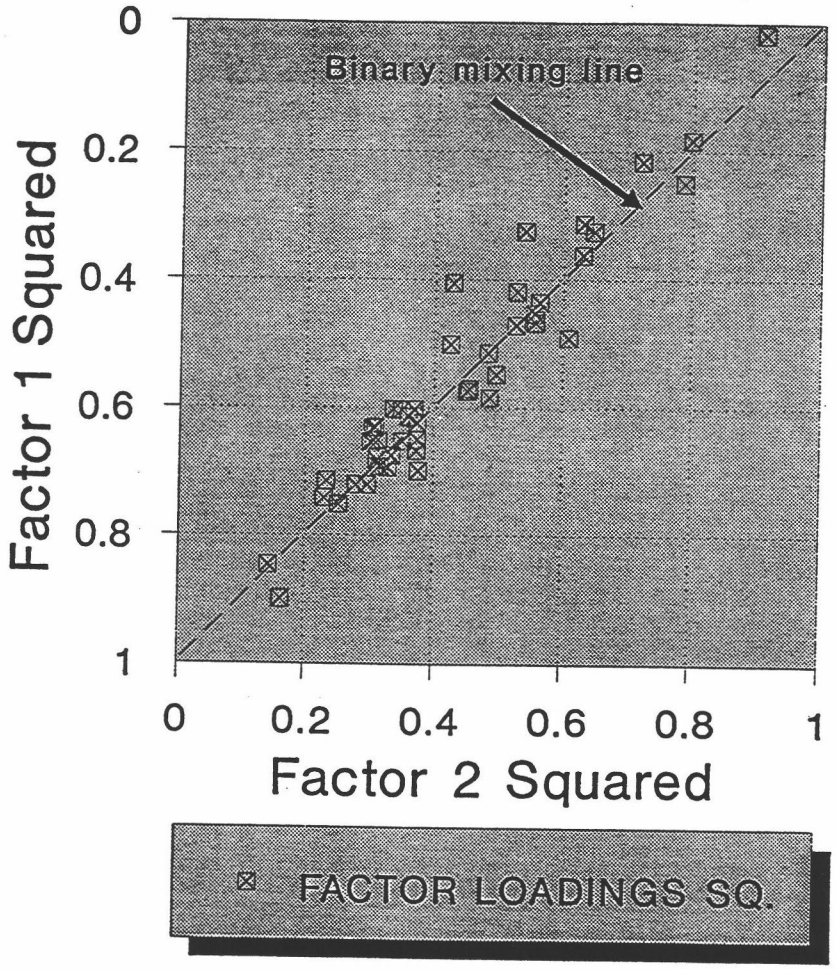


Figure II.6: Factor loadings squared.

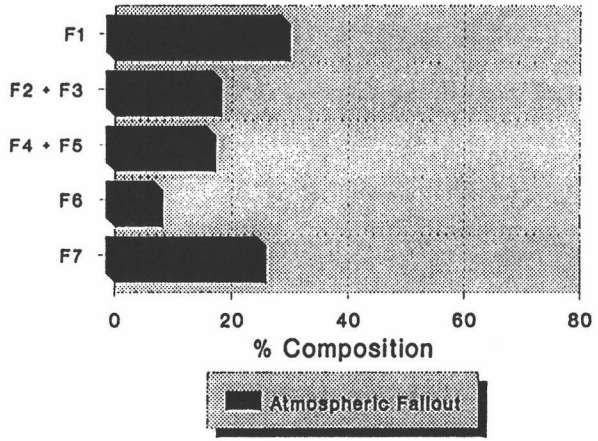
contained in the data set, the end member factors are obviously constrained to have realistic compositions. However, in order for this technique to adequately describe the data, some samples in the data set must be pure end members or subjective selection of possible end members from the data set is required.

To provide an objective means of selecting chemically reasonable end members, Leinen and Pisias (1984) developed a rotation scheme (Figure II.5c) that does not require the assumption of having sampled pure end members (Full *et al.*, 1981). Leinen and Pisias (1984) assumed that the best known statistical parameter within a data set is the vector of mean composition, so that the true end members lie between the mean concentration and the varimax axes which contain negative values. The end member compositions were found by rotating each varimax axis, one at a time, toward the mean vector until the composition of the rotated axis is reasonable (i.e. all variable concentrations are greater than or equal to zero). The criteria for choosing the number of end members used to model the data were: (1) at least 95% of the variance in the data set must be explained by the sums of squares of the end members, and (2) all end member factors that explained less than 2% of the total variance were rejected. After identifying the end member composition using this objective approach a linear programming technique (LPT) was used to determine the abundance of each end member in each sample (Wright and Doherty, 1970; Dymond, 1981). This LPT utilized the inverse technique (Dymond, 1981) to calculate small corrections to the end member compositions and abundances to better fit the observed multivariate data set (Leinen and Pisias, 1984). This helped to specify and select the compositions of the end members. The first end member composition (using LPT, Figure II.7), which explains about 93.2% of the sum of squares in Alexandria area model, is represented by the hydrocarbon fraction and dominated by aliphatics (Fraction 1, 76%). The second end member is dominated by alcohols (Fraction 6, 69%).

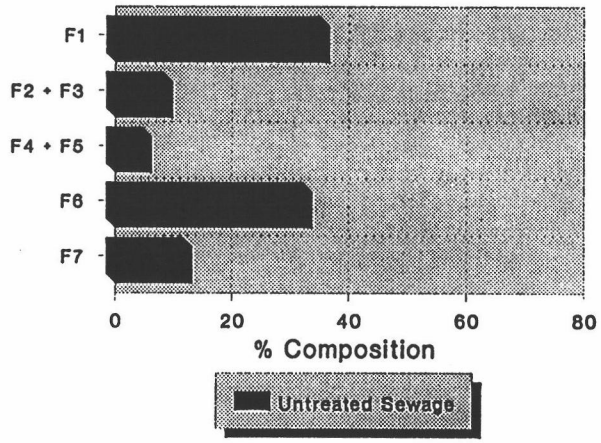
In order to assign the origin (source) of the observed factors, we used two methods:

Figure II.7: Normalized fraction yields for pure end member compositions: a) atmospheric fallout, b) sewage, and c) petroleum hydrocarbons; and d) statistically calculated end members (Q-mode factor analysis and linear programming technique) for the bottom sediments.

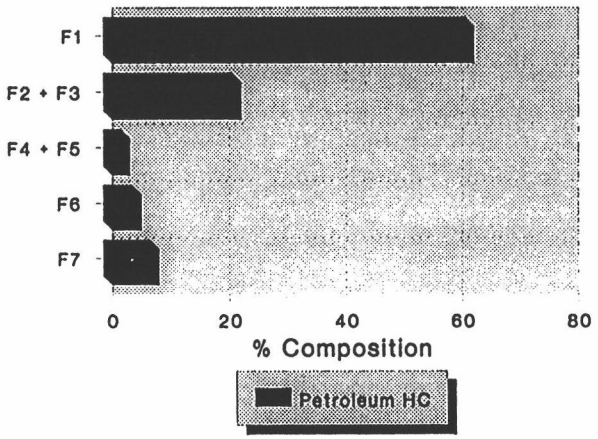
a) Lipid Fractions



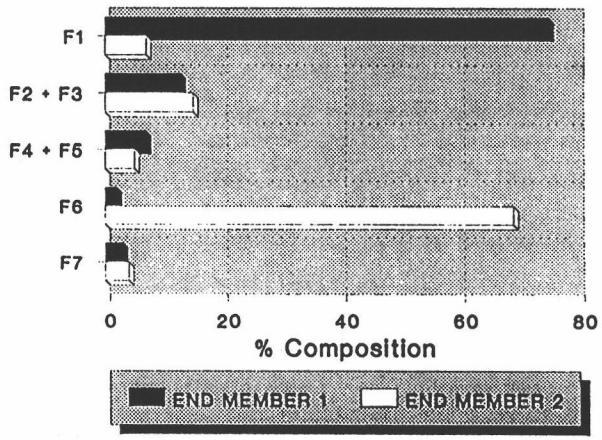
b) Lipid Fractions



c) Lipid Fractions



d) Lipid Fractions



a) statistics:

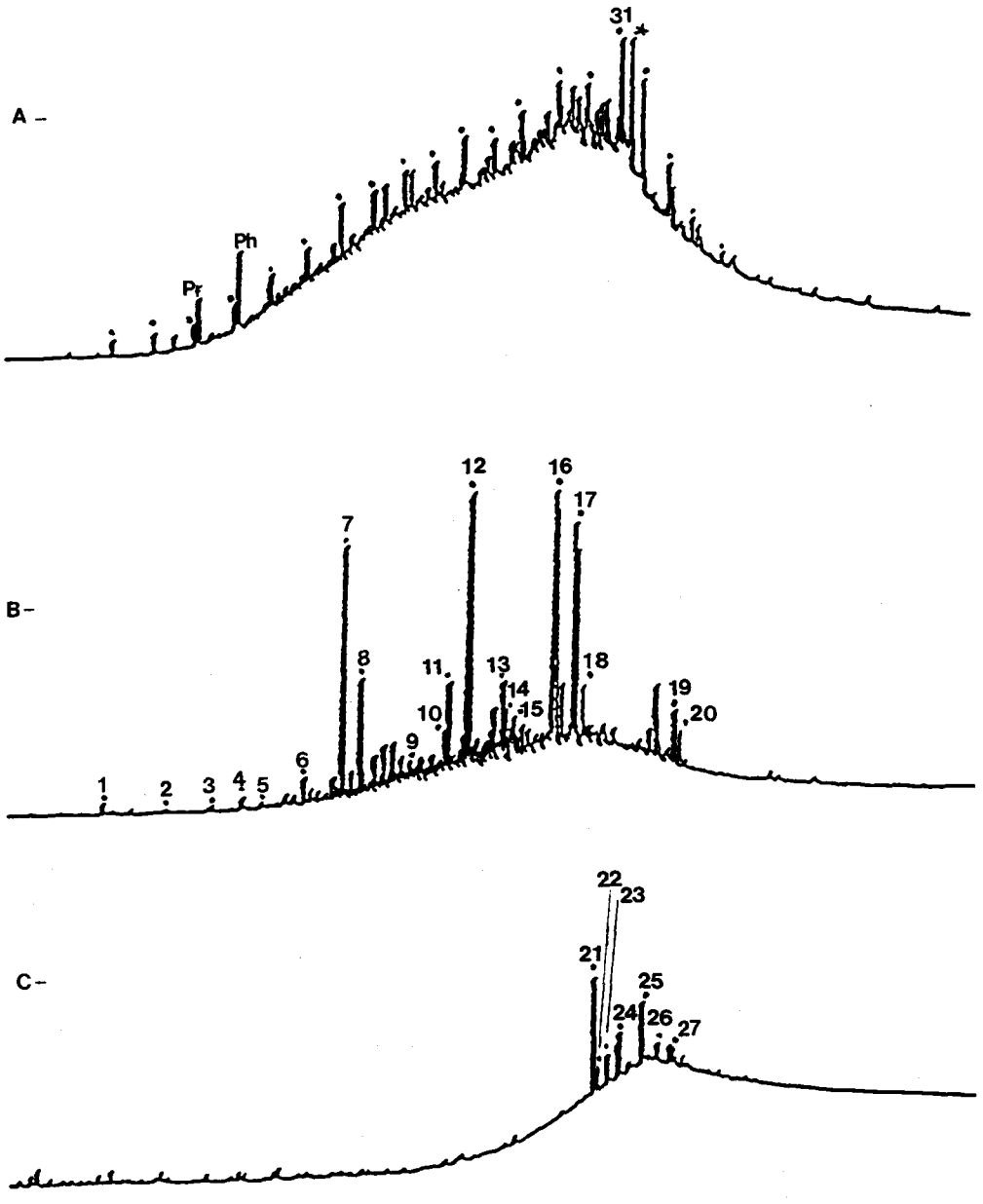
The normalized compositions of the end members were compared with the compositions of known sources (e.g., atmospheric fallout, sewage, petroleum and biogenic sources). Figure II.7 indicates that the sources of the lipids in the surficial sediments of the Alexandria coastal region are petrochemical pollution from ships and waste waters (end member 1), and domestic fecal contamination from sewage (end member 2).

b) biomarkers:

In order to confirm the sources of the end member compositions experimentally, the molecular composition of the surficial sediments was examined for the aliphatic and aromatic hydrocarbons, and alcohols. Samples believed to be pure end member sources, as for example atmospheric particle fallout, sewage and waste water, petroleum products, and biogenic samples, were characterized. This approach is ideal for confirming sources because the biomarkers are natural product compounds or their derivatives found in sediments, petroleum and sewage extracts, which provide an unambiguous link with their source and are resistant to alteration of their carbon skeletons during transport (e.g., Eglinton *et al.*, 1975; Simoneit, 1978, 1984, 1989).

The example of a GC trace of an aliphatic fraction (Figure II.8a) shows that the *n*-alkane distribution ranges from C_{14} to C_{40}, with a high level of an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons and the presence of regular isoprenoids (i.e. pristane and phytane). Advanced biodegradation is observed by the phytane/*n*-C_{18} and pristane/*n*-C_{17} ratios of >1, as well as their significant statistical correlation ($r=0.9023$, $p<0.001$; in the case of surficial sediments of zone II) with the bacterial biomass content of the water column (determined by the ATP method, Aboul-Kassim *et al.*, 1992a). An example of the petroleum biomarkers is found in the m/z 191 and 217 mass fragmentograms (Figure II.9) showing the distributions of both hopane (C_{27}-C_{35}) and sterane (C_{27}-C_{29}) series, respectively. The hopanes reflect an anthropogenic (petroleum) input, which is characterized by the 17α(H),21β(H)-hopanes and the C-22 S/R configuration for the homologs >31. The sterane hydrocarbons are comprised mainly of the 5α(H),14β(H),17β(H)-steranes, with a minor contribution of diasteranes and the

Figure II.8: Gas chromatograms representing the a) total aliphatic (*n*-alkanes=dots over peaks, *=internal standard), b) PAH and c) alcohol fractions characteristic of the Alexandria region surficial bottom sediments (Numbers indicate compound names as follows:- 1: acenaphthene, 2: methylfluorene, 3: dibenzothiophene, 4: phenanthrene, 5: anthracene, 6: fluoranthene, 7: pyrene, 8: 2,3-benzofluorene, 9: 1,1'-binaphthalene, 10: benz(a)anthracene, 11: chrysene/triphenylene, 12: benzo(b+k)fluoranthene, 13: benzo(e)pyrene, 14: benzo(a)pyrene, 15: perylene, 16: dibenzanthracene, 17:benzo(ghi)perylene, 18: anthanthrene, 19: coronene, 20: 1,2,4,5,6-dibenzopyrene, 21: 5β-cholestan-3β-ol (coprostanol), 22: 5β-cholestan-3α-ol (*epi*-coprostanol), 23: cholest-5-en-3β-ol, 24: 5α-cholestan-3β-ol, 25: 24-ethyl-5β-cholestan-3β-ol, 26: 24-ethylcholest-5-en-3β-ol, 27: 24-ethyl-5α-cholestan-3β-ol).


A –
Pr
Ph
31
B –
1
2
3
4
5
6
7
8
9
10
11
12
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17
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19
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C –
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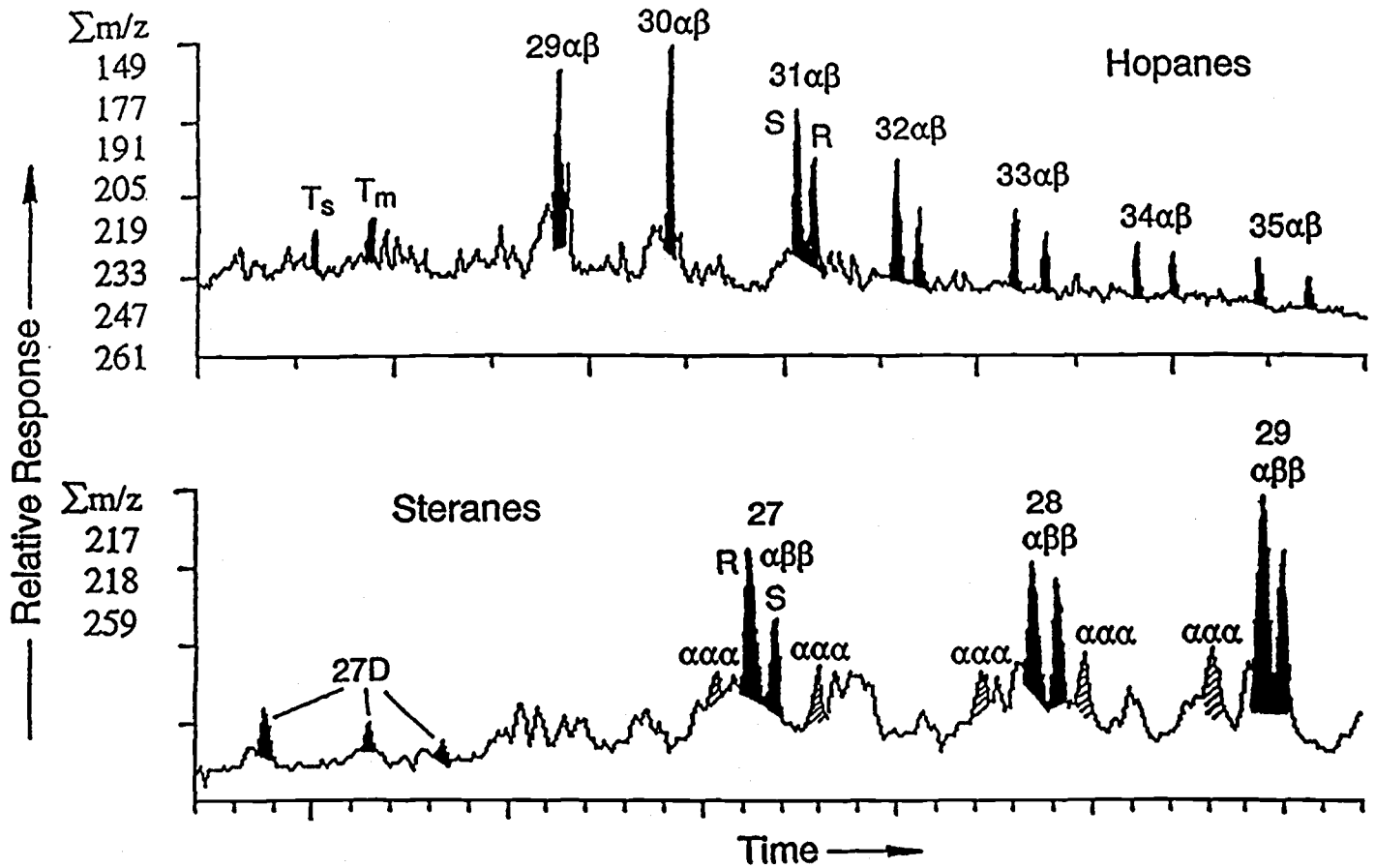
27

Figure II.9: Typical mass fragmentograms representing a) hopane (summed m/z 149,177,191,205, 219,233,247,261), and b) sterane/diasterane (summed m/z 217, 218, 259) mixtures representing the petroleum biomarkers characteristic of the Alexandria coastal sediments [T_s= 18α(H)-22,29,30-trisnorneohopane, T_m= 17α(H)-22,29,30-trisnorhopane, αβ= 17α(H),21β(H)-hopanes (R & S at C-22), αββ= 5α(H),14β(H),17β(H)-steranes (R & S at C-20), ααα=5α(H),4α(H),17α(H)-steranes (R & S at C-20), βαD=13β(H),17α(H)-diasteranes (R & S at C-20)].


Σm/z
149
177
191
205
219
233
247
261
Ts
Tm
29αβ
30αβ
31αβ
S
R
32αβ
33αβ
34αβ
35αβ
Hopanes
Σm/z
217
218
259
Steranes
27D
27
R αββ
S
ααα
ααα
ααα
28
αββ
ααα
ααα
29
αββ
Relative Response
Time

5α(H),14α(H),17α(H) configuration. The use of m/z 217 and 191 mass fragmentography, isoprenoid hydrocarbons, UCM and a CPI of one are useful in characterizing the petroleum source of end member 1 and supporting the statistical approach.

The second end member (alcohols) originates mainly from the dominance of fecal sterols (Figure II.8c) such as coprostanol [5β(H)-cholestan-3β-ol], *epi*-coprostanol [5β-cholestan-3α-ol], 24-ethyl-5β-cholestan-3β-ol and 24-ethyl-5α-cholestan-3β-ol which are indicative of the domestic sewage pollution source in the Alexandria aquatic environment. Thus, coprostanol has been used as a biomarker indicator for sewage because of its occurrence in human feces, as a result of biohydrogenation of cholesterol by internal microflora (Hatcher and McGillivary, 1979; Walker *et al.*, 1982; Venkatesan and Santiago, 1989). The biomarker correlation of the alcohol fraction with the human fecal source in the environment confirms the statistical end member 2.

The PAHs, a class of chemical carcinogenic and mutagenic pollutants, were identified and quantified by GC-MS in the Alexandria area surficial sediments (Figure II.8b). They are part of both end members 1 (13%) and 2 (15%). This may indicate a dual origin (petrochemical and thermogenic from atmospheric fallout or sewage disposal). Further examination of the individual PAHs and their alkylated homologs is needed to differentiate between sources in order to assign their transport and fate in the environment.

CONCLUSION

An extensive study of the different extractable lipid classes was carried out in order to examine the impact of anthropogenic sources of pollution on the Alexandria environment. Samples collected from various compartments of the Alexandria region (i.e., atmospheric particulate fallout, untreated sewage and waste water discharge, surficial bottom sediments) were analyzed for quantitative lipid data which were interpreted using both molecular biomarker and statistical approaches. The emission rates (loadings) of the different lipid fractions to the Alexandria environment were calculated as atmospheric particle deposition, terrestrial runoff, and sedimentary flux to evaluate the inputs.

Analysis of variance (ANOVA), applied to the data set to compare the relative magnitude of sample site and sample type variances, indicated that there are statistically significant differences in lipid concentrations for all environmental samples, except for the Σketone+ aldehyde+ester fractions of both the atmospheric fallout and waste water samples. In addition, ANOVA demonstrated the existence of significant variations in lipid compositions between sample sites and temporal variations in lipid compounds in the sediments.

Extended Q-mode factor analysis and linear programming technique were implemented to reduce the data set into meaningful statistically significant end members specific for the area, as well as to assess their contributions to each sample. Multivariate data analysis indicated the presence of two significant end members, which were further confirmed by using molecular biomarker characterization. The first end member composition, which explained 93.2% of the sum of squares in the Alexandria area model, was represented by the hydrocarbon fraction and dominated by aliphatic hydrocarbons (76%). The second end member was dominated by alcohols (69%). Further experimental assignment of end member sources (by comparison with the compositions of known sources) indicated that the main sources of the lipids in the surficial sediments of the Alexandria coastal region are petrochemical pollution from ship traffic and waste waters (end member 1), and domestic fecal contamination from sewage (end member 2).

ACKNOWLEDGEMENTS

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CHAPTER III

ALIPHATIC AND AROMATIC HYDROCARBONS IN PARTICULATE FALLOUT OF ALEXANDRIA CITY, EGYPT - SOURCES AND IMPLICATIONS

ABSTRACT

Particulate fallout samples (PFS) were collected in Alexandria city and their aliphatic and aromatic hydrocarbon compositions were determined both quantitatively and qualitatively to characterize the homologous and biomarker compounds in terms of their original sources. The results show that all samples contain aliphatic hydrocarbons, including *n*-alkanes, UCM, isoprenoids, tri- and tetracyclic terpanes, hopanes, and steranes/diasteranes. The main source of these compounds is from petrochemical contamination with trace input of terrestrial higher plant wax. In addition, polycyclic aromatic hydrocarbons, which are considered to be combustion products from fossil fuel such as petroleum, are also widely distributed in all samples.

Multivariate statistical analysis, including extended Q-mode factor analysis and linear programming technique, was performed in order to reduce the hydrocarbon data set into a meaningful number of end members (sources). This analysis indicates that there are 2 significant end members explaining 90% of the total variation among the samples, and confirming petrochemical (79.6%), and thermogenic/pyrolytic (10.4%) sources in the PFS model.

INTRODUCTION

Hydrocarbons (aliphatic and aromatic) are widespread organic compounds which are part of the carbon cycle in the contemporary environment. Natural hydrocarbons produced by terrestrial and marine plants are generally encountered at trace levels, with their characteristic components or distributions reflecting their origin and transport. Anthropogenic hydrocarbons are widely distributed and originate from different sources, such as petroleum, coal, and wood via their combustion products. Accordingly, the anthropogenic hydrocarbon sources are found mostly in heavily populated cities associated with industrial and urban activities.

The transport of pollutants by atmospheric particulate matter can expose large populations to toxic substances (carcinogenic or mutagenic), representing the environmental process of highest potential hazard to human health, especially when the proximity between humans and pollutant sources is closest. Thus, a direct cause-effect relationship between the atmospheric release of allergenic products and urban asthma outbreaks has been documented (Neff, 1979; Cretney *et al.*, 1985; Colmsjö *et al.*, 1986; Daisey *et al.*, 1986). In addition, many organic compounds, i.e. hydrocarbons, found in urban air or in fallout deposits have been shown to be mutagens or carcinogens (Ketseridis *et al.*, 1976; Levin *et al.*, 1978; Baum, 1978; Gelbon and Tśo, 1978; Grimmer *et al.*, 1981a,b; Stegeman, 1981; Ho *et al.*, 1982; Muel and Saguen, 1985, Alarcon and Cruzado, 1988; Leuenberger *et al.*, 1988; Atlas, 1990).

The importance of long-range atmospheric transport to the global distribution of pollutants and natural products is well documented (e.g., Knap, 1990). Major environmental problems in the Southeastern Mediterranean region are the result of anthropogenic activity and, over remote areas, of dust storms prevailing between September and June, mostly during the spring season (Chester *et al.*, 1977, 1984; Morales, 1979; Mamane *et al.*, 1980; Middleton, 1986; Bucher and Lucas, 1984). These dust storms are called Saharan dust (Haboob in Sudan and Khamsin in Egypt) which are carried in the atmosphere by high velocity winds with large vertical motions that are associated with cold or warm low pressure systems (Joseph *et al.*, 1973; Yaalon and

Ganor, 1979; Levin *et al.*, 1980). Thus, the dust is transported by westerly or south-westerly winds to Egypt (Lunson, 1950; Joseph *et al.*, 1973) and then to Israel (Levin and Lindberg, 1979; Ganor, 1991; Ganor *et al.*, 1991). Ganor and Mamane (1981) reported that dust storms in the eastern Mediterranean usually contain high concentrations of total particulate solids.

Alexandria City (Egypt), located in the south-eastern Mediterranean region (Figure III.1), is unique for assessing the hydrocarbon composition in the atmosphere, especially during the study period, because it receives particulate mixtures from local and Khamasin dust sources. Thus, the characterization of the hydrocarbon constituents in particulate fallout in terms of their natural or anthropogenic sources serves to define and elucidate the regional transport pattern. This is the first comprehensive characterization of the hydrocarbon components in particulate fallout in the south-eastern Mediterranean. The previous research was conducted in the western Mediterranean (Ho *et al.*, 1982; Marty *et al.*, 1984; Muel and Saguen, 1985; Saliot and Marty, 1986; Sicre *et al.*, 1987a,b; Grimalt *et al.*, 1988; Rosell *et al.*, 1991; Simó *et al.*, 1991).

The objectives in this paper are to: (a) characterize both aliphatic and aromatic hydrocarbons in the solvent extractable fraction of particulate fallout collected from Alexandria in different areas, (b) use biomarkers to characterize the different sources, and (c) carry out statistical data analyses using both univariate and multivariate statistical procedures to examine the variations in the data, determine the regions of hydrocarbon concentration and find statistically significant associations (end members) in the data set which will help to assess and identify hydrocarbon composition sources in the atmospheric dry fallout over the city.

EXPERIMENTAL METHODS

Sampling

Atmospheric particulate fallout samples (PFS) were collected from locations in Alexandria representing 4 main zones, namely the beach area, eastern and western city

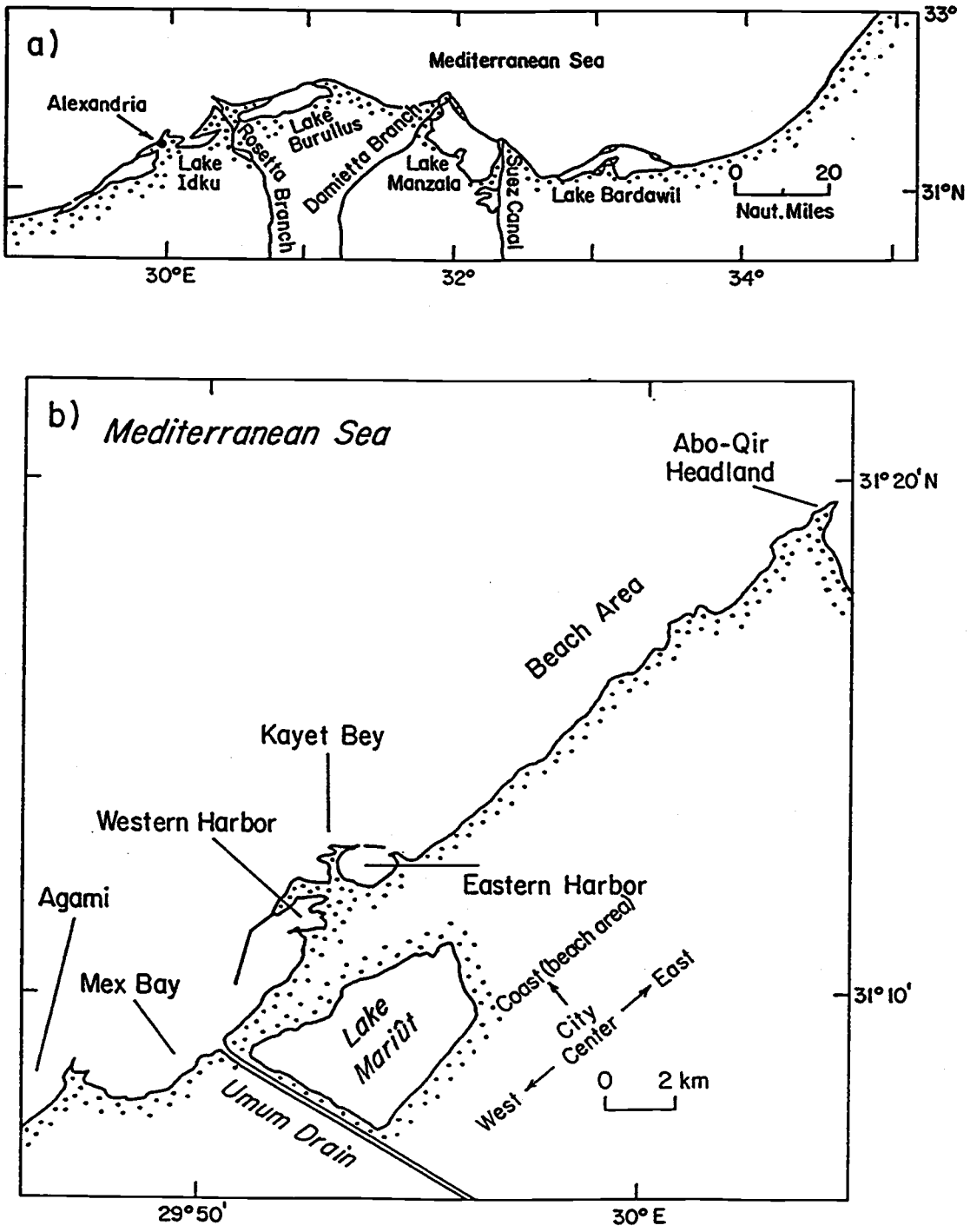


Figure III.1: The study area, a) Egypt in the southeastern Mediterranean region, b) the Alexandria City.

and central city (Figure III.1, Table III.1). Samples were collected by exposing plastic trays covered with solvent precleaned aluminum foil for typically 45-67 days.

Sample extraction and separation

To minimize contamination all glassware was cleaned with soap and water, rinsed with distilled water, heated in an oven at 550°C for 8 hrs to combust any traces of surficial organic matter, and finally rinsed twice with ultra-pure methanol and methylene chloride. The KOH used for saponification was extracted 3 times with *n*-hexane and once with methylene chloride in a separatory funnel to remove organic interferences.

An extraction protocol was designed for the qualitative and quantitative analyses of different organic compounds found in the lipids of the PFS. In brief, samples (typically 1.5 g) were extracted in a Soxhlet apparatus with methylene chloride-methanol (2:1). This extract is a measure of the amount of extractable organic matter (EOM) in a sample. All the extracts (EOM) were concentrated to 2 ml and hydrolyzed overnight with 35 ml of 6% KOH/methanol. The corresponding neutral and acidic fractions were successively recovered with *n*-hexane (4 x 30 ml). The neutral fraction was fractionated by column chromatography, using a column (50 x 1.2 cm) filled with 8 g each of alumina (top) and silica (bottom), both deactivated with 5% water. The following fractions were eluted and collected: (a) 45 ml of *n*-hexane (aliphatic hydrocarbons, F1), (b) 25 ml of 10% methylene chloride in *n*-hexane (mono-aromatic hydrocarbons, F2), (c) 40 ml of 20% methylene chloride in *n*-hexane (polycyclic aromatic hydrocarbons "PAHs", F3), followed by 3 additional fractions representing ketones, aldehydes, esters and alcohols. Here we describe the results for fraction 1 to represent the aliphatic hydrocarbons and for fractions 2&3 the aromatic hydrocarbons.

Organic carbon analysis

Organic carbon analyses were carried out for all the particulate fallout samples using a Carlo Erba NA-1500 CNS analyzer. Samples were combusted at 1000°C in an oxygen-rich medium to CO_2. The CO_2 gas is separated chromatographically, detected

Table III.1: Locations, deposition rates and TOC contents of particulate fallout samples from Alexandria, Egypt.

Zone	Zone location	Sampling time and date in 1992	Number of samples	Mean deposition rate ($mg/d/m^2$)	Total Organic Carbon		Mean conc. of EOM* (mg/g)
					Mean conc. (mg C/g)	Mean deposition rate (mg $C/d/m^2$)	
A	Beach Area	April 27-July 4	4	594±261	89.6±12.2	53±3	17.1±5.3
B	City Center	May 12-June 16	4	578±152	96.8±9.5	56±2	10.0±3.1
C	Eastern Side	May 5-June 27	3	4157±823	92.8±6.2	386±5	19.5±4.9
D	Western Side	May 6-July 7	3	185±28	127.0±18.4	24±1	11.2±2.1
Average				1378±1613	101.6±14.9	130±149	14.5±3.9

*extractable organic matter

using a thermal conductivity detector and the resulting signals are digitized, integrated, and mathematically processed along with results based on standards. The concentrations of the hydrocarbon fractions were calculated relative to the total organic carbon (TOC) content of the PFS.

Instrumental analyses

High resolution gas chromatography (HRGC) of the hydrocarbon fraction of the PFS was conducted on a Hewlett Packard (HP) *5890*A gas chromatograph (GC), equipped with a split/splitless capillary injection system and a flame ionization detector (FID). The samples were analyzed in the splitless mode using a fused silica capillary column (30 m x 0.25 mm i.d, DB-5, J & W Scientific) with a 0.25 μm film thickness and using helium as carrier gas. The analog signal was monitored and/or integrated with an HP *3393*A integrator. The GC conditions were: FID 300°C, injector 300°C, initial oven temperature 65°C, programmed to 200°C at 4°C/min, isothermal at 290°C (60 min). The gas chromatography-mass spectrometry (GC-MS) analyses of the samples were performed using a Finnigan *9610* GC (identical column with initial temperature 50°C, isothermal 6 min, programmed at 4°C/min to 310°C, isothermal 60 min) interfaced directly with a Finnigan *4021* quadruple mass spectrometer (electron impact, emission current -0.45 mA, electron energy 70eV, scanned from 50 to 650 daltons). Data were acquired and processed with a Finnigan-INCOS Model *2300* data system.

Compound identification and quantification

Compound identification was based on comparison with the retention times and mass fragmentation patterns of standard reference materials and with the help of the National Institute of Standard and Technology (NIST) standard library (incorporated in the INCOS data system). This was achieved using the following standard mixtures injected in both GC and GC-MS: (1) a series of normal alkanes ranging from *n*-C_{10} to *n*-C_{36}, (2) regular isoprenoids as pristane and phytane, and (3) a suite of about 30 polycyclic aromatic hydrocarbons (PAHs), including: naphthalene, methyl- and dimethylnaphthalene,

fluorene, 9-methylfluorene, dibenzothiophene, phenanthrene, 3-, 2-, 9- and 1-methylphenanthrene, anthracene, fluoranthene, pyrene, 2,3-benzofluorene, 1,1'-binaphthalene, benz(a)anthracene, chrysene, benzo(b+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, 9,10-diphenylanthracene, dibenz(ah)anthracene, benzo(ghi)perylene, anthanthrene, coronene, and dibenzo(ae)pyrene. Quantification was based on the application of perdeuterated compounds (e.g. n-$C_{32}D_{66}$ and d_{10}-pyrene) as internal standards for the aliphatic and aromatic fractions, respectively. In order to correct for detector response, sets of relative response factors were determined for every fraction from multiple injections.

Statistical analyses

Organic geochemical data on the hydrocarbon compositions and biomarkers was examined statistically in order to determine any significant environmental variation. All statistical analyses were performed using the SPSS/PC$^+$ statistical package (Norusis, 1986), as well as the statistical package provided on the SUN system of College of Oceanic and Atmospheric Sciences at OSU. These analyses include standard deviation (measure of dispersion), correlation between variables, extended Q-mode factor analysis and linear programming techniques.

The objectives of the statistical analyses are to verify the following points throughout the discussion of this paper:

(1) Define the organic geochemical characteristics of the PFS samples in the different regions of Alexandria City.

(2) Examine the organic geochemical relationship between the samples.

(3) Discuss the sources and occurrence of the biomarkers.

The statistical parameters used to test this organic geochemical data were calculated in the following way:

1- <u>The mean (X)</u> is the arithmetic average, i.e., the sum of the values of all observations divided by the number of observations. The range, gives the low and high values for a parameter in the data set, i.e., a measure of the dispersion of the data.

2- The standard deviation (S.D.) or standard error of a mean is a measure of the dispersion of the data around the mean. It is defined simply as the square root of variance, where the variance is the average squared deviation of all possible observations from the mean.

3- The correlation coefficient (r) expresses the standard deviation as a percentage of the mean value. It is characteristic of the spread (i.e., degree of scatter) of the variables. Pearson's coefficient of linear correlation, referred to as r, is used to assess the linear relationship between two measured variables. The correlation coefficient is expressed as:

$$r = [\text{covariance } (x,y)]/[(\text{variance } x \,.\, \text{variance } y)^{1/2}]$$

The correlation coefficient is unitless ranging from +1 to -1, where (+1) = perfect direct relationship between two variables, (-1) = one variable changes inversely in relation to the other, and, 0 = absolute lack of linear relationship.

4- Q-mode factor analysis and linear programming technique: Factor analysis (FA) is a statistical technique which effectively reduces the raw data into a smaller number of hypothetical variables called factors. There are two types of FA, known as R- and Q-mode techniques. The first is concerned with the relationships between variables while the second concerned with the interrelationships between samples. In the present work Q-mode FA will be employed. The quantitative compositions of the hydrocarbon fractions were submitted to extended Q-mode FA and linear programming technique (LPT). LPT was used to identify end member compositions (Leinen and Pisias, 1984; Aboul-Kassim and Simoneit, 1994b).

FA provides a description of the multivariate data set in terms of a few orthogonal end members (factors), which account for the variance within the data set. The importance of each variable in each end member is represented by a factor score, while the relative importance of each end member in each sample is its factor loading value. Because transformations of the original data variables during the analysis result in negative factor scores for some variables and negative concentrations for others in the end member, we used the "new rotation" technique proposed by Leinen and Pisias (1984) which does not require the assumption of having sampled pure end members. The criteria for choosing the number of end members used to model the data were: (1) at least 90% of data set

variance was explained by the sums of squares of the end members, and (2) all end member factors that explained less than 2% of the total variance were rejected. By using a partitioning by LPT, a set of equations was applied for correcting the initial end member compositions and their abundance to better fit the observed multivariate data set. This helped to specify and select the compositions of the end members.

Organic geochemical ratios

In order to build a robust data set, we used both the actual concentrations of variables and their ratios. The following calculations based on biomarker indices (Tissot and Welte, 1984) were made to show relationships among samples (Table III.2):

1- Carbon Preference Index (CPI), a measure of the ratios of odd-to-even carbon numbered *n*-alkanes, is calculated according to the following equations (Simoneit, 1989):

CPI_a(whole range, petroleum) = $[\sum(C_{13}- C_{37})/\sum(C_{14}- C_{39})]$

CPI_b (split range, bacterial/algal) = $[\sum(C_{13} - C_{19})/\sum(C_{12} - C_{18})]$

CPI_c (split range, higher plant wax)= $[\sum(C_{21} - C_{37})/\sum(C_{20} - C_{36})]$

2- Terrestrial higher plant *n*-alkane signature is calculated by subtraction of the average of the next higher and lower even carbon numbered homolog (Simoneit *et al.*, 1990) as follows:

Wax *n*-C_n = $[C_n] - 0.5[C_{(n+1)} + C_{(n-1)}]$

negative values of C_n were taken as zero.

3- Ratio of unresolved to resolved hydrocarbons (U/R) (Mazurek and Simoneit, 1983), is calculated as:

U/R = concentration of unresolved complex mixture (UCM)/concentration of $\sum$ resolved hydrocarbon peaks (mostly *n*-alkanes)

4- Triplet ratio of tricyclic and tetracyclic terpanes, a measure of biodegradation of petroleum hydrocarbons (Kvenvolden *et al.*, 1985), calculated as:

Triplet ratio = (C_{26}-tricyclic S + C_{26}-tricyclic R)/(C_{24}-tetracyclic).

Table III.2: Mean aliphatic hydrocarbon compositions relative to the weight and total organic carbon content, as well as biomarker ratios of the particulate fallout samples from Alexandria.

Compound Class	Composition	M.W.	Concentrations[a]				ID[b]
			Zone A	Zone B	Zone C	Zone D	
ALIPHATIC HYDROCARBONS							
n-Alkanes (μg/g)[c]							
n-tetradecane	$C_{14}H_{30}$	198	bd	5.3 (55)	bd	bd	a
n-pentadecane	$C_{15}H_{32}$	212	1.0 (12)	24.5 (253)	bd	bd	a
n-hexadecane	$C_{16}H_{34}$	226	0.6 (7)	13.9 (144)	bd	bd	a
n-heptadecane	$C_{17}H_{36}$	240	0.6 (7)	7.2 (74)	2.8 (30)	bd	a
n-octadecane	$C_{18}H_{38}$	254	0.6 (7)	4.4 (46)	4.5 (49)	4.2 (33)	a
n-nonadecane	$C_{19}H_{40}$	268	1.3 (14)	9.0 (93)	9.8 (106)	30.2 (238)	a
n-eicosane	$C_{20}H_{42}$	282	2.9 (32)	13.4 (138)	17.0 (183)	70.9 (558)	a
n-heneicosane	$C_{21}H_{44}$	296	4.8 (54)	21.1 (218)	25.8 (278)	142.8 (1112)	a
n-docosane	$C_{22}H_{46}$	310	5.5 (61)	29.7 (307)	28.8 (310)	163.7 (1323)	a
n-tricosane	$C_{23}H_{48}$	324	5.9 (65)	41.8 (432)	30.4 (328)	166.1 (1346)	a
n-tetracosane	$C_{24}H_{50}$	338	5.9 (66)	44.9 (464)	29.6 (314)	150.6 (1236)	a
n-pentacosane	$C_{25}H_{52}$	352	5.7 (64)	56.8 (587)	31.5 (340)	134.5 (1146)	a
n-hexacosane	$C_{26}H_{54}$	366	4.6 (51)	48.2 (498)	23.0 (248)	108.2 (852)	a
n-heptacosane	$C_{27}H_{56}$	380	4.4 (49)	59.9 (619)	26.1 (281)	95.7 (753)	a
n-octacosane	$C_{28}H_{58}$	394	4.5 (50)	64.3 (664)	19.9 (234)	90.4 (712)	a
n-nonacosane	$C_{29}H_{60}$	408	3.8 (42)	81.5 (842)	25.1 (271)	78.2 (619)	a
n-triacontane	$C_{30}H_{62}$	422	3.2 (36)	64.2 (663)	18.1 (195)	62.3 (490)	a
n-hentriacontane	$C_{31}H_{64}$	436	2.3 (26)	55.6 (574)	14.4 (155)	46.4 (365)	a
n-dotriacontane	$C_{32}H_{66}$	450	1.1 (12)	30.3 (313)	7.5 (81)	26.5 (209)	a
n-tritriacontane	$C_{33}H_{68}$	464	0.6 (7)	22.8 (235)	4.5 (49)	20.3 (160)	a
n-tetratriacontane	$C_{34}H_{70}$	478	0.5 (6)	12.9 (133)	4.8 (52)	10.7 (84)	a
n-pentatriacontane	$C_{35}H_{72}$	492	0.4 (9)	8.9 (91)	0.7 (78)	7.2 (78)	a
n-hexatriacontane	$C_{36}H_{74}$	506	bd	3.2 (33)	0.6 (7)	6.0 (47)	a
n-heptatriacontane	$C_{37}H_{76}$	520	bd	2.2 (23)	bd	4.0 (32)	a
n-octatriacontane	$C_{38}H_{78}$	534	bd	0.9 (10)	bd	bd	a

Table III.2: Continued.

Compound Class	Composition	M.W.	Concentrations[a] Zone A	Zone B	Zone C	Zone D	ID[b]
Σ n-alkanes			60 (673)	727 (7509)	325 (3666)	937 (11515)	
Terrestrial wax *n*-alkanes (μg/g)[c,d]							
n-pentadecane			bd	14.6 (153.8)	bd	bd	
n-heptadecane			bd	bd	0.6 (5.9)	bd	
n-nonadecane			bd	0.1 (1.1)	bd	bd	
n-heneicosane			0.6 (6.7)	12.7 (133.8)	2.9 (31.2)	21.8 (171.0)	
n-tricosane			0.2 (1.7)	4.4 (46.5)	1.5 (15.8)	6.4 (50.0)	
n-pentacosane			0.5 (5.4)	10.1 (106.0)	5.5 (59.0)	9.4 (74.1)	
n-heptacosane			0.3 (3.3)	3.6 (37.7)	3.7 (40.0)	bd	
n-nonacosane			0.4 (4.5)	16.9 (178.2)	5.3 (56.5)	2.3 (18.1)	
n-hentriacontane			0.2 (2.1)	8.2 (86.3)	1.7 (17.8)	2.0 (16.0)	
n-tritriacontane			bd	1.1 (11.8)	bd	1.7 (13.2)	
n-pentatriacontane			bd	0.7 (7.7)	0.8 (8.9)	1.5 (12.1)	
n-heptatriacontane			bd	0.1 (1.4)	bd	bd	
ΣTerrestrial wax *n*-alkanes			2.0 (23.7)	72.5 (764.5)	2.7 (29.4)	45.1 (354.4)	
UCM (μg/g)[c]			186 (2086)	2562 (28611)	1717 (19174)	5903 (72545)	
Isoprenoids (μg/g)[c]							
2,6,10,14-tetramethylpentadecane (pristane)	$C_{18}H_{38}$	254	0.2 (2)	1.2 (13)	0.6 (7)	bd	a
2,6,10,14-tetramethylhexadecane (phytane)	$C_{19}H_{40}$	268	1.4 (15)	1.7 (17)	1.6 (17)	2.1 (16)	a
Σ Isoprenoids			1.6 (17)	2.9 (30)	2.2 (24)	2.1 (16)	
Tricyclic Terpanes (ng/g)							
C_{19}-tricyclic	$C_{19}H_{42}$	262	bd	0.01 (0.10)	0.01 (0.11)	0.02 (0.16)	b
C_{20}-tricyclic	$C_{20}H_{44}$	276	0.01 (0.12)	0.02 (0.21)	0.04 (0.43)	0.05 (0.39)	b
C_{21}-tricyclic	$C_{21}H_{46}$	290	bd	0.01 (0.11)	0.01 (0.11)	0.01 (0.08)	b
C_{23}-tricyclic	$C_{23}H_{42}$	318	0.03 (0.33)	0.06 (0.62)	0.11 (1.19)	0.14 (1.10)	b

Table III.2: Continued.

Compound Class	Composition	M.W.	Concentrations[a] Zone A	Zone B	Zone C	Zone D	ID[b]
C_{24}-tricyclic	$C_{24}H_{44}$	332	0.02 (0.23)	0.04 (0.41)	0.09 (0.97)	0.09 (0.71)	b
C_{25}-tricyclic	$C_{25}H_{46}$	346	0.02 (0.23)	0.04 (0.39)	0.10 (1.08)	0.11 (0.87)	b
C_{26}-tricyclic (S)	$C_{26}H_{48}$	360	0.01 (0.11)	0.02 (0.21)	0.05 (0.54)	0.02 (0.16)	b
C_{26}-tricyclic (R)	$C_{26}H_{48}$	360	0.01 (0.11)	0.01 (0.10)	0.04 (0.43)	0.03 (0.24)	b
C_{28}-tricyclic	$C_{28}H_{52}$	388	0.01 (0.11)	0.02 (0.21)	0.06 (0.65)	0.05 (0.39)	c
C_{29}-tricyclic	$C_{29}H_{54}$	402	0.01 (0.11)	0.04 (0.40)	0.08 (0.86)	0.11 (0.87)	c
ΣTricyclics			0.14 (1.41)	0.27 (2.76)	0.59 (6.39)	0.63 (4.97)	
Tetracyclic terpanes (ng/g)							
C_{24}-tetracyclic (17,21-*seco*-hopane)	$C_{24}H_{42}$	330	0.01 (0.12)	0.02 (0.21)	0.07 (0.75)	0.03 (0.24)	b
C_{28}-tetracyclic (18,14-*seco*-hopane)	$C_{28}H_{50}$	386	0.01 (0.11)	0.03 (0.31)	0.06 (0.65)	0.08 (0.63)	b
C_{29}-tetracyclic (18,14-*seco*-hopane)	$C_{29}H_{52}$	400	bd	0.04 (0.41)	0.11 (1.19)	0.11 (0.87)	b
ΣTetracyclics			0.02 (0.23)	0.09 (0.93)	0.24 (2.59)	0.22 (1.74)	
Pentacyclic triterpanes (ng/g)							
18α(H)-22,29,30-trisnorneohopane (Ts)	$C_{27}H_{46}$	370	0.03 (0.33)	0.10 (1.03)	0.33 (3.56)	0.44 (3.46)	a
17α(H)-22,29,30-trisnorhopane (Tm)	$C_{27}H_{46}$	370	0.10 (1.12)	0.13 (1.34)	0.68 (7.33)	0.48 (3.78)	b
17α(H),21β(H)-norhopane	$C_{29}H_{50}$	398	0.48 (5.36)	0.94 (9.71)	2.23 (24.03)	2.01 (15.82)	b
17β(H),21α(H)-norhopane	$C_{29}H_{50}$	398	0.05 (0.56)	0.20 (2.07)	0.16 (1.72)	0.20 (1.57)	b
17α(H),21β(H)-hopane	$C_{30}H_{52}$	412	0.35 (3.91)	1.05 (10.85)	2.50 (26.94)	2.26 (17.79)	b
17β(H),21α(H)-hopane	$C_{30}H_{52}$	412	bd	bd	0.25 (2.69)	bd	b
17α(H),21β(H)-homohopane (22S)	$C_{31}H_{54}$	426	0.27 (3.11)	0.55 (5.68)	1.79 (19.29)	1.49 (11.73)	b
17α(H),21β(H)-homohopane (22R)	$C_{31}H_{54}$	426	0.18 (2.11)	0.43 (4.44)	1.24 (13.36)	1.06 (8.34)	b
Gammacerane	$C_{30}H_{52}$	412	0.05 (0.56)	0.07 (0.72)	0.18 (1.94)	0.10 (0.79)	c
17α(H),21β(H)-bishomohopane (22S)	$C_{32}H_{56}$	440	0.15 (1.67)	0.36 (3.72)	0.92 (9.91)	0.96 (7.56)	b
17α(H),21β(H)-bishomohopane (22R)	$C_{32}H_{56}$	440	0.12 (1.34)	0.26 (2.69)	1.04 (11.21)	0.77 (6.06)	b
17α(H),21β(H)-trishomohopane (22S)	$C_{33}H_{58}$	454	0.12 (1.34)	0.26 (2.68)	0.91 (9.81)	0.73 (5.75)	b
17α(H),21β(H)-trishomohopane (22R)	$C_{33}H_{58}$	454	0.10 (1.12)	0.19 (1.96)	0.50 (5.39)	0.49 (3.86)	b
17α(H),21β(H)-tetrakishomohopane (22S)	$C_{34}H_{60}$	468	0.11 (1.23)	0.19 (1.97)	0.54 (5.82)	bd	b
17α(H),21β(H)-tetrakishomohopane (22R)	$C_{34}H_{60}$	468	0.07 (0.78)	0.16 (1.65)	0.42 (4.53)	bd	b

Table III.2: Continued.

Compound Class	Composition	M.W.	Concentrations[a] Zone A	Zone B	Zone C	Zone D	ID[b]
17α(H),21β(H)-pentakishomohopane (22S)	$C_{35}H_{62}$	482	0.10 (1.12)	0.21 (2.17)	0.75 (8.08)	0.49 (3.86)	b
17α(H),21β(H)-pentakishomohopane (22R)	$C_{35}H_{62}$	482	0.09 (1.00)	0.10 (1.03)	0.63 (6.79)	0.49 (3.87)	b
ΣPentacyclics			2.40 (26.70)	5.20 (53.70)	15.10 (162.40)	12.00 (94.20)	
Diasteranes (ng/g)							
13α(H),17β(H)-diacholestane (20S)	$C_{27}H_{48}$	372	0.01 (0.11)	0.02 (0.21)	0.05 (0.54)	0.06 (0.47)	b,d
13α(H),17β(H)-diacholestane (20R)	$C_{27}H_{48}$	372	0.01 (0.11)	0.02 (0.22)	0.09 (0.97)	0.05 (0.39)	b,d
ΣDiasteranes			0.02 (0.22)	0.04 (0.43)	0.14 (1.51)	0.11 (0.86)	
Steranes (ng/g)							
5α(H),14α(H),17α(H)-cholestane (20S)	$C_{27}H_{48}$	372	0.02 (0.22)	0.04 (0.41)	0.21 (2.26)	0.40 (3.15)	b
5α(H),14β(H),17β(H)-cholestane (20R)	$C_{27}H_{48}$	372	0.03 (0.33)	0.02 (0.21)	0.31 (3.34)	0.33 (2.60)	b
5α(H),14β(H),17β(H)-cholestane (20S)	$C_{27}H_{48}$	372	0.03 (0.34)	0.02 (0.21)	0.18 (1.94)	0.20 (1.57)	b
5α(H),14α(H),17α(H)-cholestane (20R)	$C_{27}H_{48}$	372	0.02 (0.21)	0.07 (0.72)	0.21 (2.26)	0.41 (3.23)	b
5α(H),14α(H),17α(H)-ergostane (20S)	$C_{28}H_{50}$	386	0.03 (0.33)	0.09 (0.93)	0.06 (0.66)	0.19 (1.50)	b
5α(H),14β(H),17β(H)-ergostane (20R)	$C_{28}H_{50}$	386	0.04 (0.46)	0.03 (0.27)	0.30 (3.23)	0.32 (2.52)	b
5α(H),14β(H),17β(H)-ergostane (20S)	$C_{28}H_{50}$	386	0.03 (0.33)	0.05 (0.52)	0.25 (2.69)	0.27 (2.13)	b
5α(H),14α(H),17α(H)-ergostane (20R)	$C_{28}H_{50}$	386	0.03 (0.32)	0.04 (0.41)	0.21 (2.26)	0.32 (2.52)	b
5α(H),14α(H),17α(H)-sitostane (20S)	$C_{29}H_{52}$	400	0.03 (0.31)	0.06 (0.62)	0.24 (2.59)	0.38 (2.99)	b
5α(H),14β(H),17β(H)-sitostane (20R)	$C_{29}H_{52}$	400	0.05 (0.56)	0.04 (0.41)	0.32 (3.45)	0.39 (2.98)	b
5α(H),14β(H),17β(H)-sitostane (20S)	$C_{29}H_{52}$	400	0.03 (0.32)	0.05 (0.43)	0.31 (3.34)	0.31 (2.44)	b
5α(H),14α(H),17α(H)-sitostane (20R)	$C_{29}H_{52}$	400	0.03 (0.31)	0.09 (0.92)	0.24 (2.59)	0.32 (2.52)	b,d
ΣSteranes			0.37 (4.05)	0.60 (6.02)	2.84 (30.61)	3.84 (30.15)	
BIOMARKER RATIOS[d]							
pristane/phytane			0.14	0.70	0.40	0.14	
pristane/n-C_{17}			0.33	0.17	0.21	1.00	
phytane/n-C_{18}			2.33	0.39	0.36	0.50	
CPI_a			1.10	1.20	0.50	1.10	
CPI_b			1.30	1.40	1.20	1.20	

Table III.2: Continued.

Compound Class		Composition	M.W.	Concentrations[a] Zone A	Zone B	Zone C	Zone D	ID[b]
CPI_c				0.80	1.10	0.30	0.90	
U/R				3.60	6.52	5.30	6.30	
Triplet				1.81	1.50	1.29	2.08	
Homohopane Index (HHI) for	C_{31}			0.60	0.56	0.59	0.58	
	C_{32}			0.56	0.58	0.46	0.55	
	C_{33}			0.55	0.58	0.65	0.60	
	C_{34}			0.61	0.54	0.56	-	
	C_{35}			0.53	0.68	0.54	0.54	
Sterane epimerization	(ααα)			0.50	0.40	0.50	0.54	
	(αββ)			0.38	0.56	0.49	0.44	

[a]expressed as weight g/particulate fallout; values in parantheses are concentrations relative to g TOC, bd=below detection.
[b]ID=Compound identification (a, positive; b, probable; c, possible; d, tentative), for more details see Rogge *et al.*, 1993a.
[c]values relative to organic carbon were rounded off.
[d]see text (section organic geochemical ratios) for more details.

5- Homohopane index (HHI), is the ratio between the epimer at C-22 S and R for the 17α(H)-homohopane series (C_{31} - C_{35}):

HHI = [22S/(22S+22R)].

6- Sterane epimerization parameter at C-20 is calculated for C_{29} as:

5α(H),14α(H),17α(H)-C_{29}-sterane = [(20S)/(20S+20R)].

RESULTS AND DISCUSSION

The sampling locations in Alexandria, dates, TOC content, and the deposition rates of the PFS are given in Table III.1. High deposition rates occurred in the eastern zone of the city (overall average 4157 mg/d/m^2), while low values occurred in the western part (overall average 185 mg/d/m^2). On the other hand, TOC values were inversely proportional to the deposition rate of particulate fallout, recording a maximum in zone D and a lower value in zone C (127.0 and 92.8 mg/d/m^2, respectively, Table III.1). The fluxes of TOC ranged between 24 and 386 mg C/d/m^2, with an overall average of 130 mg C/d/ m^2 characteristic for Alexandria fallout particulate matter, but comprising only 9 % of the total fallout solid mass.

The total solvent extractable organic matter (EOM) was a maximum of 19.5 mg/g PFS for zone C and a low of 10.0 mg/g for zone B (Table III.1), with an average of 14.5 mg/g. The EOM yield relative to TOC reached a maximum of 19% in zone A, a low of 11% in zone B, and averaged 14%. The average total hydrocarbon (HC) content of the EOM was 37%, and was comprised of 68% aliphatic and 32% aromatic hydrocarbons.

Aliphatic hydrocarbon composition

Normal and isoprenoid alkanes, and an envelope (hump) of an UCM of branched and cyclic hydrocarbons were present and ranged in carbon chain length from C_{14} - C_{38} (Figure III.2). Table III.2 lists the concentrations for the different aliphatic hydrocarbons relative to both weight and TOC. The *n*-alkane concentrations in the study area relative to TOC are shown as an overview in Figure III.3. All zones exhibit a minor predominance of the odd carbon *n*-alkanes from C_{23} to C_{31} which indicates a trace input of terrestrial

Figure III.2: GC traces of *n*-alkanes (dots over peaks, IS = internal standard) of particulate fallout samples from the a) eastern, b) western, c) beach, and d) city center areas of Alexandria City, Egypt.

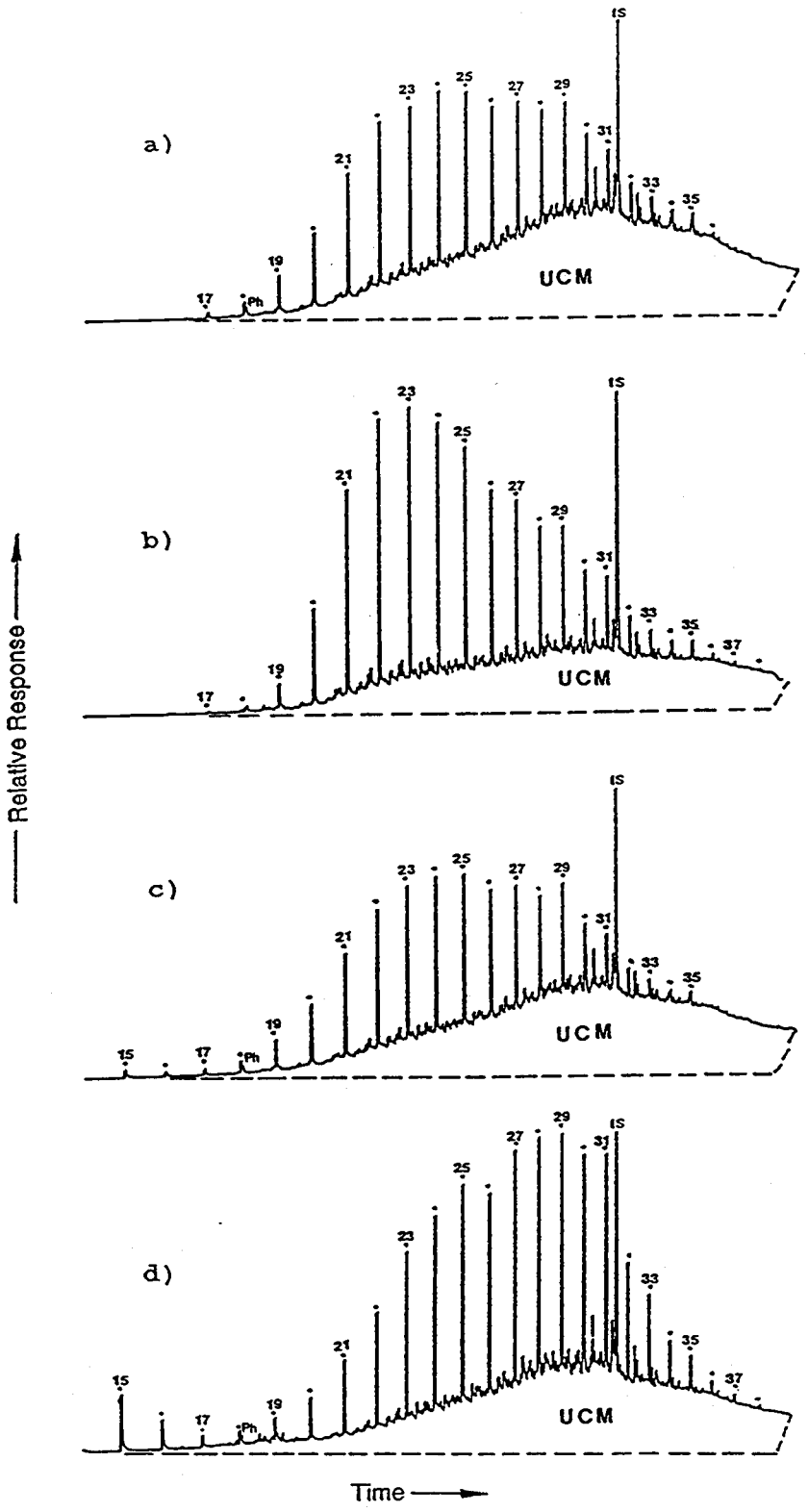
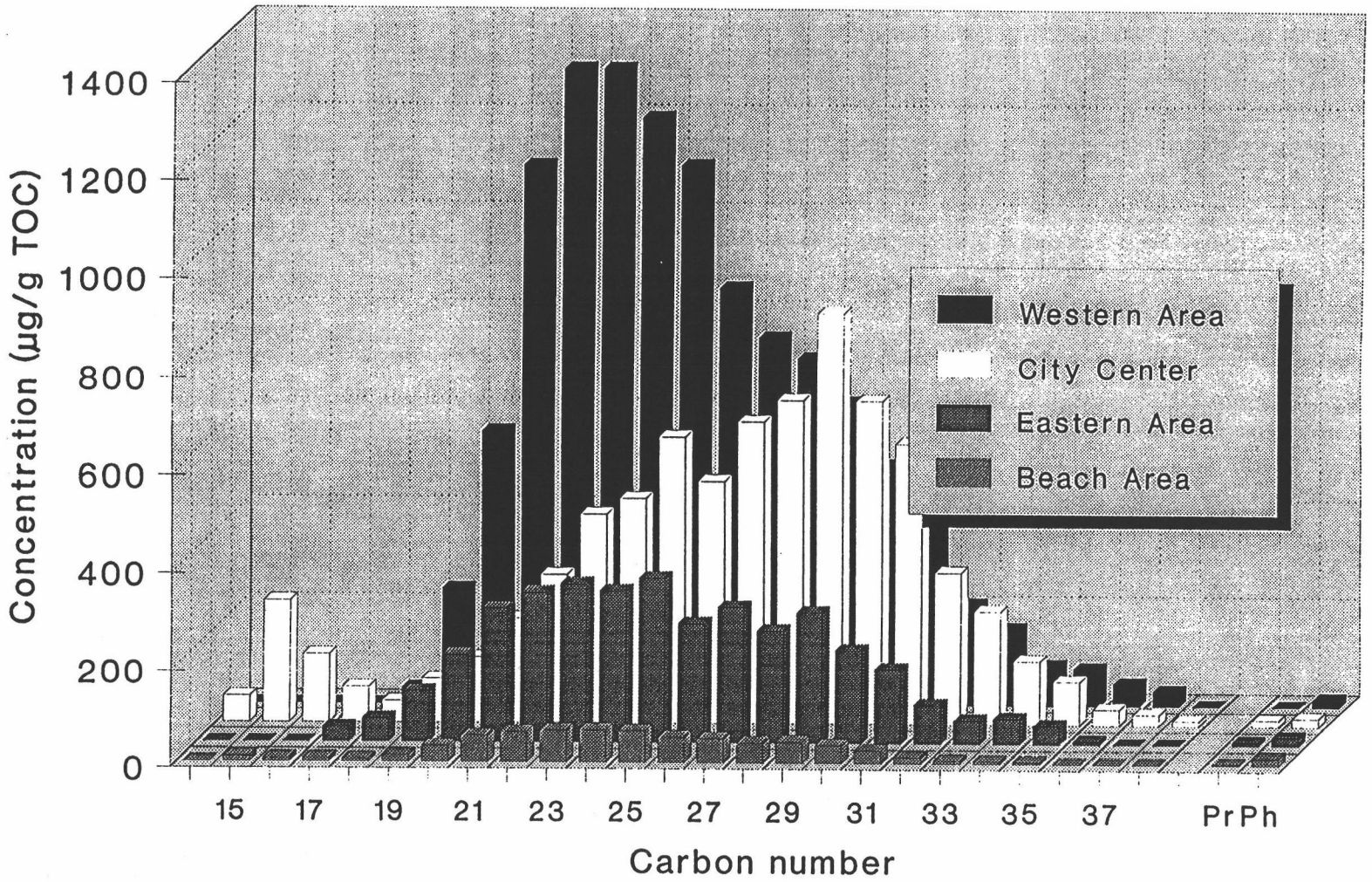

a)
b)
c)
d)
UCM
IS
Ph
Relative Response
Time

Figure III.3: Aliphatic hydrocarbon concentrations relative to organic carbon content of the PFS from Alexandria.


Concentration (µg/g TOC)
1400
1200
1000
800
600
400
200
0
15
17
19
21
23
25
27
29
31
33
35
37
PrPh
Carbon number
Western Area
City Center
Eastern Area
Beach Area

plant wax. The total *n*-alkane concentrations were 673, 7509, 3666 & 11515 µg/g OC, for zones A-Z, respectively. Figure III.2 indicates that the hydrocarbon distributions have different contributions from both petroleum and biogenic sources.

The identification of the homologous *n*-alkanes in the hydrocarbon fractions allowed the determination of the CPI, C_{max}, UCM and wax *n*-alkanes for each sample set. Each provides supportive evidence for the relative incorporation of both biogenic and anthropogenic components.

The CPI (Mazurek and Simoneit, 1983) which is a measure of biologically synthesized *n*-alkanes was determined for these samples. CPI values of automobile exhaust particulate matter, diesel soot and motor oil are near unity (Simoneit *et al.*, 1980; 1991; Stephanou, 1992). On the other hand, major alkanes present in waxes of plants and algae (Douglas and Eglinton, 1966; Simoneit *et al.*, 1991), pollen (Hallgren and Larsson, 1963), and fungi (Oró *et al.*, 1966; Weete, 1976) are generally odd-carbon numbered, with CPI values higher than unity. CPI values can therefore indicate the relative contributions of *n*-alkanes from natural compared to artificial sources. Thus, a low CPI (~1) indicates significant hydrocarbon pollution. In the PFS from Alexandria (Table III.2), the CPI_a(full range) values had an average of 1.0, with small differences between the sampling sites, indicating significant petroleum pollution.

A more sensitive method to calculate CPI is to split the carbon number range into low (C_{13}- C_{19}) and high (C_{20}- C_{37}) ends (Mazurek and Simoneit, 1983). This split demonstrates the relative input of contemporary biogenic versus anthropogenic materials with greater clarity, i.e. the low end (C_{13}- C_{19}) is produced by microbiota or is present in volatile fossil fuels (e.g. diesel) (Simoneit, 1985, Simoneit *et al.*, 1991, Rogge *et al.*, 1993a). On the other hand, the high weight range (C_{20} - C_{37}) occurs in higher plant waxes and in fossil fuel detritus of urban areas (Simoneit, 1985; Simoneit *et al.*, 1980, 1991; Standley and Simoneit, 1987, Rogge *et al.*, 1993a,b). The CPI_b for the PFS was relatively high for zone B (1.4), while the CPI_c was a low of 0.3 for zone C (Table III.2).

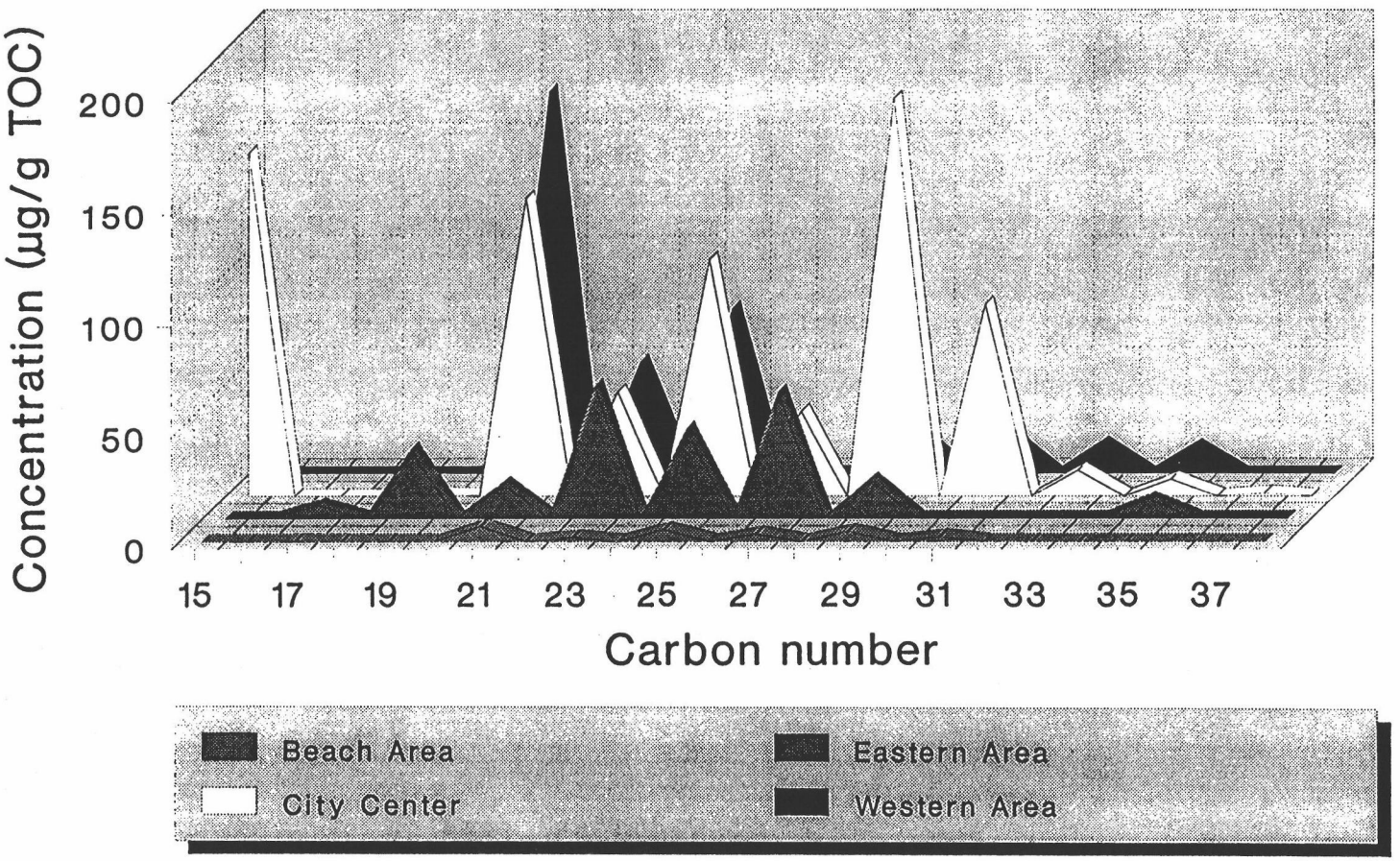
Because the *n*-alkanes of petroleum and terrestrial origins are mixed together in the PFS, a subtraction of the corresponding *n*-alkane concentration with CPI_a=1 was

carried out (Simoneit *et al.*, 1990) to determine the distribution signatures of the residual plant wax alkanes. Table III.2 shows the mean terrestrial wax *n*-alkane series relative to the weight and TOC content of the PFS, while Figure III.4 shows the relation among the remaining odd carbon numbered alkanes. It is obvious that each sample has a different *n*-alkane distribution derived from epicuticular waxes and representing about 0.3% of the total resolved aliphatic hydrocarbons. They range between 23.7-764.5 µg/g OC, with an average of 293 µg/g OC.

The determination of the C_{max} can also give an indication of the relative source input (Mazurek and Simoneit, 1983). In general, a $C_{max} \geq C_{25}$ for *n*-alkanes reflects the incorporation of higher plant wax and C_{max} at lower carbon numbers (Figures III.2&III.3) may indicate a major input from microbial or petroliferous sources. The dominant C_{max} determined for the *n*-alkanes of the PFS are C_{29} (zone B), C_{25} (zones A & C), and C_{23} (zone D). These C_{max} support the interpretation of a minor terrestrial contribution to the fallout, while different C_{max} values may result from regional differences in source strengths.

Another diagnostic parameter is the UCM of branched and cyclic hydrocarbons. This UCM is interpreted here to derive from utilization of petroleum products (Simoneit, 1984; 1985; Simoneit *et al.*, 1991; Rogge *et al.*, 1993a). The high value, i.e. 72.6 mg/g OC, occurred in zone B, while a low value of 2.1 mg/g OC occurred in zone A (Table III.2), with a regional average of 30.6 mg/g OC. The value of the U/R ratio (Mazurek and Simoneit, 1983) is also used as a criterion to assess anthropogenic input. The U/R values for the hydrocarbons from the different zones (Table III.2) ranged from 3.5 to 6.3 (mean 4.3). Plant wax hydrocarbons have U/R <0.1, i.e. they have no UCM (Simoneit, 1984; Mazurek and Simoneit, 1983). A U/R value >2 reflects significant contamination by petroleum products (e.g. Mazurek and Simoneit, 1983; Simoneit *et al.*, 1990, 1991). Matsumoto and Hanya (1980) gave a U/R ratio of 2.6-9.2, with an average of 5.6 for atmospheric fallout in the Tokyo area, reflecting varying degrees of urban pollution. The strong inverse correlation between U/R and CPI of these samples ($r=-0.9684$, $p \leq 0.001$)

Figure III.4: Wax *n*-alkane concentrations relative to organic carbon content of the PFS from Alexandria.


Concentration (µg/g TOC)
200
150
100
50
0
15
17
19
21
23
25
27
29
31
33
35
37
Carbon number
Beach Area
City Center
Eastern Area
Western Area

can be explained by the admixture of petroleum contaminants which reduces the CPI to values of about 1.

Biomarkers

The second main group of organic compounds studied in the aliphatic fraction of the EOM from the PFS are the molecular biomarkers. They are specific organic indicator compounds (found in geological and environmental samples) that can be utilized for genetic source correlations (Simoneit and Mazurek, 1982; Simoneit, 1984, 1986a,b). Such molecules are characterized by their restricted occurrence, source specificity, molecular stability, and suitable concentration for analytical detection (Simoneit, 1984). Biomarkers have been utilized as confirmation indicators for petroleum residues, higher plant waxes and pyrogenic components in the solvent extractable organic matter of aerosol and PFS (Alpert and Hopke, 1980; Matsumoto and Hanya, 1980; Mazurek and Simoneit, 1983; Simoneit, 1977, 1984, Simoneit *et al.,* 1980, 1990, 1991, Simoneit and Mazurek, 1982; Stephanou, 1992). The biomarkers examined in this study are the isoprenoids, tri- and tetracyclic terpanes, 17α(H),21β(H)-hopanes, steranes, and diasteranes. The following will examine these biomarkers in more details.

Isoprenoid Hydrocarbons

Pristane (2,6,10,14-tetramethylpentadecane), phytane (2,6,10,14-tetramethylhexadecane), and lower molecular weight homologs are geologic alteration products of phytol and are not primary constituents of most terrestrial biota (Didyk *et al.,* 1978; Rowland, 1990; Peters and Moldowan, 1993). The presence of these isoprenoid biomarkers in the PFS hydrocarbon fractions coupled with UCM confirms an origin from petroleum mainly from vehicular exhausts. The concentration of pristane in the PFS ranged between 2-13 μg/g OC, with an average of 3.1 μg/g OC (Table III.2). On the other hand, phytane had a higher concentration with a maximum of 17 μg/g OC (zones B&C) and a low of 15 μg/g OC (zone A) (Table III.2).

Tricyclic terpanes

Tricyclic terpanes (Appendix I) are important geochemical tracers occurring in almost all crude oils (except those derived from terrestrial source materials) and range from $C_{19}H_{34}$ to $C_{45}H_{86}$, possibly higher (Aquino Neto *et al.*, 1982, 1983; Moldowan *et al.*, 1983; Peters and Moldowan, 1993). The tricyclic terpane series present in the PFS ranges from $C_{19}H_{36}$ to $C_{29}H_{52}$, with no C_{22} and C_{27}, and a C_{23} predominance (Figure III.5a, m/z 191 key ion for the series). The C_{23} tricyclane was 0.1-1.2 ng/g OC (Figure 6), with an average characteristic for Alexandria of 0.76 ng/g OC (Table III.2). Higher concentrations of the tricyclic series occurred in zones C and D. The total tricyclic terpane series concentration is 3.87 ng/g OC. The occurrence and variation in the relative distribution of the homologs of this series, as determined by GC-MS, in these samples makes them useful tracers for petroleum source identification.

Tetracyclic terpanes

Another group of biomarkers found in the PFS comprises the tetracyclic terpanes, which are derivatives of the hopanes (Aquino Neto *et al.*, 1983). Both 17,21- and 8,14-*seco*-hopanes (Appendix I) are found in fossil fuels, and the 17,21-*seco*-hopanes were proposed to be derived from either thermocatalytic degradation of hopane precursors during geological maturation, microbial ring opening of hopanoids during early diagenesis, or cyclization of squalene to only ring-D (Trendel *et al.*, 1982). In the case of the 8,14-*seco*-hopanes, a ring-C opened hopane structure was suggested (Peter and Moldowan, 1993). The PFS contained a C_{24}-(17,21-*seco*-hopane) and C_{28}& C_{29}-(8,14-*seco*-hopanes) (Figure III.5a) which were quantified for the different zones (Table III.2, Figure III.6). The total tetracyclic terpanes in the study area ranged from 0.23 to 2.59 ng/g OC, with an average of 1.37 ng/g OC. Kvenvolden *et al.*(1985) used the triplet ratio to evaluate oil biodegradation, where a ratio of 2.0-2.2 indicated biodegraded oil. In the FPS the triplet ratio ranged between 1.3-2.1 (Table III.2) suggesting that biodegradation may have commenced.

Figure III.5: Mass fragmentograms representing a) tri- and tetracyclic (m/z 191), b) hopane (summed m/z 149, 177, 191, 205, 219, 233, 247, 261), and c) sterane/diasterane (summed m/z 217, 219, 259) series representing the anthropogenic biomarkers in the PFS from Alexandria [T= tricyclane, TT= tetracyclane, T_s= 18α(H)-22,29,30-trisnorneohopane, T_m= 17α(H)-22,29,30-trisnorhopane, αβ= 17α(H),21β(H)-hopanes (R&S at C-22), G= gammacerane, αββ= 5α(H),14β(H),17β(H)-steranes (R&S at C-20), ααα=5α(H),4α(H),17α(H)-steranes (R&S at C-20), αβD=13β(H),17α(H)-diasteranes (R & S at C-20)].

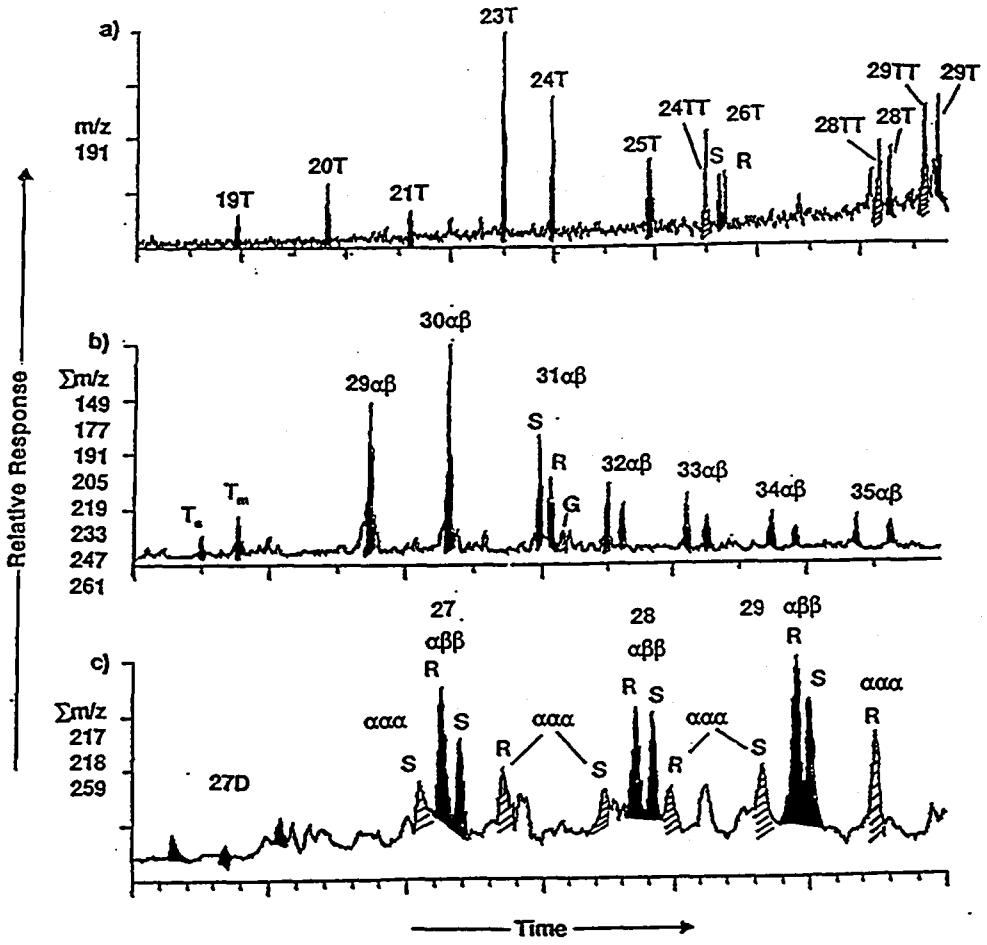
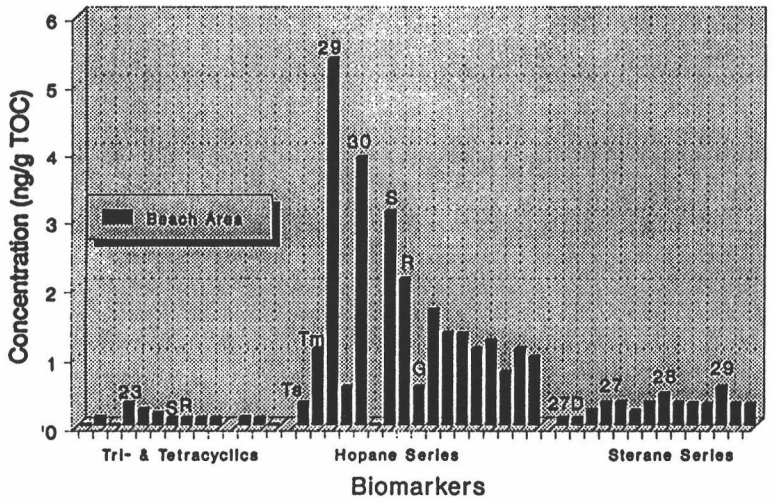
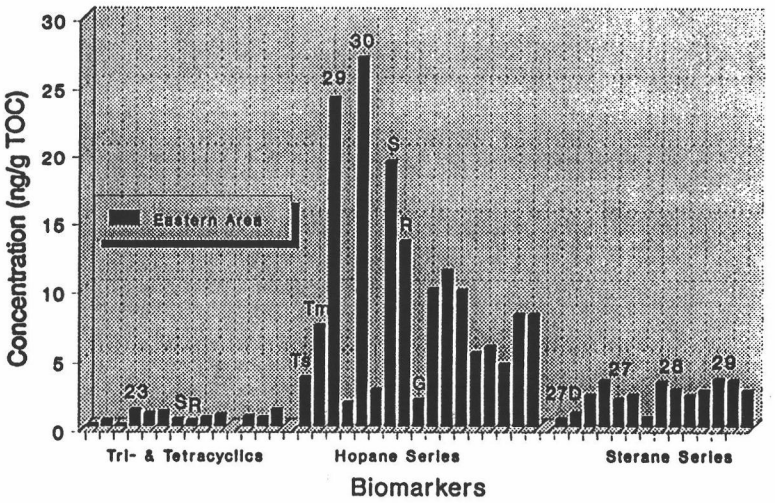
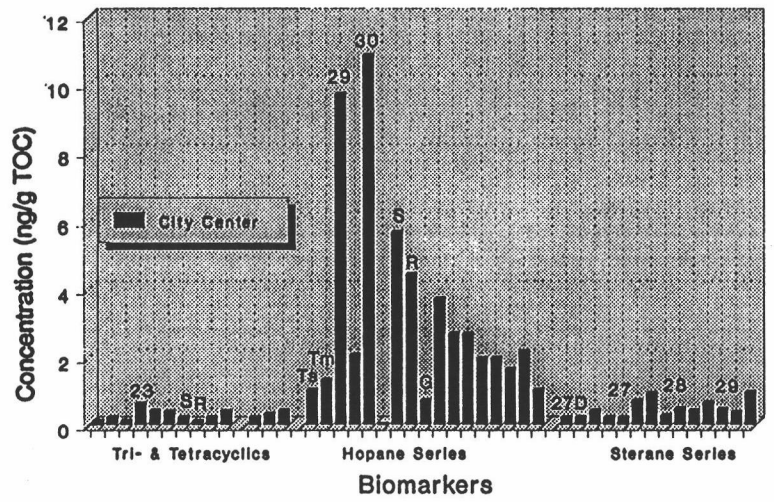
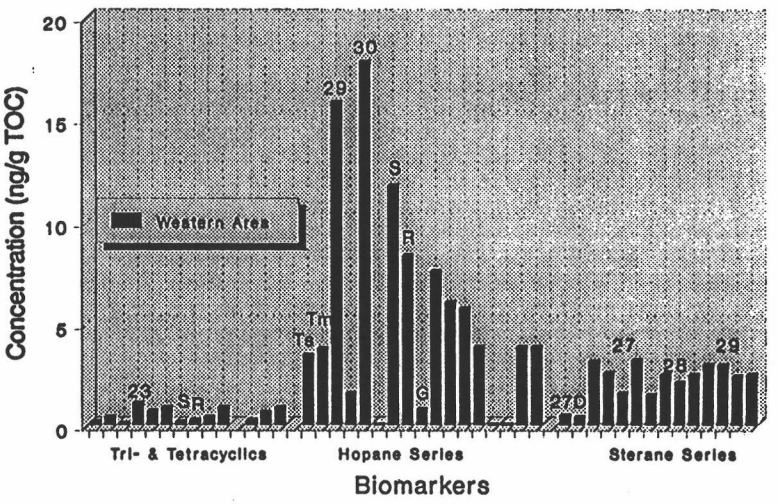

a)
m/z
191
19T
20T
21T
23T
24T
25T
24TT
S
R
26T
28TT
28T
29TT
29T
b)
Σm/z
149
177
191
205
219
233
247
261
T_s
T_m
29αβ
30αβ
31αβ
S
R
G
32αβ
33αβ
34αβ
35αβ
c)
Σm/z
217
218
259
27D
27 αββ R
28 αββ R S
29 αββ R S
ααα S
ααα R S
ααα R S
ααα S
ααα R
Relative Response
Time

Figure III.6: Biomarker composition relative to organic carbon content of the PFS from Alexandria.


Concentration (ng/g TOC)
Beach Area
23
SR
Ts
Tm
29
30
S
R
G
27D
27
28
29
Tri- & Tetracyclics
Hopane Series
Sterane Series
Biomarkers


Concentration (ng/g TOC)
Eastern Area
23
SR
Ts
Tm
29
30
S
R
G
27D
27
28
29
Tri- & Tetracyclics
Hopane Series
Sterane Series
Biomarkers


Concentration (ng/g TOC)
City Center
23
SR
Ts
Tm
29
30
S
R
G
27D
27
28
29
Tri- & Tetracyclics
Hopane Series
Sterane Series
Biomarkers


Concentration (ng/g TOC)
Western Area
23
SR
Ts
Tm
29
30
S
R
G
27D
27
28
29
Tri- & Tetracyclics
Hopane Series
Sterane Series
Biomarkers

Pentacyclic triterpanes

The predominant triterpenoid hydrocarbons from petroleum found in atmospheric particulate matter are the 17α(H),21β(H)-hopanes (Appendix I, Simoneit, 1984). The identification of these compounds is based primarily on their mass spectra and GC retention time. Their occurrence is determined by GC-MS using the m/z 191 ion intensity which is the base peak of most triterpanes (Philp, 1985). An example of the m/z 191 data is shown in Figure III.5b, where the predominant homolog is 17α(H),21β(H)-hopane, with subordinate amounts of 18α(H)-22,29,30-trisnorneohopane, T_s; 17α(H)-22,29,30-trisnorhopane,T_m; 17α(H),21β(H)-norhopane; and the 17β(H),21α(H)-hopane series; and the extended C_{31} - C_{35} 17α(H),21β(H)-hopanes. The hopane series (C_{27} - C_{35}) was present in the PFS of all zones from Alexandria and showed a predominance of 17α(H)-hopane in zones B, C & D, while zone A had a predominance of 17α(H)-norhopane. The distribution patterns of the m/z 191 fragmentograms are represented as bar graphs to facilitate pattern comparison (Figure III.6). The distributions of the hopane series are similar for auto and diesel exhausts (Simoneit, 1985 ; Rogge *et al.*, 1993a), confirming vehicular emissions as the major source of petroleum residues in PFS. Gasoline and diesel fuels do not contain these triterpanes, but they are present in lubricating oil (Simoneit, 1985). This indicates that lubricants adsorbed as vapor microdroplets on particles carry the biomarker signature of fossil fuels to vehicular emissions (Simoneit, 1984, 1985). The concentrations of all hopanes in PFS are listed in Table III.2 and the total hopanes ranged from 26.7 ng/g OC in zone A to 162.4 ng/g OC in zone C. In typical petroleums, the extended α-hopane homologs $>C_{31}$ have the epimers at C-22 at an equilibrium ratio {S/(S+R)} of 0.6 (HHI, Seifert and Moldowan, 1978). The HHI (Table III.2) for the PFS varies from 0.46 to 0.68.

Steranes and diasteranes

Steranes and diasteranes (Appendix I) are biomarkers present in fossil fuels and are also useful indicators for emissions from vehicular traffic in urban areas (Simoneit, 1984, 1985). Both steranes and diasteranes were detected and quantified in the PFS by their m/z 217, 218 and 259 fragmentograms (Figure III.5 c,d) and their yields are given

in Table III.2. The steranes have mainly the 5α(H),14β(H),17β(H)-configuration and a minor amount of the 5α(H),14α(H), 17α(H)-configuration. The abundances of the steranes are presented in Figure III.6. The epimerization ratio at C-20 of the C_{29} sterane is high (0.40-0.54, Table III.2) which indicates that the PFS contain mature petroleum residues.

To summarize, coupling CPI, C_{max}, UCM, U/R and wax *n*-alkane values with quantitation of biomarker data allows the definition of the different sources for the aliphatic hydrocarbon fraction of the PFS (terrestrial vs. anthropogenic). Experimental analysis allowed only the determination of different sources in the PFS and not source strengths (cf. the statistical part).

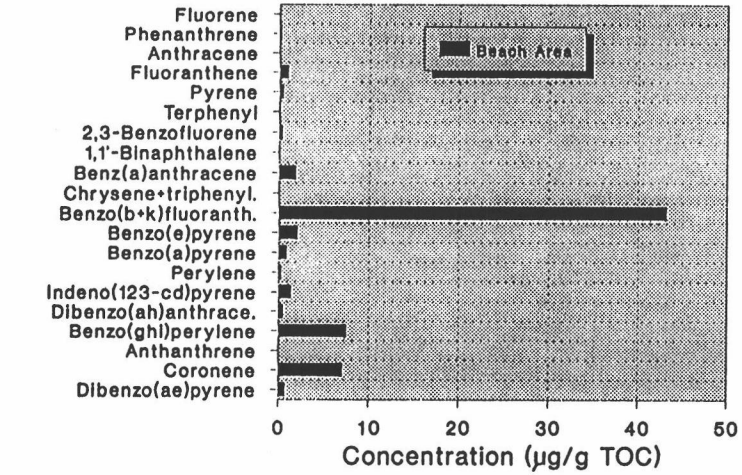
Polycyclic aromatic hydrocarbons

The second main class of compounds in the PFS consists of PAHs. They are considered to be a class of chemical carcinogens and mutagenic pollutants, derived from anthropogenic sources, such as vehicular exhaust (Rogge *et al.*, 1993a; Tong and Karasek, 1984), emissions from coke ovens (Lao *et al.*, 1975), refining (Wade, 1983), and other processes involving high temperature pyrolytic reactions and incineration (Badger, 1962). PAHs emitted to the atmosphere as combustion products cool rapidly and condense on particles in the ambient air.

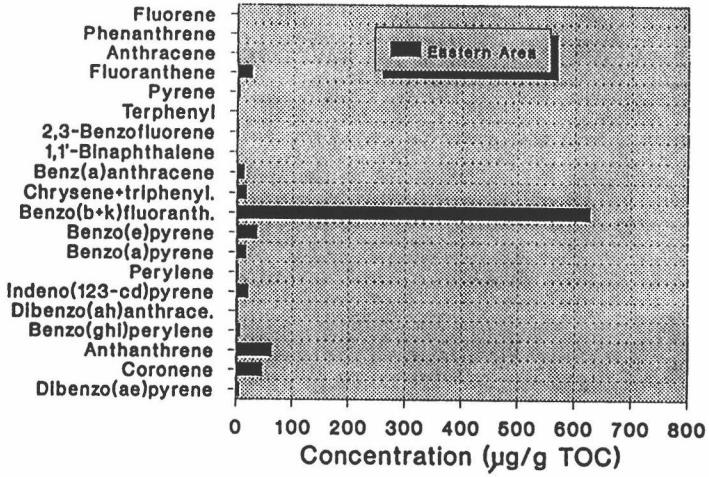
The mean concentration of individual PAHs in the PFS from Alexandria are given in Table III.3 and account for all detectable PAH by GC and GC-MS. Regardless of the sampling site, the PAH mixtures are similar with some alkylated homologs observed mainly for phenanthrene, pyrene, perylene and benz(ae)anthracene. The PAHs showed a predominance of benz(b+k)fluoranthene, benzo(ghi)perylene, and coronene, with a terphenyl present in zone D, probably from the heavy industry in that area and their concentrations relative to OC are shown in Figure III.7. The total unsubstituted PAH had a maximum concentration of 895 µg/g OC in zone C and a minimum of 71 µg/g OC in zone A, with a regional average of 362 µg/g OC (Table III.3).

Figure III.7: PAH compositions relative to organic carbon content of the PFS from Alexandria.

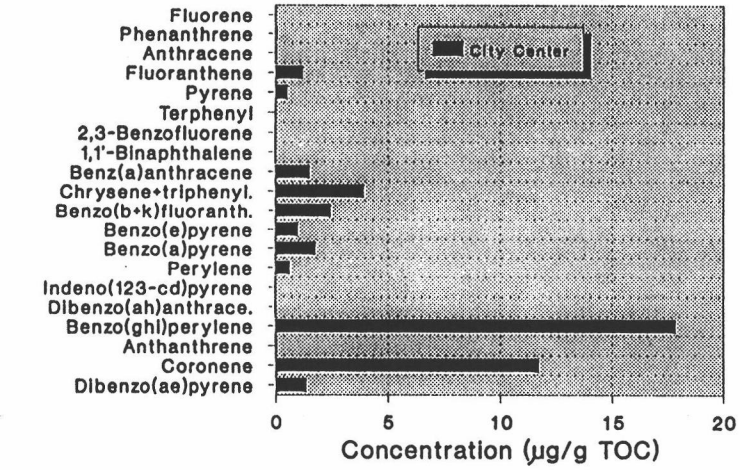
Unsubstituted PAHs



Unsubstituted PAHs



Unsubstituted PAHs



Unsubstituted PAHs

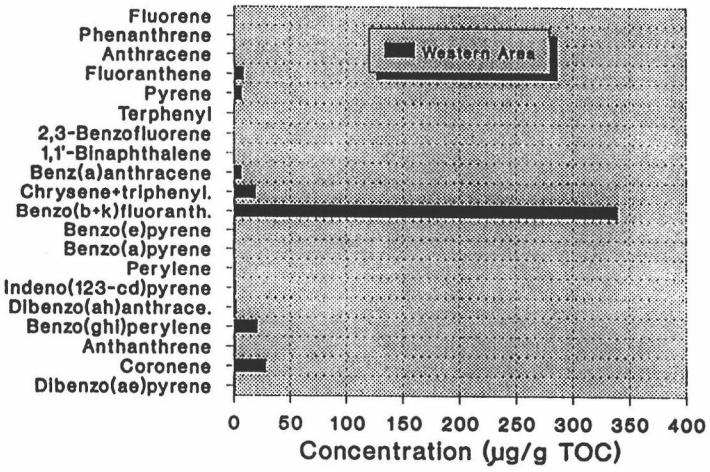


Table III.3: Mean polycyclic aromatic hydrocarbon compositions relative to the weight of the particulate fallout samples from Alexandria.

Table III.3: Continued.

Compound Class	Composition	M.W.	Concentrations[a] Zone A	Zone B	Zone C	Zone D	ID[b]
Polycyclic aromatic hydrocarbons (PAHs, ng/g)							
Phenanthrene	$C_{14}H_{10}$	178	11.1 (124)	6.7 (69)	7.6 (82)	4.4 (34)	a
Anthracene	$C_{14}H_{10}$	178	bd	5.8 (60)	9.2 (99)	5.8 (46)	a
Fluoranthene	$C_{16}H_{10}$	202	83.9 (935)	117.8 (1220)	2440.0 (26290)	1070.0 (8440)	a
Pyrene	$C_{16}H_{10}$	202	36.1 (402)	50.6 (523)	404.8 (4360)	838.9 (6600)	a
Terphenyl	$C_{18}H_{14}$	230	bd	bd	bd	5.1 (40)	b
2,3-Benzofluorene	$C_{17}H_{12}$	216	28.3 (316)	0.5 (5)	141.9 (1530)	0.5 (4)	a
Benz(a)anthracene	$C_{18}H_{12}$	228	167.6 (1870)	147.3 (1520)	1200.0 (13000)	814.0 (6410)	a
Chrysene/triphenylene	$C_{18}H_{12}$	228	333.2 (3718)	379.3 (3920)	1590.0 (17180)	2460.0 (19400)	a
Benzo(b+k)fluoranthene	$C_{20}H_{12}$	252	3870.0 (43200)	238.4 (2460)	58270.0 (627990)	43080.0 (339150)	a
Benzo(e)pyrene	$C_{20}H_{12}$	252	185.4 (2070)	96.9 (1000)	3400.0 (36660)	119.4 (939)	a
Benzo(a)pyrene	$C_{20}H_{12}$	252	78.2 (873)	173.2 (1790)	1620.0 (17420)	28.7 (226)	a
Perylene	$C_{20}H_{12}$	252	21.5 (239)	62.9 (649)	293.9 (3170)	151.3 (1190)	a
Indeno(123-cd)pyrene	$C_{22}H_{12}$	276	124.9 (1390)	bd	1980.0 (21310)	206.8 (1630)	b
Dibenz(ah)anthracene	$C_{22}H_{14}$	278	43.6 (487)	bd	204.9 (2210)	251.9 (1980)	a
Benzo(ghi)perylene	$C_{22}H_{12}$	276	674.0 (7520)	1730.0 (17840)	654.3 (7050)	2630.0 (20670)	a
Anthanthrene	$C_{22}H_{12}$	276	bd	4.8 (50)	5880.0 (63470)	93.6 (1520)	a
Coronene	$C_{24}H_{12}$	300	637.9 (7120)	1130.0 (11710)	4340.0 (46740)	3570.0 (28120)	a
Dibenzo(ae)pyrene	$C_{24}H_{14}$	302	66.0 (737)	132.4 (1370)	560.1 (6040)	95.1 (962)	a
ΣPAHs			6361.7 (71001)	4276.6 (44186)	82996.7 (894601)	55425.5 (437361)	
Alkyl-substituted PAHs (ng/g)							
3-Methylphenanthrene (3MP)	$C_{15}H_{12}$	192	7.3 (82)	bd	477.8 (5140)	61.1 (481)	a
2-Methylphenanthrene (2MP)	$C_{15}H_{12}$	192	6.7 (75)	bd	352.2 (3800)	110.9 (873)	a
9-Methylphenanthrene (9MP)	$C_{15}H_{12}$	192	9.5 (106)	bd	166.4 (1790)	128.4 (1010)	a
1-Methylphenanthrene (1MP)	$C_{15}H_{12}$	192	10.6 (118)	bd	253.2 (2730)	104.8 (825)	a
Dimethylphenanthrene	$C_{16}H_{14}$	206	114.1 (1270)	bd	4510.0 (48590)	1420.0 (11190)	b
Trimethylphenanthrene	$C_{17}H_{16}$	220	97.4 (1090)	bd	5750.0 (61970)	1650.0 (12960)	b
Tetramethylphenanthrene	$C_{18}H_{18}$	234	41.9 (468)	bd	4900.0 (31530)	bd	b

Table III.3: Continued.

Compound Class	Composition	M.W.	Concentrations[a] Zone A	Zone B	Zone C	Zone D	ID[b]
Pentamethylphenanthrene	$C_{19}H_{20}$	248	64.1 (716)	bd	2930.0 (52760)	bd	d
Σ Phenanthrene Series			351.6 (3925)	bd	19339.6 (208310)	3475.2 (27339)	
Methylpyrene/fluoranthene	$C_{17}H_{12}$	216	bd	bd	1530.0 (16500)	578.1 (4550)	b
Dimethylpyrene	$C_{18}H_{14}$	230	120.9 (1350)	bd	4780.0 (51470)	1510.0 (11850)	b
Trimethylpyrene	$C_{20}H_{16}$	244	bd	bd	5890.0 (63470)	2740.0 (21560)	d
Tetramethylpyrene	$C_{19}H_{18}$	258	bd	bd	2430.0 (26180)	408.8 (3220)	b
Σ Pyrene Series[c]			120.9 (1350)	bd	14630.0 (157600)	5236.9 (41180)	
Methylperylene	$C_{21}H_{14}$	266	208.3 (2320)	bd	2400.0 (25840)	112.0 (8780)	b
Dimethylperylene	$C_{22}H_{16}$	280	238.4 (2660)	bd	5270.0 (56790)	1350.0 (10590)	b
Trimethylperylene	$C_{23}H_{18}$	294	172.7 (1930)	bd	4170.0 (44950)	358.4 (2820)	b
Tetramethylperylene	$C_{24}H_{20}$	308	161.9 (1810)	bd	3930.0 (42320)	452.2 (3560)	b
Σ Perylene Series[c]			781.3 (8720)	bd	15770.2 (169900)	3280.6 (25750)	
Methylbenz(a)anthracene	$C_{19}H_{14}$	242	156.6 (1750)	bd	392.0 (4220)	2840.0 (22350)	b
Dimethylbenz(a)anthracene	$C_{20}H_{16}$	256	139.9 (1560)	bd	1027.0 (11070)	1770.0 (13910)	b
Trimethylbenz(a)anthracene	$C_{21}H_{18}$	270	107.1 (1200)	bd	617.1 (6650)	617.2 (4860)	b
Tetramethylbenz(a)anthracene	$C_{22}H_{20}$	284	bd	bd	554.0 (5980)	464.5 (3660)	b
ΣBenz(a)anthracene Series[c]			403.6 (4510)	bd	2590.1 (27920)	5691.7 (44780)	
Σ Total PAHs + alkyl PAHs (µg/g)			8.0 (89.5)	4.3 (44.2)	135.3 (1446.6)	73.1 (576.4)	

[a]expresses as weight/g particulate fallout; values in parantheses are concentrations relative to g TOC; bd= below detection limit (concentrations are <1 ng/g PFDs or 10 ng/g OC).
[b]ID=Compound identification (a, positive; b, probable; c, possible; d, tentative), for more details see Rogge *et al.*, 1993a.
[c]The parent PAH is assumed as example.

The distribution of the alkylated and parent PAHs are presented in Figure III.8, showing the relative abundance of the predominant components. Generally the proportion of alkylated to parent PAH depends on the combustion temperature (Adams *et al.*, 1982). Thus, coal and wood smokes contain a phenanthrene mixture maximizing at the parent PAH with an exponential drop to the C_4-homologs (LaFlamme and Hites, 1978; Simoneit, 1985). In contrast, vehicular emissions exhibit a pattern of low amounts of phenanthrene and maximum at the C_1-homologs, and petroleum input is characterized by a distribution increasing uniformly from less to more alkylated homologs up to C_5 and greater. In the PFS, the alkylated PAHs of the phenanthrene, pyrene, perylene and benz(ae)anthracene series maximize at C_3, C_3, C_2 and C_1, respectively (Figure III.8). Relatively high concentrations of 2- and 3-methyl phenanthrene (MP) compared to 1- and 9-MP were observed for the PFS (Table III.3) indicate a thermogenic/alteration. This can be explained in terms of the rearrangement of the MP, favoring the thermodynamically more stable 2- and 3-positions at high temperatures (Radke *et al.*, 1982).

Data interpretation and source confirmation

Multivariate statistical analysis was performed in order to reduce the data set of the hydrocarbon fraction into a number of factors (end members or sources). These factors represent in an organic geochemical sense, the combined effect of several geochemical processes or factors. The correlation matrix of the PFS reveals similarities in behavior of pairs of components but does not conveniently identify groups of components which behave similarity, as in factor analysis.

After extended Q-mode FA and LPT, two significant end members were obtained explaining 90% of the total variation in the data set. The first end member explains 79.6% of the total sum of squares of the Alexandria PFS hydrocarbon model (Figure III.9). This end member is represented by long-chain *n*-alkanes (77.1%), isoprenoid hydrocarbons (1.54% Pr, 1.82% Ph), α-hopanes (5.6%), and steranes/diasteranes (2.4%). Also, traces of the tri- and tetracyclic terpanes contributed, with low molecular weight PAH and alkyl PAH representing 4.5% (Figure III.9). The presence of the aliphatic biomarkers as well

Figure III.8: Alkyl PAH homolog distribution of the phenanthrene, pyrene, perylene, and benz(a)anthracene series for the PFS from Alexandria (C_1, C_2, C_3, and C_4 represent the PAH with 1, 2, 3, and 4 carbon atom alkyl substituents, respectively).

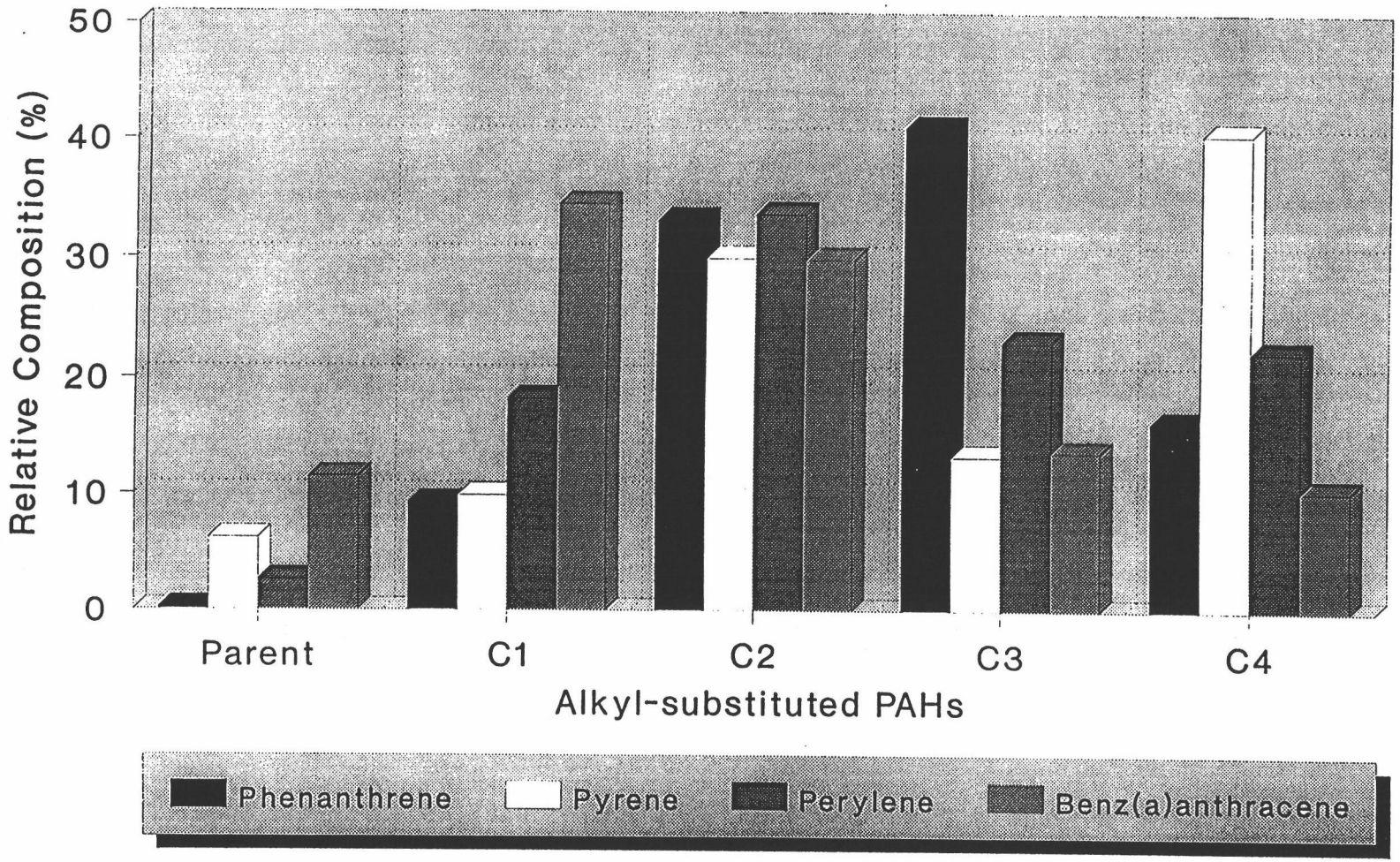
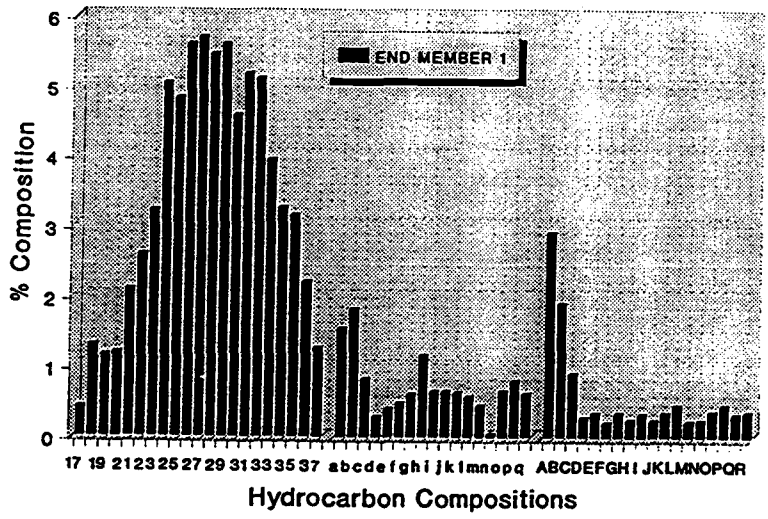
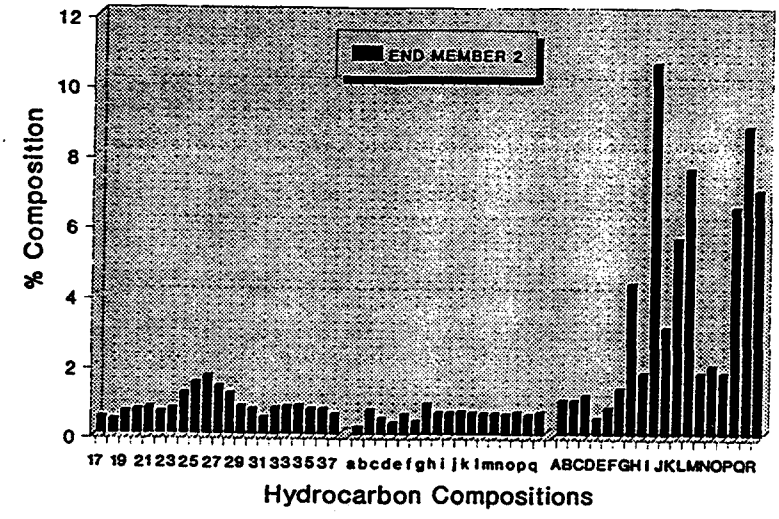

Relative Composition (%)
50
40
30
20
10
0
Parent
C1
C2
C3
C4
Alkyl-substituted PAHs
Phenanthrene
Pyrene
Perylene
Benz(a)anthracene

Figure III.9: End member compositions of the PFS from Alexandria after Q-mode FA and LPT [Numbers indicate *n*-alkane carbon skeleton; letters a-q indicate aliphatic biomarkers: a= pristane; b= phytane; c= ∑tricyclanes; d= ∑tetracyclanes; e & f= C_{27}-hopane (T_s) and (T_m), respectively; g & h= C_{29}- and C_{30}-hopanes, respectively; i to m= C_{31}- to C_{35}-homohopanes (S+R), respectively; n= C_{27}-diasteranes (S+R); o to q= C_{27} to C_{29} steranes (S+R, ααα+αββ), respectively; letters A-R indicate the aromatic hydrocarbons: A= ∑phenanthrenes, B= anthracene; C= fluoranthene; D= ∑pyrenes; E= terphenyl; F= 2,3-benzofluorene; G= ∑benz(a)anthracene; H= chrysene/ triphenylene; I= benzo(b+k)fluoranthene; J= benzo(e)pyrene; K= benzo(a)pyrene; L= ∑perylenes; M= indeno(123-cd)pyrene; N= dibenz(ah)anthracene; O= benzo(ghi)- perylene; P= anthanthrene; Q= coronene; and R= dibenzo(ae)pyrene].


END MEMBER 1
% Composition
0
1
2
3
4
5
6
17 19 21 23 25 27 29 31 33 35 37 abcdefghijklmnopq ABCDEFGHIJKLMNOPQR
Hydrocarbon Compositions


END MEMBER 2
% Composition
0
2
4
6
8
10
12
17 19 21 23 25 27 29 31 33 35 37 abcdefghijklmnopq ABCDEFGHIJKLMNOPQR
Hydrocarbon Compositions

as the low molecular weight alkyl PAHs confirm a petrochemical end member in the Alexandria PFS model, derived mainly from vehicular exhaust.

The second end member (Figure III.9) represented 10.4% of the total variation in the data set of the hydrocarbon fractions. It is dominated mainly by high molecular weight PAH, consisting of benz(a)anthracene (4.5%), benzofluoranthene (10.6%), benzo(a)- and benzo(e)pyrene (8.8%), perylene (7.6%), anthanthrene (6.8%), coronene (8.9%), and dibenzo(ae)pyrene (7%). Since combustion processes occur rapidly (considering a radical formation mechanism, Haynes, 1991), PAH formation and growth by the addition of hydrocarbon radicals also occurs quickly, leading to heavy PAH condensation on particles. Thus, the presence of high molecular weight PAH in the second end member confirms its origin from thermogenic/pyrolytic sources in the PFS model. In addition, a minor insignificant end member, describing <2.0% of the sample variations, was characterized and dominated by odd carbon numbered *n*-alkanes maximizing between C_{19} to C_{33} (the composition was calculated according to Simoneit *et al.,* 1990), representing the trace terrestrial plant wax contribution to the Alexandria PFS model.

In order to assess the different sources and origins of PAHs present in the PFS, a comparison was made between characteristic ratios calculated from well characterized emission sources and the same ratios for these samples. Nevertheless, the use of such ratios as definitive identification criteria assumes that only minor modification has occurred from emission of the PAH to their deposition (Lee *et al.,* 1980; Gibson *et al.,* 1986; Grimalt *et al.,* 1988). It has been shown that the degradation rate of PAHs on atmospheric particles depends on the nature of the particles (Valerio *et al.,* 1984; Valerio and Lazzarotto, 1985; Behymer and Hites, 1985), where PAHs appear to be better preserved from alteration when associated with soots. Nielsen (1988) and Masclet *et al.* (1986) reported the rapid decay of benzo(a)pyrene relative to benzo(e)pyrene increased with distance from their source. In the present study, this ratio was 0.79, 0.40, 0.71 and 0.83 for zones A-D, respectively, which may indicate that zone B (the city center) is the source for the benzopyrenes and the ratio increases as the particles are transported to the other zones. Based on the comparisons in Table III.4, it can be concluded that more than

Table III.4: Comparison between characteristic ratios deduced from the PAH compositions of several potential source inputs and those from the particulate fallout samples from Alexandria.

Source	Ratios*				References
	(1) P/(P+An)	(2) Ban/(Ban+Chr)	(3) BeP/(BeP+BaP)	(4) Inpy/(Inpy/Bper)	
Alexandria City					Present study
Zone A	0.58	0.34	0.79	0.16	
Zone B	0.96	0.21	0.40	0.00	
Zone C	0.50	0.34	0.71	0.76	
Zone D	0.48	0.19	0.83	0.08	
Crude oil	0.98	0.16	0.87	-	Grimmer et al. (1985), Neff (1979)
Used motor oil	0.78	0.50	0.64	0.25	Grimmer et al. (1981b)
Car emission, gasoline	0.77	-	0.53	0.18	Grimmer and Hildebrandt (1975)
Coal soot	-	-	0.30	0.56	Cretney et al. (1985)
Coke oven emission	0.67	0.43	0.23	-	Lao et al. (1975)

*Abbreviations stand for the following ratios: 1. phenanthrene/(anthracene+phenanthrene), 2. benz(a)anthracene/(benz(a)anthracene +chrysene+triphenylene), 3. benzo(e)pyrene/(benzo(e)pyrene+benzo(a)pyrene), 4. indeno(123-cd)pyrene/(indeno(123-cd)pyrene +benzo(ghi)perylene).

one source is contributing PAHs to the PFS. Values of the ratios such as [P/(P+An)] and [BeP/(BeP+BaP)] are close to those for crude oil, its products and vehicular exhaust as well as coke oven emissions. Furthermore, the [Inpy/(Inpy+Bper)] values are similar to vehicular emissions in zones A and D, and the [Ban/(Ban+Chr)] are intermediate between crude oil and/or coke oven emissions. In short, a dominant pyrolytic origin can be assigned to the PAH composition of the PFS. Vehicular emissions and higher temperature combustion processes (i.e., industrial emissions) appear to be the major sources for these PAHs.

Since carcinogenicity depends mainly on the type and quantity of the hydrocarbon (aromatic) compounds, human exposure in Alexandria (especially in the west, Tables III.2&III.3) to atmospheric particulate matter could become a public health concern, especially with the high concentrations, which is considered as the most important cause of lung cancer and asthma (IRLG, 1979; Reif, 1981). Because the present study is preliminary for that area, future research for health risk assessment should consider some or all of the following points: (1) point source assessment - the determination of all possible input sources in the area with complete compositional analyses for these sources, (2) hazard identification - the determination of specific chemicals with detrimental health effects, (3) dose-response assessment - the determination of the magnitude of exposure and the probability of the occurrence of a health effect, and (4) exposure assessment - the determination of the extent of human exposure before or after application of regulatory controls. Thus, this exposure-response relationship would be based on consistent evidence provided by chemical analyses and information on the occurrence of human lung disease.

CONCLUSION

Particulate fallout samples from a coastal area in the Southeastern Mediterranean (Alexandria, Egypt) contain both anthropogenic and traces of terrestrial organic compounds, which are specific to their emission sources. The anthropogenic components comprise mainly petroleum residues, confirmed by UCM, U/R, pristane, phytane, CPI, C_{max}, tricyclic (C_{19} - C_{29}) and tetracyclic (C_{24}, C_{28} and C_{29} *seco*-hopanes) terpanes, triterpanes ($\alpha\beta$-hopanes), steranes ($\alpha\beta\beta$ configuration with a minor amount of the $\alpha\alpha\alpha$), diasteranes, and thermogenic/pyrogenic PAH, ranging from fluorene to coronene with minor alkyl-PAH series. The trace terrestrial wax *n*-alkane source, determined by subtracting the average alkane distribution (CPI=1), was observed in the PFS mainly by the predominance of C_{21}, C_{25}, C_{27}, C_{29}, and C_{31}.

The multivariate statistical analyses, including both extended Q-mode FA and LPT, reduced the hydrocarbon data set into 2 significant end members (sources), explaining 90% of the variation among the PFS. These multivariate techniques represented a useful method for end member source confirmation, representing petrochemical (79.6%), and thermogenic/pyrolytic (10.9%) sources.

ACKNOWLEDGEMENT

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CHAPTER IV

PETROLEUM HYDROCARBON FINGERPRINTING AND SEDIMENT TRANSPORT ASSESSED BY MOLECULAR BIOMARKER AND MULTIVARIATE STATISTICAL ANALYSES IN THE EASTERN HARBOR OF ALEXANDRIA, EGYPT.

ABSTRACT:

The Eastern Harbor (EH) of Alexandria, a heavily polluted southeastern Mediterranean basin, is subjected to petroleum contamination from two different sources. Surficial bottom sediments sampled inside and outside the harbor were analyzed for organic geochemical markers in order to assess and track the aliphatic hydrocarbon signature in the bottom sediments. The aliphatic hydrocarbon compositions were determined both quantitatively and qualitatively for the alkanes, UCM, and biomarkers, including acyclic isoprenoids, tri- and tetracyclic terpanes, hopanes, and steranes/diasteranes. The data indicated a petroleum product end member characteristic of the EH. In order to differentiate among the possible petroleum sources in the area, biodegradation indices derived from the biomarker data were calculated for two possible end member sources, namely untreated sewage and petrochemicals, then compared statistically and experimentally with the data for the surficial bottom sediments. As a result, high levels of sewage derived-petroleum hydrocarbons were dominant in the area rather than direct input from boating activities or urban runoff. A multivariate statistical approach, including both factor analysis and linear programming technique, was used to determine the end member compositions and evaluate sediment partitioning and transport in the EH area.

INTRODUCTION

The Eastern Harbor (EH) of Alexandria, which receives about 22% of the land drainage from Alexandria City, is subjected to major inputs of organic chemicals in largely unknown amounts from agricultural and street runoff, untreated sewage and waste water discharges, atmospheric fallout, and ship and boat traffic. The EH basin has not been investigated for petroleum pollution as other areas of the Mediterranean (Albaigés, 1980; Albaigés and Cuberes, 1980; Albaigés *et al.,* 1984; Solanas *et al.,* 1982; Grimalt and Albaigés, 1990; Grimalt *et. al.,* 1984, 1986, 1990; Saliot *et al.,* 1990, 1991). It has long been recognized that one way to investigate the geochemical setting and/or history of any contaminated environment is through its sedimentary record (Eglinton *et al.,* 1975; Prahl, 1985; Prahl *et al.*, 1980; Readman et al., 1986a,b). The application of the concept that surficial sediments of the EH act as pollutant sinks could provide an integrated picture of the events that occurred in the water column (Aboul-Kassim and Simoneit, 1994a; Kennicut II *et al.,* 1994). In this regard, surficial sediments have been used to determine the petroleum contamination of the EH. In order to understand the fate and distribution of the petroleum pollution, the sources origins and movements of sediments in the EH would have to be determined because the hydrodynamic influences on sediment movement are poorly understood.

This is a preliminary investigation of a selected group of organic constituents, mainly aliphatic hydrocarbons, in the surficial sediments of the EH area. The objectives include the characterization and assessment of petroleum hydrocarbon signatures from different anthropogenic sources, and determining the suitability of these hydrocarbons for defining the origin and net movement of sediment in the EH by multivariate statistical analyses.

THE STUDY AREA

The EH is a relatively shallow semi-closed basin, situated between longitudes 29°53' to 29°54'E and latitudes 31°12' to 31°13'N (Figure IV.1). The harbor issheltered from the sea by an artificial break water, leaving two openings (Boughaz and Silsila)

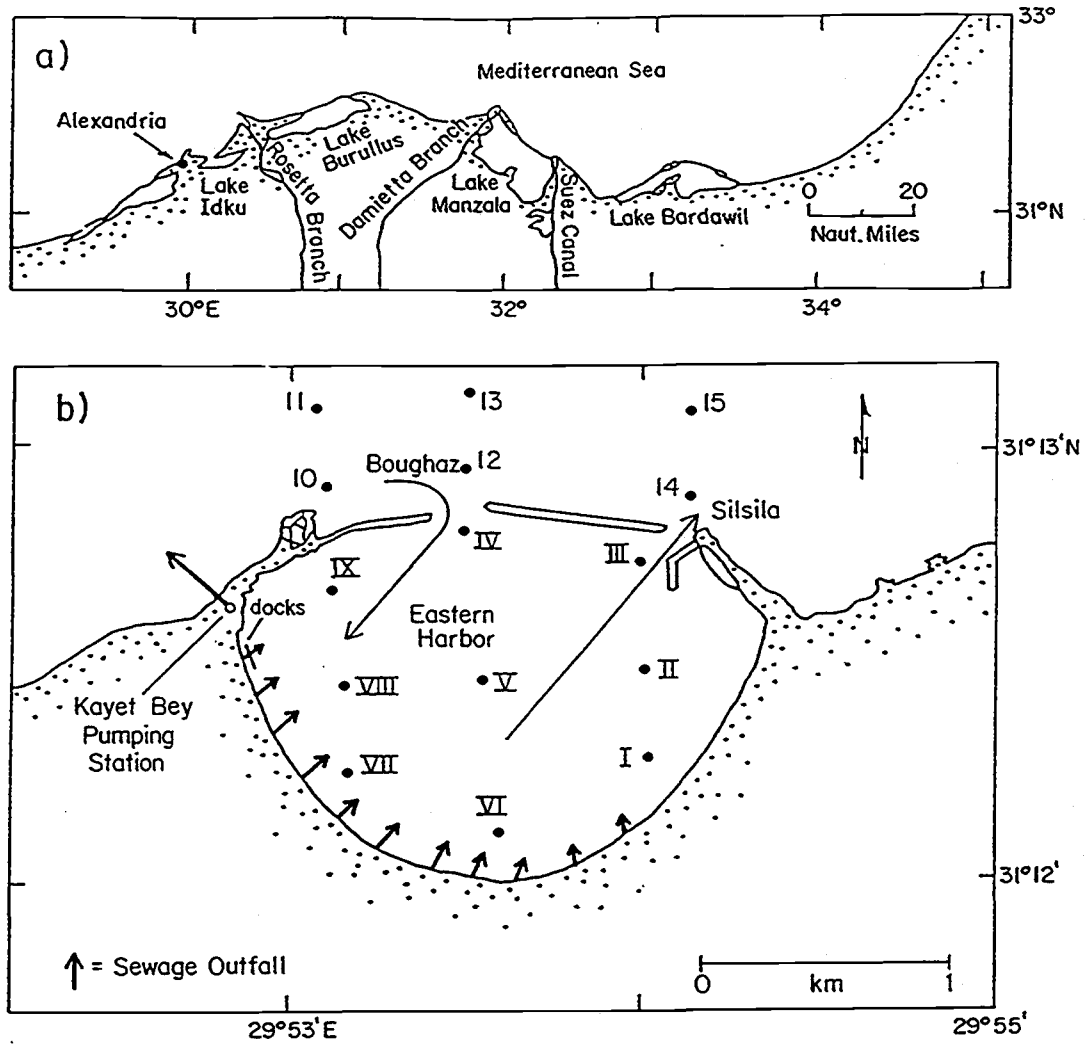


Figure IV.1: The study area, a) the Alexandria region in the eastern Mediterranean Sea, b) the Eastern Harbor, Alexandria (arrows indicate possible sediment movement).

through which the exchange of the harbor water and the neritic Mediterranean waters take place. The area of the EH is about 2.5 km^2 with an average depth of 6 m. The harbor water is influenced by waste water (both untreated sewage and industrial) disposal from the central part of Alexandria City which is pumped into the Mediterranean Sea from the Kayet Bey pumping station. Inside the EH (Figure IV.1), 11 small sewage outlets discharge on average 15,000 m^3/day during winter and 10,000 m^3/day during summer of unprocessed sewage directly into the harbor (Aboul-Kassim et al., 1992). In addition, petroleum contamination is introduced to the EH from runoff during rainy periods, ship and boat traffic, and atmospheric fallout. On the other hand, the region outside the harbor is subjected to petroleum contamination from different sources, such as ship and boat traffic, the Alamein oil field, and the Suez-Mediterranean piplelinne terminal (SUMED).

EXPERIMENTAL METHODS

Sampling

Surface sediment samples were collected from both inside (stations I-IX) and outside (stations 10-15) the EH with a grab sampler (Figure IV.1). Samples were removed from the middle of the grab, wrapped in aluminum foil and stored frozen at -20°C. Before extraction, the samples were freeze-dried and sieved to pass through 250 μm. Pure end member sources, e.g., untreated sewage and waste waters (representing 5 outfalls in the EH) and tarry surficial sediment samples, believed to contain solely petroleum residues, were collected in front of the main docks inside and outside the harbor (Figure IV.1). These samples were also kept frozen at -20°C to prevent organic matter alteration.

Extraction and fractionation

To minimize contamination, all glassware was cleaned with soap and water, rinsed with distilled water, heated in an oven at 550°C for 8 hr to combust any traces of surficial organic matter, and finally rinsed twice with ultra-pure methanol and methylene chloride. The KOH used for saponification was extracted 3 times with *n*-hexane and once with methylene chloride in a separatory funnel to remove organic interferences.

An extraction protocol was designed for the qualitative and quantitative analyses of the hydrocarbons with the biomarkers. Briefly, surficial bottom sediment samples (10 g) were extracted with methylene chloride-methanol (2:1, 250 ml) in a Soxhlet apparatus for 48 hr. The untreated sewage and waste water samples (sewage end member) were liquid/liquid extracted in separatory funnels using *n*-hexane followed by chloroform. Portions of the tarry surficial sediment samples (petrochemical end member) were sonicated with *n*-hexane followed by chloroform. These extracts are a measure of the amount of extractable organic matter (EOM) in the samples. Extracts were vacuum evaporated to near dryness, desulfurized with activated copper, and hydrolyzed overnight with 35 ml of 6% KOH-methanol. Neutral components were recovered with *n*-hexane (4 x 30 ml) and fractionated by column chromatography (column 50 x 1.2 cm, with 8 g each of alumina on top and silica below, both deactivated with 5% water). The following fractions were eluted and collected: (I) 45 ml of *n*-hexane (aliphatic hydrocarbons), followed by 5 additional fractions representing monoaromatic and polycyclic aromatic hydrocarbons, ketones, aldehydes, esters and alcohols. Here, we describe the results for fraction 1 representing the aliphatic hydrocarbons.

Organic carbon analysis

Organic carbon analyses were carried out for all sediment samples using a Carlo Erba NA-1500 CNS analyzer. Samples were combusted at 1000°C in an oxygen-rich medium to CO_2. The CO_2 gas was separated chromatographically, detected using a thermal conductivity detector, and the resulting signals were digitized, integrated, and mathematically processed along with results based on standards. Concentrations of the hydrocarbon fractions were calculated relative to the sedimentary organic carbon content (TOC).

Instrumental analyses

High resolution gas chromatography (GC) was conducted on a Hewlett Packard (HP) *5890*A gas chromatograph, equipped with a split/splitless capillary injection system

and a flame ionization detector (FID). The samples were analyzed in the splitless mode using a fused silica capillary column (30 m x 0.25 mm i.d, DB-5, 0.25 μm film thickness, J & W Scientific) and helium as carrier gas. The analog signal was monitored and/or integrated with an HP *3393*A integrator. The GC conditions were: FID 300°C, injector 300°C, oven temperature initially 65°C, programmed to 200°C at 4°C/min, isothermal at 290°C (60 min). The gas chromatography-mass spectrometry (GC-MS) analyses were performed with a Finnigan *9610* GC (identical column with initial temperature 50°C, isothermal 6 min, programmed at 4°C/min to 310°C, isothermal 60 min) interfaced directly to a Finnigan *4021* quadrupole mass spectrometer (electron impact, emission current -0.45 mA, electron energy 70eV, scanned from 50 to 650 daltons). Data were acquired and processed with a Finnigan-INCOS Model *2300* data system.

Compound identification and quantification

Compound identification was based on comparison with the GC retention times and mass fragmentation patterns of standard reference materials and with the help of the National Institute of Standards and Technology (NIST) standard library (incorporated in the INCOS data system). The following standard mixtures were injected on both GC and GC-MS: (1) a series of *n*-alkanes ranging from C_{10} to C_{36}, and (2) regular isoprenoids as pristane and phytane. Quantification was based on the application of perdeuterated compounds, e.g., *n*-$C_{32}D_{66}$, as internal standards. In order to correct for detector response, sets of relative response factors were determined for the aliphatic fraction (C_{10} to C_{36}) from multiple injections.

Statistical analyses

Data for the aliphatic biomarkers was examined statistically in order to determine any significant environmental variations. All statistical analyses were performed using the SPSS/PC$^+$ statistical package (Norusis, 1986) as well as the statistical package provided on the SUN system of College of Oceanic and Atmospheric Sciences at OSU. These analysis include a measure of dispersion (standard deviation), a correlation analysis

between variables, extended Q-mode factor analysis, and linear programming techniques. The objectives of the statistical analyses were to define the organic geochemical characteristics of the surficial sediments in the EH, examine the geochemical relationships between samples, and assess the sources and occurrence of the aliphatic biomarkers.

RESULTS AND DISCUSSION

Total yields

The total solvent extractable organic matter (EOM) was a maximum of 91.1 mg/g dry sediment for station IX and a minimum of 1.0 mg/g for station IV (Table IV.1), with averages of 5.6 and 2.9 mg/g for inside and outside the EH, respectively. The EOM to TOC was a maximum of 36.2% for station VII, a low of 1.3% for station II, and averaged 15.0 and 20.5% for inside and outside the EH, respectively (Table IV.1).

Hydrocarbons

Normal and isoprenoid alkanes and an envelope (hump) of an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons were present as shown in the typical GC traces (Figure IV.2). The *n*-alkanes ranged in chain length from C_{13} - C_{35} with a carbon number predominance near unity (Table IV.1). The concentrations of the different aliphatic hydrocarbons as weights and relative to TOC are given in Table IV.2. The EOM concentrations relative to TOC and the total *n*-alkanes relative to the UCM are shown as an overview in Figure IV.3. Isoprenoid hydrocarbons were present in all samples as norpristane, pristane and phytane which confirm the petroleum related origin of the *n*-alkanes and UCM (Figure IV.2; e.g., Simoneit, 1978, 1982a,b; Simoneit and Kaplan, 1980; Peters and Moldowan, 1993). The distribution of these isoprenoids and their ratios for all samples points to a common petrochemical source in the EH environment.

Because mixtures of *n*-alkanes from petroleum and terrestrial origins were detected in some stations (Figure IV.2b) inside the harbor area, a substraction of the corresponding *n*-alkane concentrations with a CPI=1 was carried out to determine the distribution

Figure IV.2: GC traces of the total aliphatic hydrocarbons (*n*-alkanes = dots over peaks, * = internal standard) for the surficial sediments of the Eastern Harbor of Alexandria. The biodegradation sequence proceeds from samples numbered from a-d (stations 10, VI, V & III, respectively).

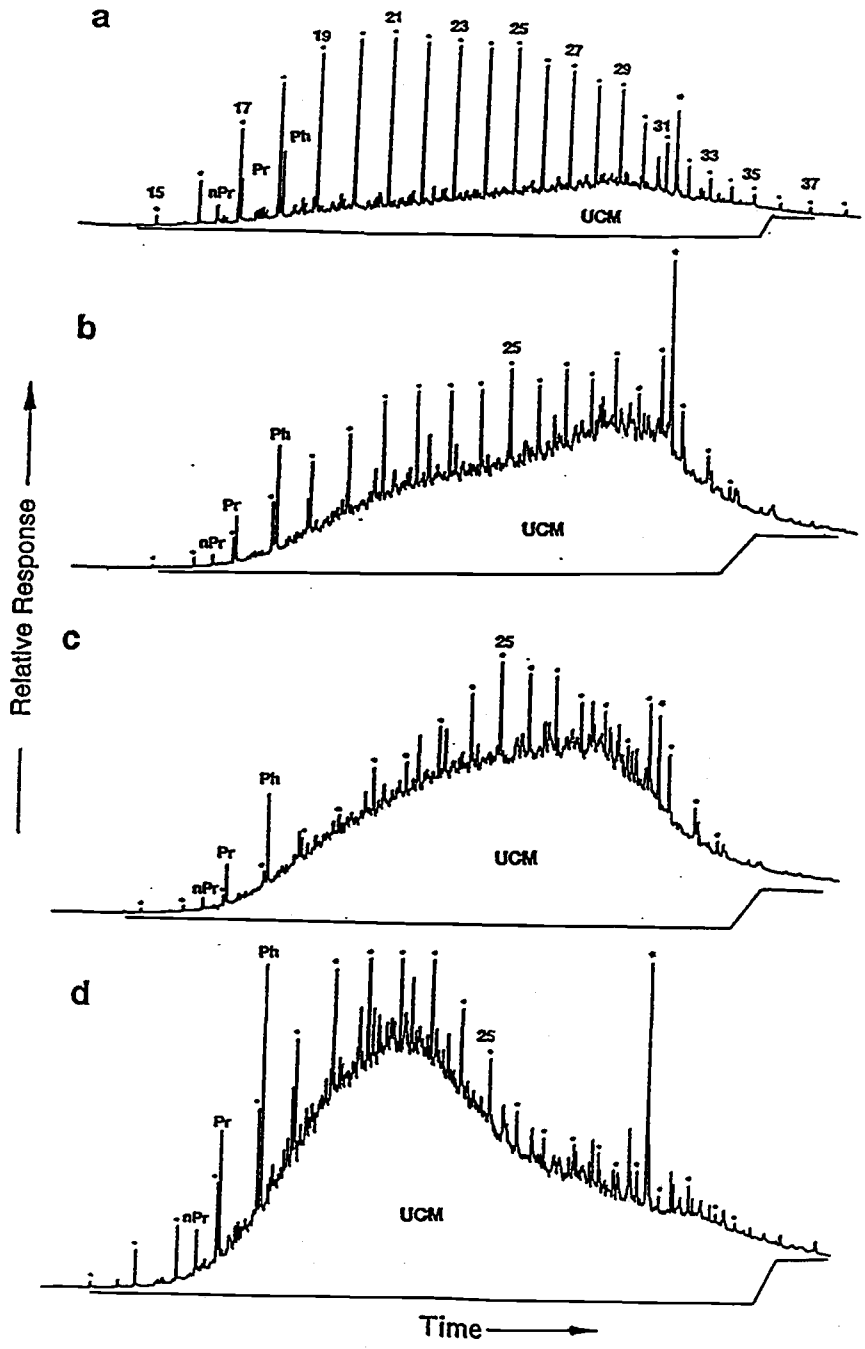

a
15
17
19
21
23
25
27
29
31
33
35
37
nPr
Pr
Ph
UCM
b
25
Ph
Pr
nPr
UCM
c
25
Ph
Pr
nPr
UCM
d
Ph
25
Pr
nPr
UCM
Relative Response
Time

Figure IV.3: Yield of: a) EOM and TOC, and both b) total *n*-alkane and UCM, and c) wax *n*-alkane concentrations relative to TOC in the study area.

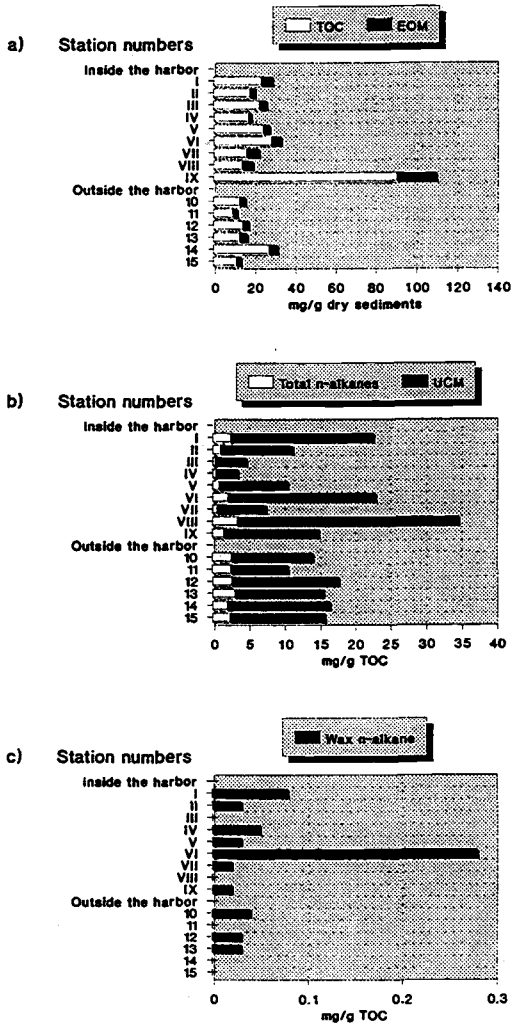

a)
Station numbers
TOC
EOM
Inside the harbor
I
II
III
IV
V
VI
VII
VIII
IX
Outside the harbor
10
11
12
13
14
15
0 20 40 60 80 100 120 140
mg/g dry sediments
b)
Station numbers
Total n-alkanes
UCM
Inside the harbor
Outside the harbor
0 5 10 15 20 25 30 35 40
mg/g TOC
c)
Station numbers
Wax n-alkane
Inside the harbor
Outside the harbor
0 0.1 0.2 0.3
mg/g TOC

Table IV.1: Geochemical analyses of the surficial bottom sediments of the Eastern Harbor of Alexandria.

Sample Location	Sample Station	TOC (mg/g)	EOM (mg/g)	EOM/OC (%)	Σ Total n-alkanes μg/g dry weight	Σ Total n-alkanes mg/g TOC	UCM[a] μg/g dry weight	Organic Geochemical Parameters U/R[b]	Pr/Ph	Pr/C_{17}	Ph/C_{18}	CPI[c]	T_s/T_m	$\frac{C_{23}\ Tri}{C_{30}\alpha\beta}$	Triplet Ratio	$\frac{C_{29}\ \alpha\beta}{C_{30}\ \alpha\beta}$	$C_{31}\alpha\beta\frac{S}{S+R}$	$\frac{\alpha\beta DC_{27}}{\alpha\alpha\alpha C_{29}}$	$\alpha\alpha\alpha C_{29}\frac{S}{S+R}$
Inside the harbor																			
	I	23.6	5.5	23.3	59.08	2.50	478.5	8.1	0.54	3.03	5.42	1.35	0.81	0.13	1.61	0.81	0.63	0.31	0.61
	II	18.1	2.3	1.3	19.24	1.05	184.7	9.6	0.36	2.32	3.20	1.20	0.85	0.07	1.39	0.78	0.56	0.41	0.60
	III	22.8	3.5	15.4	8.01	0.35	98.5	12.3	0.19	3.64	11.54	0.96	0.68	0.11	1.54	0.80	0.60	0.35	0.59
	IV	17.3	1.0	5.8	7.14	0.42	53.6	7.5	0.41	2.79	2.18	1.14	0.73	0.07	2.27	0.86	0.71	0.43	0.67
	V	24.5	3.1	12.7	21.19	0.86	237.3	11.2	0.55	2.13	3.35	1.17	0.78	0.06	1.33	0.78	0.67	0.22	0.59
	VI	28.7	4.5	15.7	60.82	2.12	602.1	9.9	0.37	2.21	2.18	0.97	0.78	0.10	2.00	0.71	0.59	0.39	0.62
	VII	16.3	5.9	36.2	9.61	0.60	113.4	11.8	0.35	3.00	4.78	1.25	0.61	0.08	1.67	0.94	0.59	0.30	0.51
	VIII	14.1	5.2	3.7	49.14	3.48	437.3	8.9	0.46	3.71	3.10	1.32	0.78	0.11	1.61	0.81	0.70	0.39	0.56
	IX	91.0	19.1	21.0	142.77	1.56	1213.5	8.5	0.40	3.81	4.72	1.40	0.80	0.10	1.64	0.77	0.67	0.36	0.61
	average	28.5	5.6	15.0	41.89	1.41	380.0	9.8	0.40	2.96	4.50	1.20	0.76	0.09	1.64	0.81	0.63	0.35	0.60
	SD±	22.5	5.0	10.3	42.50	1.09	345.2	1.6	0.10	0.62	2.71	0.50	0.07	0.02	0.28	0.06	0.05	0.06	0.04
Outside the harbor																			
	10	12.9	2.6	20.2	34.41	2.65	148.0	4.3	0.90	0.50	0.55	1.52	0.87	0.01	1.23	0.79	0.58	0.45	0.56
	11	9.6	2.0	20.4	24.91	2.57	77.2	3.1	0.65	0.70	0.61	1.46	0.67	0.08	-	0.80	0.56	0.36	0.55
	12	14.4	2.9	20.3	38.26	2.65	218.1	5.7	0.71	0.56	0.50	1.50	0.70	0.07	1.47	0.82	0.53	0.50	0.52
	13	12.9	3.6	28.0	39.55	3.08	162.2	4.1	0.62	0.91	0.81	1.35	0.61	-	-	0.92	0.53	0.21	0.57
	14	27.6	4.2	15.3	54.70	2.05	399.3	7.3	0.38	1.40	0.71	0.94	0.68	0.12	1.32	0.90	0.61	0.34	0.50
	15	11.4	2.1	18.6	27.31	2.40	152.9	5.6	0.70	0.78	0.82	1.10	0.63	0.05	1.35	0.88	0.55	0.14	0.39
	average	14.8	2.9	20.5	36.55	2.57	193.0	5.0	0.66	0.81	0.67	1.31	0.69	0.07	1.34	0.85	0.56	0.33	0.52
	SD±	5.9	0.8	3.8	9.76	0.34	101.0	1.4	0.15	0.30	0.12	0.22	0.08	0.04	0.08	0.05	0.03	0.13	0.06

[a]UCM: unresolved complex mixture of aliphatic hydrocarbons.
[b]U/R: unresolved complex mixture/resolved n-alkanes.
[c]CPI: carbon predominance index; $CPI = 0.5\{[(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})] + [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32})]\}$.

Table IV.2: Mean aliphatic hydrocarbon compositions relative to the weight and total organic carbon of the surficial bottom sediments from the Eastern Harbor, Alexandria.

Compound Class	Formula	M.W	Average Concentrations[a]				ID[b]
			Inside the harbor		Outside the harbor		
			A	B	A	B	
n-ALKANES (µg/g)							
n-hexadecane	$C_{16}H_{34}$	226	0.27	9.46	bd	bd	a
n-heptadecane	$C_{17}H_{36}$	240	0.69	24.07	0.40	19.12	a
n-octadecane	$C_{18}H_{38}$	254	1.89	66.07	0.96	45.76	a
n-nonadecane	$C_{19}H_{40}$	268	2.30	80.34	1.43	68.25	a
n-eicosane	$C_{20}H_{42}$	282	3.52	122.84	2.00	95.55	a
n-heneicosane	$C_{21}H_{44}$	296	3.44	119.85	2.51	119.95	a
n-docosane	$C_{22}H_{46}$	310	2.84	92.96	2.70	128.99	a
n-tricosane	$C_{23}H_{48}$	324	2.67	99.10	2.92	139.57	a
n-tetracosane	$C_{24}H_{50}$	338	3.14	109.72	3.03	144.86	a
n-pentacosane	$C_{25}H_{52}$	352	2.86	99.60	3.13	149.81	a
n-hexacosane	$C_{26}H_{54}$	366	3.36	117.36	2.86	136.84	a
n-heptacosane	$C_{27}H_{56}$	380	2.57	89.47	2.96	141.45	a
n-octacosane	$C_{28}H_{58}$	394	2.15	75.03	2.45	117.39	a
n-nonacosane	$C_{29}H_{60}$	408	2.19	76.53	2.37	113.29	a
n-triacontane	$C_{30}H_{62}$	422	1.27	44.32	1.69	80.87	a
n-hentriacontane	$C_{31}H_{64}$	436	2.05	71.55	1.63	77.97	a
n-dotriacontane	$C_{32}H_{66}$	450	2.52	87.98	1.14	54.43	a
n-tritriacontane	$C_{33}H_{68}$	464	1.38	48.14	0.77	37.02	a
n-tetratriacontane	$C_{34}H_{70}$	478	0.78	27.06	0.41	19.45	a
n-pentatriacontane	$C_{35}H_{72}$	492	bd	bd	0.37	17.57	a
n-hexatriacontane	$C_{36}H_{74}$	506	bd	bd	0.31	15.01	a

Table IV.2: Continued.

Compound Class	Formula	M.W	Average Concentrations[a]				ID[b]
			Inside the harbor		Outside the harbor		
			A	B	A	B	
n-heptatriacontane	$C_{37}H_{76}$	520	bd	bd	0.26	12.28	a
n-octatriacontane	$C_{38}H_{78}$	534	bd	bd	0.25	11.77	a
ΣTotal *n*-alkane			41.89	1411.46	36.55	1747.17	a
UCM			410.50	13831.50	182.80	8738.06	
Isoprenoids (μg/g)							
2,6,10,14-tetramethylpentadecane (pristane)	$C_{19}H_{38}$	254	1.52	53.12	0.23	11.09	a
2,6,10,14-tetramethylhexadecane (phytane)	$C_{19}H_{40}$	268	4.14	144.25	0.55	26.11	a
ΣTotal isoprenoids			5.66	187.30	0.78	38.20	
Tricyclic Terpanes (ng/g)							
C_{23}-tricyclic	$C_{23}H_{42}$	318	2.21	77.09	2.03	97.03	b
C_{24}-tricyclic	$C_{24}H_{44}$	332	1.51	52.67	2.48	118.54	b
C_{25}-tricyclic	$C_{25}H_{46}$	346	1.26	43.95	1.91	91.30	b
C_{26}-tricyclic (S)	$C_{26}H_{48}$	360	0.58	20.23	0.54	25.81	b
C_{26}-tricyclic (R)	$C_{26}H_{48}$	360	0.61	21.28	0.55	28.84	b
C_{28}-tricyclic	$C_{28}H_{50}$	388	0.71	24.42	0.63	30.11	c
C_{29}-tricyclic	$C_{29}H_{52}$	402	1.07	37.33	0.70	33.46	c
ΣTricyclics			7.95	277.33	8.83	422.07	
Tetracyclic terpanes (ng/g)							
C_{24}-tetracyclic	$C_{24}H_{42}$	330	2.72	94.89	1.41	67.40	b
C_{26}-tetracyclic	$C_{26}H_{50}$	386	0.91	31.74	0.70	33.46	b

Table IV.2: Continued.

Compound Class	Formula	M.W	Average Concentrations[a]				ID[b]
			Inside the harbor		Outside the harbor		
			A	B	A	B	
C_{29}-tetracyclic	$C_{29}H_{52}$	400	0.93	32.44	0.64	30.59	b
ΣTetracyclics			4.56	159.02	2.75	131.45	
Pentacyclic triterpanes (ng/g)							
18α(H)-22,29,30-trisnorneohopane (Ts)	$C_{27}H_{46}$	370	4.38	152.79	2.14	102.29	b
17α(H)-22,29,30-trisnorhopane (Tm)	$C_{27}H_{46}$	370	5.98	208.61	3.12	149.14	b
17α(H),21α(H)-norhopane	$C_{29}H_{50}$	398	26.91	938.73	14.97	715.57	b
17α(H),21α(H)-hopane	$C_{30}H_{52}$	412	33.82	1179.79	16.72	799.22	b
17α(H),21β(H)-homohopane (22S)	$C_{31}H_{54}$	426	15.27	532.68	7.99	381.92	b
17α(H),21β(H)-homohopane (22R)	$C_{31}H_{54}$	426	6.32	220.47	5.09	243.30	b
17α(H),21β(H)-bishomohopane (22S)	$C_{32}H_{56}$	440	10.92	380.93	5.61	268.16	b
17α(H),21β(H)-bishomohopane (22R)	$C_{32}H_{56}$	440	5.46	190.47	4.91	234.71	b
17α(H),21β(H)-trishomohopane (22S)	$C_{33}H_{58}$	454	8.75	305.24	3.54	169.21	b
17α(H),21β(H)-trishomohopane (22R)	$C_{33}H_{58}$	454	3.81	132.91	1.86	88.81	b
17αH(),21β(H)-tetrakishomohopane (22S)	$C_{34}H_{60}$	468	6.10	212.79	3.07	146.75	b
17α(H),21β(H)-tetrakishomohopane (22R)	$C_{34}H_{60}$	468	3.34	116.51	1.54	73.61	b
17α(H),21β(H)-pentakishomohopane (22S)	$C_{35}H_{62}$	482	6.36	221.86	2.52	120.46	b
17α(H),21β(H)-pentakishomohopane (22R)	$C_{35}H_{62}$	482	1.94	67.68	1.36	65.01	b
ΣPentacyclics			139.36	4861.44	74.44	3558.23	
Diasteranes (ng/g)							
13α(H),17β(H)-diacholestane (20S)	$C_{27}H_{48}$	372	0.46	16.05	0.32	15.30	b,d
13α(H),17β(H)-diacholestane (20R)	$C_{27}H_{48}$	372	0.69	24.07	0.49	23.42	b,d

Table IV.2: Continued.

Compound Class	Formula	M.W	Average Concentrations[a]				ID[b]
			Inside the harbor		Outside the harbor		
			A	B	A	B	
ΣDiasteranes			1.15	40.12	0.81	38.72	
Steranes (ng/g)							
5α(H),14α(H),17α(H)-cholestane (20S)	$C_{27}H_{48}$	372	1.32	46.05	0.65	31.07	b
5α(H),14β(H),17β(H)-cholestane (20R)	$C_{27}H_{48}$	372	3.04	106.05	1.78	85.08	b
5α(H),14β(H),17β(H)-cholestane (20S)	$C_{27}H_{48}$	372	1.91	66.63	1.28	61.18	b
5α(H),14α(H),17α(H)-cholestane (20R)	$C_{27}H_{48}$	372	1.24	43.26	0.68	32.50	b
5α(H),14α(H),17α(H)-ergostane (20S)	$C_{28}H_{50}$	386	1.26	43.95	1.12	53.54	b
5α(H),14β(H),17β(H)-ergostane (20R)	$C_{28}H_{50}$	386	2.96	103.26	3.02	144.36	b
5α(H),14β(H),17β(H)-ergostane (20S)	$C_{28}H_{50}$	386	3.10	108.14	2.72	130.02	b
5α(H),14α(H),17α(H)-ergostane (20R)	$C_{28}H_{50}$	386	1.11	38.72	0.88	42.06	b
5α(H),14α(H),17α(H)-sitostane (20S)	$C_{29}H_{52}$	400	2.45	85.47	2.04	97.51	b
5α(H),14β(H),17β(H)-sitostane (20R)	$C_{29}H_{52}$	400	4.60	160.47	2.57	122.85	b
5α(H),14β(H),17β(H)-sitostane (20S)	$C_{29}H_{52}$	400	3.69	128.72	2.78	132.88	b
5α(H),14α(H),17α(H)-sitostane (20R)	$C_{29}H_{52}$	400	0.45	15.70	2.04	97.51	b,d
ΣSteranes			27.82	970.47	21.56	1030.57	

[a]A: concentration relative to dry weight sediment, concentration relative to organic carbon, bd: below detection limit.
[b]for more details, see Rogge *et.al.* (1993).
*CPI=0.5[[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})]+[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})]].
**U/R ratio=unresolved complex mixutre/resolved *n*-alkanes.

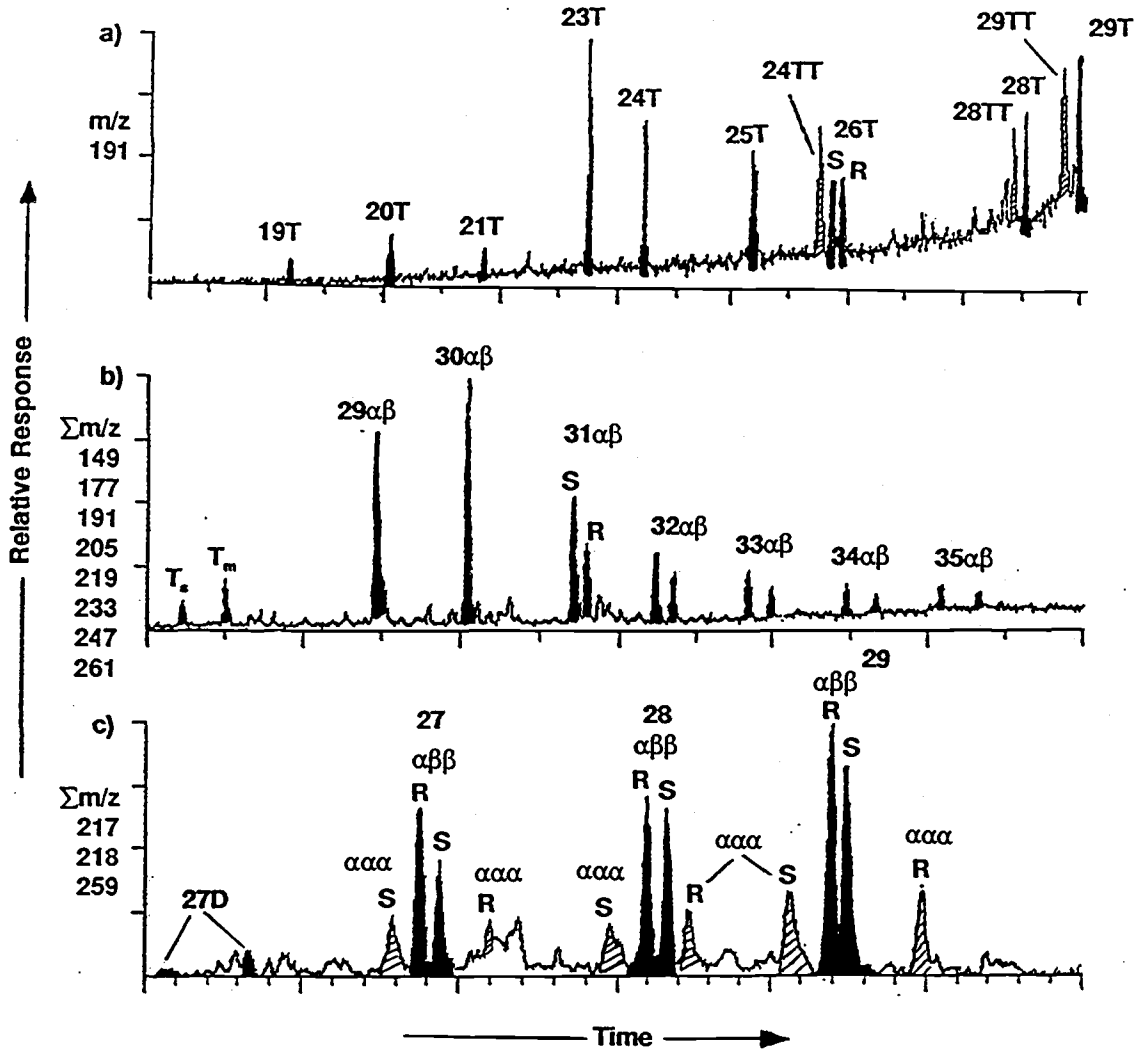
signatures of the residual plant wax alkanes. Thus, the terrestrial higher plant wax *n*-alkane signature was calculated by subtracting the average of the next higher and lower even carbon numbered homolog (Simoneit *et al.*, 1990) as follows: Wax *n*-C_n = [C_n] - 0.5[$C_{(n+1)}$+$C_{(n-1)}$], where negative values of C_n were taken as zero. These samples have slightly different *n*-alkane distribution, derived from epicuticular waxes with C_{max} of C_{21}, C_{25}, C_{27}, C_{29} and C_{31}, and amounting to 11.9% (0.05 mg/g TOC) and 13.2% (0.28 mg/g TOC) of the total *n*-alkanes of samples IV & VI, respectively (Figure IV.3).

Besides the chromatographically resolved compounds, an UCM of hydrocarbons eluting between *n*-C_{16} and *n*-C_{33} is present in all samples (Figure IV.2), with a maximum of 1214 µg/g dry sediment for station IX and a minimum of 77 µg/g for station 11 (Table IV.1). The U/R ratio is higher for samples inside than outside the harbor (Table IV.1). This is also indicative of high petroleum contributions to the sediments (Simoneit, 1978; Simoneit and Kaplan, 1980), which will now be confirmed by the identification of petroleum biomarkers (Seifert and Moldowan, 1979; Simoneit and Kaplan, 1980; Simoneit *et al.*, 1980; Simoneit, 1986; Peters and Moldowan, 1993). A direct linear correlation is observed between both *n*-alkanes (C_{13}-C_{35}) and UCM ($p \leq 0.01$) indicating a common (petrochemical) origin of these aliphatic hydrocarbons. The absence of this correlation with the aromatic components in these samples indicates a different source for the aromatic hydrocarbons in the harbor.

Biomarkers

A typical example of the distributions of the tri- and tetracyclic terpanes (key ion m/z 191), hopanes (∑m/z 149, 177, 191, 205, 219, 233, 247, 261) and steranes/diasteranes (∑m/z 217, 218, 259) is shown in Figure IV.4. The tricyclic terpane series is present in all surficial bottom sediments rangeing from C_{19} to C_{29}, with no C_{22} & C_{27}, and a C_{23} predominance (Figure IV.4, Table IV.2; Aquino Neto *et al.*, 1983). The tetracyclic terpanes are comprised of a C_{24}-(17,21-*seco*-hopane) and C_{28} and C_{29}-(8,14-*seco*-hopanes) (Figure IV.4, Table IV.2; Aquino Neto *et al.*, 1983). Kvenvolden *et al.* (1985) used the triplet ratio of the two C_{26} tricyclanes to the C_{24} tetracyclane to evaluate

Figure IV.4: Typical mass fragmentograms representing: a) tri- and tetracyclic terpanes (m/z 191), b) hopanes (summed m/z 149, 177, 191, 205, 219, 233, 247, 261), and c) steranes/diasteranes (summed m/z 217, 218, 259) representing the petroleum biomarkers in the surficial bottom sediments of the harbor [T=tricyclic, TT=tetracyclic, T_s= 18α(H)-22,29,30-trisnorneohopane, T_m= 17α(H)-22,29,30-trisnorhopane, αβ=17α(H),21β(H)-hopanes (R&S at C-22), αββ= 5α(H),14β(H),17β(H)-steranes (R&S at C-20), ααα=5α(H),4α(H),17α(H)-steranes (R&S at C-20), βαD=13β(H),17α(H)-diasteranes (R & S at C-20)].


a)
m/z
191
19T
20T
21T
23T
24T
25T
24TT
26T
S
R
28TT
28T
29TT
29T
b)
Σm/z
149
177
191
205
219
233
247
261
T_s
T_m
29αβ
30αβ
31αβ
S
R
32αβ
33αβ
34αβ
35αβ
c)
Σm/z
217
218
259
27D
αααS
27
αββ
R
S
αααR
αααS
28
αββ
R
S
αααR
S
αααS
29
αββ
R
S
αααR
Relative Response
Time

oil biodegradation, where a ratio of 2.0-2.2 indicated heavy biodegraded petroleum. For the EH bottom sediments, the triplet ratio ranged from 1.2 to 2.3, suggesting that biodegradation may have commenced. The hopane distribution is characterized by the predominance of 17α(H),21β(H)-hopane with subordinate amounts of 18α(H)-22,29,30-trisnorneohopane (T_s), 17α(H)-22,29,30-trisnorhopane (T_m), 17α(H),21β(H)-norhopane, and the extended 17α(H),21β(H)-homohopanes (Table IV.2). The homohopane series is found as the C-22 diastereomers with the 22S and 22R configuration for C_{31} to C_{35}. Steranes predominate over diasteranes and were quantified (Table IV.2). The regular steranes are comprised mainly of the 5α(H),14β(H),17β(H)-steranes, ranging from C_{27} to C_{29} with a dominance of C_{29}, a minor amount of the 5α(H),14α(H),17α(H)-steranes, and traces of 13α(H),17β(H)-diasteranes.

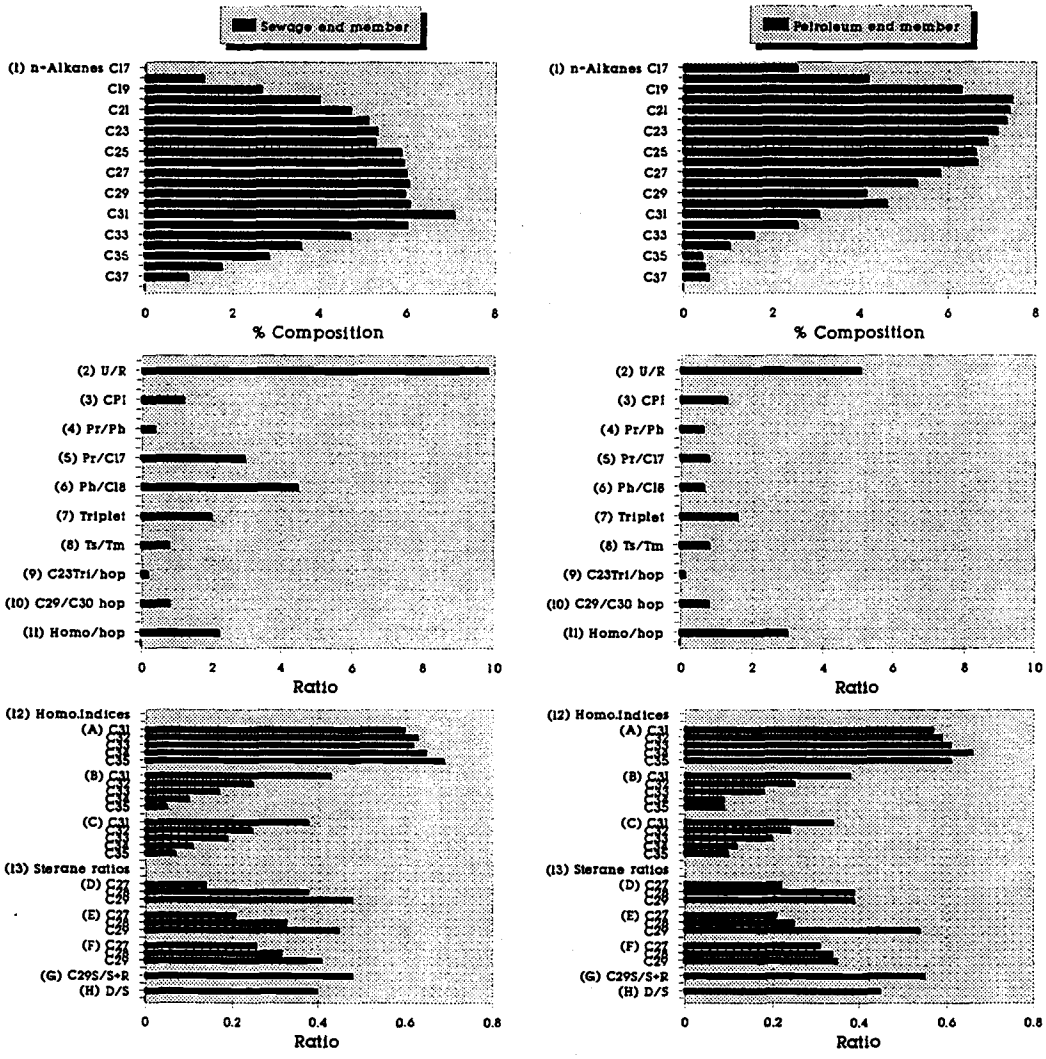
Three traditional maturity indicators for the biomarkers (Mackenzie, 1984) are considered (Table IV.1). The S/R ratios of the C_{31}-αβ hopanes are equal and fully mature (averages 0.63 and 0.56 for inside and outside the EH, respectively, Table IV.1). The ratios of the trisnorhopanes, T_s/T_m (Table IV.1), which in this case may have maturity and/or source implications have a narrow range of 0.61-0.87 with no observable trend between samples, indicating a common petrochemical source in the area. The S/(S+R) ratios (0.5 at equilibrium) of the 5α(H),14α(H),17α(H)-C_{29} steranes show a significant range (0.39-0.67, Table IV.1). This ratio can be changed due to biodegradation (e.g., Chosson *et al.*, 1992). In addition, the relative values of the C_{23}-tricyclic terpane/C_{30}-hopane and of the C_{27}-αβ diasterane/C_{29}-ααα sterane ratios do not vary among the samples (Table IV.1). Thus, coupling the *n*-alkane distributions, CPI, isoprenoid hydrocarbons, UCM, U/R, and biomarkers (tri- and tetracyclics, hopanes and steranes/diasteranes) and their ratios (Tables IV.1 and IV.2) allows the confirmation of one dominant end member of a petrochemical origin.

The aliphatic hydrocarbon compositions of the surficial sediments (inside and outside the EH) indicate a predominance of petrochemicals which can be compared with two possible end members, i.e., untreated sewage/waste water and petroleum hydrocarbons from boating. Since heavy petroleum pollution (as in the EH) enhances microbiological activity, biodegradation was observed in most of the samples from the study area. In such

situations, a strong depletion or total absence of *n*-alkanes is common (Figure IV.3), resulting in GC signatures with a prominent UCM (Bailey *et al.,* 1973a,b; Connan *et al.,* 1980). The shorter chain *n*-alkanes are depleted if moderate biodegradation has occurred (Prince *et al.,* 1994). The absence of this feature for some stations outside the EH is rather unusual and may be explained by a recent input of petroleum products. Peters and Moldowan (1991) report that microbial attack on the αβ-homohopanes favors the order $C_{35}>C_{34}>C_{33}>C_{32}>C_{31}$ and 22R>22S. For steranes, biodegradation proceeds as follows: $\alpha\alpha\alpha$20R(C_{27}-C_{29}) > $\alpha\alpha\alpha$20S C_{27} > $\alpha\alpha\alpha$20S C_{28} > $\alpha\alpha\alpha$20S $C_{29} \geq \alpha\beta\beta$(20S+20R)$C_{27}$-$C_{29}$ (Chosson *et al.,* 1992; Peters and Moldowan, 1993). Preferential degradation of the $\alpha\alpha\alpha$20R sterane epimers, like the 22R αβ-homohopanes, appears to reflect enzymatic specificity in the bacteria for the biological over the geological stereochemistry (Philp, 1985). Microorganisms typically degrade petroleum by utilizing the less complex hydrocarbon compounds first (Seifert and Moldowan, 1979; Zhang *et al.,* 1988), thus, *n*-alkanes and acyclic isoprenoids are attacked prior to steranes and triterpanes. However, biodegradation is considered to be quasi-sequential (Peters and Moldowan, 1991) in that more resistant compound classes can be attacked prior to complete utilization of less resistant classes. Because aliphatic hydrocarbons have different rates of biodegradation depending on the medium in which they are found, the use of biodegradation indices is a way to differentiate between petroleum contaminants derived from sewage or from direct input by boating. Thus, biomarker biodegradation indices were calculated for these samples and the main differences between the sources based on these are shown in Figure IV.5.

Based on the biomarker biodegradation ratio distribution (Figure IV.5), it is obvious that the sewage end member can be differentiated from the petroleum hydrocarbon end member. In general, the sewage end member is characterized by a lower ratio of each carbon number *n*-alkane to the total *n*-alkanes (Figure IV.5, ratio #1), with a C_{max} ranging from C_{27} - C_{33} (the C_{max} of the petroleum end member ranges from C_{19} - C_{23}), higher ratios of U/R, Pr/C_{17}, Ph/C_{18}, triplet, C_{23}-tri/hop, and lower ratios of Pr/Ph and homo/hop compared to the petroleum hydrocarbon end member. This confirms a high

Figure IV.5: Comparison between source end members based on aliphatic hydrocarbons, biomarker indices, and biodegradation indices. Numbers represent indices as: (1) % composition of each odd *n*-alkane; (2) U/R: ratio between unresolved complex mixture/resolved alkanes; (3) CPI: ratio of odd-to-even carbon number *n*-alkanes, where CPI=0.5{[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})]+[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})]}; (4) Pr/Ph: pristane to phytane ratio; (5) Pr/C_{17}: pristane to *n*-C_{17}; (6) Ph/C_{18}: phytane to *n*-C_{18}; (7) Triplet ratio=[(C_{26}-tricyclic S + C_{26}-tricyclic R)/C_{24}-tetracyclic] (Kvenvolden *et al.*, 1985); (8) T_s/T_m =[18α(H)-22,29,30-trisnorneohopane/17α(H)-22,29,30-trisnorhopane]; (9) C_{23}Tri/hop =[C_{23}-tricyclic/17α(H),21β(H)-hopane]; (10) C_{29}/C_{30}hop = [17α(H),21β(H)-29-norhopane/17α(H),21β(H)-hopane]; (11) homo/hop = {[17α(H),21β(H)-homohopanes (22R+S) for C_{31} - C_{35}]/17α(H),21β(H)-hopane}; (12) Homo.Indices (maturity indices), where: (A) = ratio between the S and R epimer at C-22 for the extended 17α(H),21β(H)-homohopane series (C_{31} - C_{35}), e.g. for C_{31} = αβC_{31} [S/(S+R)], (B) = ratio between each 17α(H),21β(H)-22 R homohopane homolog to the total extended homohopane R homologs (C_{31} - C_{35}), e.g. for C_{31} = [αβC_{31}R /αβ C_{31}-C_{35} R], (C) = same as in (B) but C-22 S instead of R; (13) Sterane ratios: ratio between the R and S epimer at C-20 for C_{27} - C_{29} for both ααα and αββ configurations, where: (D) = ratio of αααR to the total αααR for C_{27} - C_{29}, e.g. C_{27} = [(αααR C_{27} /αααR(C_{27}+C_{28}+C_{29}), (E) = same as in (D) but αααS not R, (F) = same as in (D) but αββ(S+R) instead of αααS/R, (G)C_{29}S/S+R= ratio of αααC$_{29}$[S/(S+R)], (H) D/S =αβC_{27}-diasterane/αααC$_{29}$-sterane.


Sewage end member
(1) n-Alkanes C17
C19
C21
C23
C25
C27
C29
C31
C33
C35
C37
0
2
4
6
8
% Composition
(2) U/R
(3) CPI
(4) Pr/Ph
(5) Pr/C17
(6) Ph/C18
(7) Triplet
(8) Ts/Tm
(9) C23Tri/hop
(10) C29/C30 hop
(11) Homo/hop
0
2
4
6
8
10
Ratio
(12) Homo.Indices
(A)
(B)
(C)
(13) Sterane ratios
(D) C27
C28
C29
(E) C27
C28
C29
(F) C27
C28
(G) C29S/S+R
(H) D/S
0
0.2
0.4
0.6
0.8
Ratio
Petroleum end member
(1) n-Alkanes C17
C19
C21
C23
C25
C27
C29
C31
C33
C35
C37
0
2
4
6
8
% Composition
(2) U/R
(3) CPI
(4) Pr/Ph
(5) Pr/C17
(6) Ph/C18
(7) Triplet
(8) Ts/Tm
(9) C23Tri/hop
(10) C29/C30 hop
(11) Homo/hop
0
2
4
6
8
10
Ratio
(12) Homo.Indices
(A)
(B)
(C)
(13) Sterane ratios
(D) C27
C28
C29
(E) C27
C28
C29
(F) C27
C28
(G) C29S/S+R
(H) D/S
0
0.2
0.4
0.6
0.8
Ratio

biodegradation rate for the sewage end member. In the case of the homohopane indices (Figure IV.5, ratios #12A-C), the ratio between the C-22 S and R epimer for the extended homohopane series (C_{31} - C_{35}), e.g. C_{31}= $\alpha\beta C_{31}$[S/(S+R)], indicate an increase with increasing carbon number, with higher values for the sewage end member. The ratios of the 22 R αβ-homohopanes to the total extended 22R homohopanes (C_{31} - C_{35}), e.g. for C_{31} = [$\alpha\beta C_{31}$R /$\alpha\beta$ C_{31}-C_{35} R], or the same ratio for C-22 S instead of R, decrease with increasing carbon number. The Sterane ratios (Figure IV.5, ratios #13D-F), the R and S epimer at C-20 for C_{27} - C_{29} of both ααα and αββ configurations increase with increasing carbon number more pronounced for the sewage than the petroleum end member. In addition, lower ratios of $\alpha\alpha\alpha C_{29}$ S/(S+R) (0.48) and βC_{27}-diasterane/$\alpha\alpha\alpha C_{29}$-sterane (0.40) and (Figure IV.5, ratios #13 G and H, respectively) indicate a higher biodegradation rate for sewage than for the petrochemicals

Statistical analyses

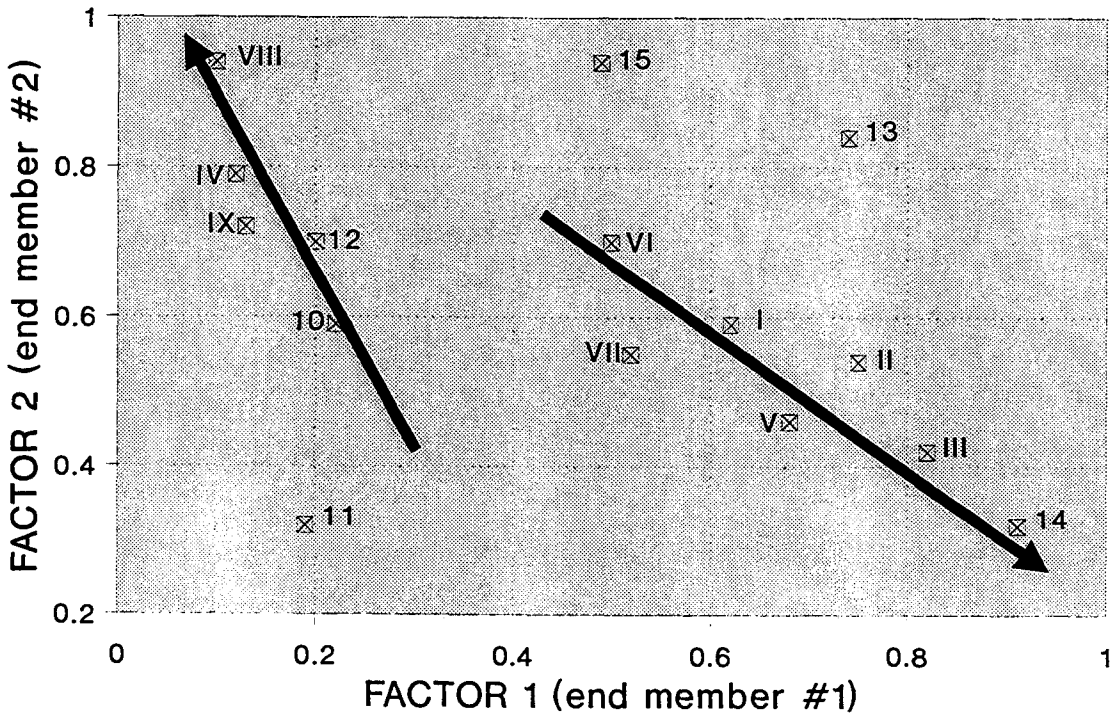
The quantitative composition of the aliphatic hydrocarbon fractions relative to TOC, as well as the biomarker biodegradation ratios, were submitted to extended Q-mode factor analysis and linear programming technique (LPT). Q-mode factor analysis is devoted exclusively to the interpretation of the inter-object relationships rather than covariance relationships explored with R-mode. LPT was used to identify end member compositions (Leinen and Pisias, 1984; Aboul-Kassim and Simoneit, 1994a,b). Factor analysis provides a description of the multivariate data set in terms of a few orthogonal end members (factors), which account for the variance within the data set. The importance of each variable in each end member is represented by a factor score, while the relative importance of each end member factor in each sample is its factor loading value. Because transformations of the original data variables during the analysis result in negative factor scores for some variables and negative concentrations for others in the end member when using varimax rotation (Aboul-Kassim and Simoneit, 1994a), we used the "new rotation" technique proposed by Leinen and Pisias (1984) which corrects the negative values and does not necessarily require the assumption of having sampled pure end members. However, we used both the new rotation technique as well as sampling pure end member

sources (Aboul-Kassim and Simoneit, 1994a,b). The criteria for choosing the number of end members used to model the data were: (1) at least 90% of data set variance was explained by the sums of squares of the end members, and (2) all end member factors that explained less than 2% of the total variance were rejected. By using a partitioning by LPT, a set of equations was applied for correcting the initial end member compositions and their abundance to better fit the observed multivariate data set (Leinen and Pisias, 1984).

The first result from factor analysis on these samples yields two significant principal factor loading scores, providing information about sample variations of 65.4% and 26.1% (maximum cumulative information 91.5%), respectively. These sources could be confirmed after using the new rotation on the composition scores. The two resultant end members fit statistically and experimentally with the source end members, representing petroleum hydrocarbons (Figure IV.5) derived from untreated sewage (end member #1) and from direct input due to ship and boat traffic (end member #2). In addition, a minor unsignificant end member, describing 0.065% of the sample variations, was characterized with a predominance of C_{25}, C_{29} and C_{31}, representing the trace input of terrestrial plant wax *n*-alkanes in the harbor area.

In order to determine sediment transport in the study area and to know to what extent these two contaminant sources can move, we used the gradient change in factor loading values (Figure IV.6) as a tool, where a high factor loading at a station means that a large amount of the total information for that site is explained by that factor. The individual squared loading of one factor represents the fraction which that factor contributes to the sample (e.g., if a sample has a factor #1 loading of 0.7, then $(0.7)^2$= 0.49 or 49% of the sample is from factor #1). Thus, the distributions of the factors were obtained for each sample. The factor loadings of factor #1 (sewage derived) for the EH stations indicate that sample 14 outside the harbor has the highest loading (0.91), sample III has the second highest loading (0.81), samples II & V have the third highest loadings, and so on (Figure IV.6). Thus, the increase of factor loading values in the order of stations VI<VII<I<V<II<III<14 indicates that particulate matter or surficial sediment from the eastern side of the harbor and close to the sewage outfalls (Figure IV.1) may be

Figure IV.6: Factor loadings and possible sediment transport (arrows indicate sediment movement).


FACTOR 2 (end member #2)
1
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1
FACTOR 1 (end member #1)
VIII
15
13
IV
IX
12
VI
10
I
VII
II
V
III
14
11

transported in a northeast direction (Figure IV.6) even outside the harbor through the Silsila opening (Figure IV.1).

In the case of factor #2 (oil derived), the highest factor loading values are between stations VIII and IV, followed by stations IX, 12, and then 10. Thus, particulate matter or surficial sediment may move from outside to inside the harbor in a southwest direction through the Boughaz opening (Figure IV.1). This can be supported by the biodegradation indices for the sediments, where extensive transport results in more severe biodegradation. Thus, an increase in the biodegradation sequence was observed in the same order of these stations, with increases in U/R, Pr/C_{17}, Ph/C_{18}, and decreases in total *n*-alkanes, Pr/Ph, CPI, $C_{31}\alpha\beta[S/(S+R)]$, and $\alpha\beta DC_{27}/\alpha\alpha\alpha C_{29}$ (Table IV.1). Station 11, which is closer to end member #2, (Figure IV.6) may contribute less to particle or sediment movement toward the harbor. On the other hand, stations 15 and 13 exhibit no particle or sediment movement and are derived from end member #1.

CONCLUSION:

Aliphatic hydrocarbons from petrochemical sources have been identified in surficial sediments of the Eastern Harbor of Alexandria. The petroleum origin was indicated by the pristane/phytane ratio, UCM signal, low carbon preference index, and the presence of petroleum biomarkers such as tri-, tetra-, and pentacyclic terpanes and steranes/diasteranes. Biodegradation parameters were used to differentiate between petroleum hydrocarbons derived from discharge of untreated sewage and waste water or from direct input by ship and boat traffic in the area.

The multivariate statistical analyses represented a useful method to confirm the end member sources and to assess suspended particulate matter or sediment transport in the area using the gradient change in factor loading values. Aliphatic hydrocarbons derived from untreated sewage (representing 65% of the sample variation) are transported from stations close to sewage outfalls in a northeast direction through the Silsila opening, while petroleum hydrocarbons derived from ship and boat traffic move from outside to inside the harbor through the Boughaz opening.

ACKNOWLEDGEMENTS:

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CHAPTER V

LIPID GEOCHEMISTRY OF SURFICIAL SEDIMENTS FROM THE ALEXANDRIA COASTAL ENVIRONMENT. I- ALIPHATIC HYDROCARBONS - CHARACTERIZATION AND SOURCES

ABSTRACT

Samples of surficial bottom sediments collected from six main zones along the Alexandria coast (Egypt) have been analyzed and characterized in terms of their contents of biogenic and anthropogenic hydrocarbon biomarkers. The distributions, structures, and applicability of these compounds in determining sample sources are discussed using the biomarker multi-tracer approach. By means of multivariate statistical analyses (Q-mode cluster analysis, extended Q-mode factor analysis, and linear programming technique), the hydrocarbon tracers were grouped according to their probable input sources and the sampling stations according to the relative importance of each source contribution.

Homologous long chain *n*-alkanes (C_{15} - C_{38}), CPI, UCM, and biomarkers such as pristane, phytane, tricyclic (C_{19} - C_{29}) and tetracyclic (C_{24}, C_{28} and C_{29}) terpanes, 17α(H),21β(H)-hopanes (C_{27} - C_{35}), 5α(H),14β(H),17β(H)-steranes (C_{27} - C_{29}) with a minor amounts of 5α(H),14α(H),17α(H)-steranes and 13α(H),17β(H)-diasteranes were found to be the most suitable indicators to differentiate between sewage/industrial pollution and natural background sources. Several ratios of the terrestrial and anthropogenic biomarkers were calculated for every station in each zone. These ratios, the aliphatic hydrocarbon concentrations (relative to TOC), and the statistical findings from the multivariate techniques indicate strong signals of petroleum/industrial and biogenic/terrestrial aliphatic hydrocarbons in the Alexandria coastal region.

INTRODUCTION

Egypt, a southeastern Mediterranean country, has excellent and productive coasts along the Mediterranean Sea with many beaches (Figure V.1). The future of these coasts and their beaches depends mainly on the care and effort spent on their environmental protection. Among them, Alexandria City, chosen as a model, is the main port of Egypt as well as an industrial and touristic place. The region receives organic pollution from different sources including atmospheric fallout deposition (Aboul-Kassim and Simoneit, 1994a), outfall of partially treated domestic sewage and waste water (Aboul-Kassim *et al.*, 1992a), as well as ship and boat pollution (sewage, petroleum and engine oil; Aboul-Kassim and Simoneit, 1994b). Thus, to provide base-line data for the preservation of the Alexandria coastal environment, we carried out a research project called Organic Tracers of Pollution in the Environment of the South-Eastern Mediterranean (OTPESEM). It is new in the area and studies the characterization, distribution, transport and fate of several organic pollutants. Alexandria city is a heavily polluted environment. When this OTPESEM project has set up the organic pollution multi-tracer model, the application of the same model to other coastal areas on national and multinational scales will aid the comparison of data bases, the characterization of biomarkers specific for each environment, the exchange ideas and data, as well as the provision of a basis for legislation to conserve the marine environment.

Aliphatic hydrocarbons, a diverse suite of compounds, are an important lipid fraction in the multi-tracer OTPESEM model. In the coastal and marine environment, these aliphatic hydrocarbons are sequestered and preserved in surficial sediments. Their sources are natural from photosynthesis by marine biota inhabiting the surface waters and transport as part of particulate matter from land runoff and/or industrial anthropogenic inputs. Thus, the assessment of aliphatic hydrocarbons in surficial sediments of the coastal environment of Alexandria should record changes in rates of sewage/industrial and natural vegetation inputs, as well as variations in the predominance of certain sources and/or irregular local emissions. This is the first study conducted to characterize the different hydrocarbon components in surficial sediments of the south-eastern Mediterranean, since most of the previous work was done in the western Mediterranean (Albaigés, 1980;

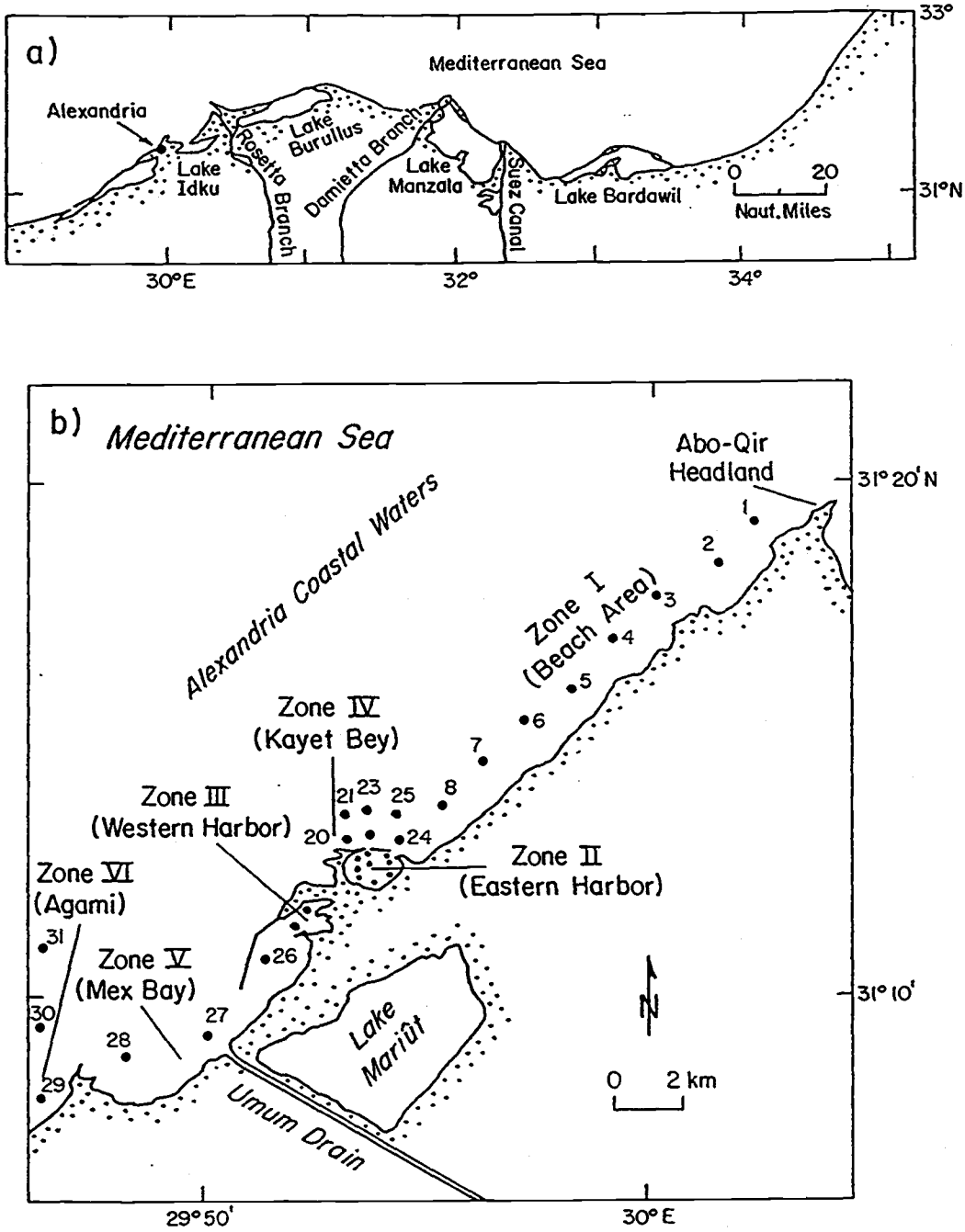


Figure V.1: The study area, a) Egypt in the southeastern Mediterranean region, b) the Alexandria coastal region.

Albaigés and Cuberes, 1980; Albaigés *et al.*, 1984; Solanas *et al.*, 1982; Grimalt and Albaigés, 1990; Grimalt *et al.*, 1984, 1986, 1990; Saliot *et al.*, 1990, 1991).

In order to distinguish and evaluate the different anthropogenic versus biogenic sources, the aliphatic hydrocarbon composition of surficial sediments from various sources must be determined and the proportion of each must be identified in the samples. The direct approach for source characterization and partitioning would be to isolate the aliphatic hydrocarbon fractions from the lipids of pure end member sources, to determine their qualitative and quantitative compositions, and then to assess their relative importance in each sample (Aboul-Kassim and Simoneit, 1994c). Thus, using this multi-tracer biomarker approach with multivariate statistical analysis techniques will accurately partition sediment samples according to their probable input sources.

The present study is an initial investigation of a selected group of organic constituents, mainly aliphatic hydrocarbons, in the surficial sediments of the Alexandria region. The objectives are to: (a) characterize aliphatic hydrocarbons in the solvent extractable lipids of sediments from the Alexandria coastal areas, (b) use the multi-tracer biomarker approach to assess the different hydrocarbon sources, and (c) carry out statistical data analysis using both univariate and multivariate procedures to examine the variations in the data, determine the regions of hydrocarbon concentrations, group samples according to their probable input sources, and find statistically significant associations (end members) in the data set which will help to assess and identify the different sources of the hydrocarbons in the study area.

STUDY AREA

Alexandria is the second largest city and the principal summer resort of Egypt. It is one of the densely populated regions of the eastern Mediterranean (about 3.5 million inhabitants), receiving about 1 million tourists in summer who come to use its beaches for recreation. Alexandria encompasses 40% of the nation's industry and has the main commercial and yachting harbors. Its coastal waters are highly polluted with untreated domestic sewage and industrial waste waters, discharged into the sea through several outfalls along the coast (Table V.1). The problem of organic pollution of Alexandria has

Table V.1: General characteristics of the land runoff in the Alexandria coastal environment.

Table V.1: General characteristics of the land runoff in the Alexandria coastal environment.

Zone	No. of samples	Name	Type of anthropogenic input	Flow rate (10^6 m^3/yr)	Area (km^2)	Mean depth (m)
I	8	Beach area	- untreated sewage and waste waters (18 outfalls)	34.0	30.0	12.0
II	9	Eastern Harbor	- untreated sewage and waste waters (11 outfalls)	36.0	2.5	6.0
III	2	Western Harbor	- brackish water (from NubariaCanal) - waste water (from 16 tanning factories)	33.0 0.5	7.5	10.0
IV	6	Kayet Bey pumping station	- sewage and waste waters (the main metropolitan outfall)	112.0	4.5	11.0
V	3	Mex Bay	- agricultural - chlor-alkali waste water	2200.0 12.8	19.4	9.8
VI	3	Agami (The control zone)	- minute local emissions		12.5	15.0

been and is still being discussed on a national and multinational scale. The Alexandria coastal area, when considered in general, is one of the major pollution-stressed areas of the Mediterranean region. The problem has been attributed to industrial versus agricultural derived pollutants on one hand and sewage derived pollutants on the other. The domination of either depends mainly on the dispersal location.

The study area (Figure V.1) lies off Alexandria between 31° 08' to 31° 26'N and 29° 47 to 30° 04'E, extending for about 38 km from Agami to Abo-Qir headland. According to the type of regional impact, the coastal waters can be divided into six main zones (Table V.1). Zone I (beaches) receives a significant amount of untreated sewage; zones II (Eastern Harbor) and III (Western Harbor), the main trading and fishing harbors of the city, receive waste water and untreated sewage; zone IV (Kayet Bey) receives domestic sewage from the main metropolitan pumping station; zone V (Mex Bay) receives various industrial waters from several outfalls such as agricultural and chlor-alkali plants; and zone VI (Agami) is regarded as the reference area receiving little local discharge. The area, mean depth and flow rates are given in Table V.1.

EXPERIMENTAL METHODS

Sampling

Surficial bottom sediments were collected from six main zones with a grab sampler (Figure V.1). Samples were removed from the middle of the grab, wrapped in aluminum foil and stored frozen at -20°C. Before extraction, the samples were freeze-dried and sieved to pass through 250 μm. End member samples, e.g., untreated sewage and waste waters (representing 11 outfalls in the Alexandria region), four tarry surficial sediment samples believed to contain solely petroleum residues, and three offshore sediment samples (~300 m deep) from the Egyptian continental shelf believed to contain both marine and terrestrial input sources, were collected. These samples were also kept frozen at -20°C to prevent organic matter alteration.

Grain size analyses of the surficial sediments were determined according to Folk (1974), utilizing sieving to separate sand from clay and silt fractions. The scale for grain sizes ranges from 1ϕ to 4ϕ for sand, 4ϕ to 8ϕ for silt and above 8ϕ for clay.

Extraction and fractionation

To minimize contamination, all glassware was cleaned with soap and water, rinsed with distilled water, heated in an oven at 550°C for 8 hr to combust any traces of surficial organic matter, and finally rinsed twice with ultra-pure methanol and methylene chloride. The KOH used for saponification was extracted 3 times with *n*-hexane and once with methylene chloride in a separatory funnel to remove organic interferences.

An extraction protocol was designed for the qualitative and quantitative analyses of the aliphatic hydrocarbons with the biomarkers. Briefly, surficial bottom sediment samples (10 g) were extracted with methylene chloride-methanol (2:1, 250 ml) in a Soxhlet apparatus for 48 hr. The untreated sewage and waste water samples were liquid/liquid extracted in separatory funnels using *n*-hexane followed by chloroform. Portions of the tarry surficial sediment samples were sonicated with *n*-hexane followed by chloroform. These extracts are a measure of the amount of extractable organic matter (EOM) in the samples. Extracts were vacuum evaporated to near dryness, desulfurized with activated copper, and hydrolyzed overnight with 35 ml of 6% KOH-methanol. Neutral components were recovered with *n*-hexane (4 x 30 ml) and fractionated by column chromatography (column 50 x 1.2 cm, with 8 g each of alumina on top and silica below, both deactivated with 5% water). The following fractions were eluted and collected: (I) 45 ml of *n*-hexane (aliphatic hydrocarbons), followed by 5 additional fractions representing monoaromatic and polycyclic aromatic hydrocarbons, ketones, aldehydes, esters and alcohols. Here, we describe the results for fraction 1 representing the aliphatic hydrocarbons.

Organic carbon analysis

Organic carbon analyses were carried out for all sediment samples using a Carlo Erba NA-1500 CNS analyzer. Samples were combusted at 1000°C in an oxygen-rich medium to CO_2. The CO_2 gas was separated chromatographically, detected using a thermal conductivity detector, and the resulting signals were digitized, integrated, and mathematically processed along with results based on standards. Concentrations of the

hydrocarbon fractions and their molecular biomarkers were calculated relative to the sedimentary organic carbon content (TOC).

Instrumental analyses

High resolution gas chromatography (GC) was conducted on a Hewlett Packard (HP) *5890*A gas chromatograph, equipped with a split/splitless capillary injection system and a flame ionization detector (FID). The samples were analyzed in the splitless mode using a fused silica capillary column (30 m x 0.25 mm i.d, DB-5, 0.25 μm film thickness, J & W Scientific) and helium as carrier gas. The analog signal was monitored and/or integrated with an HP *3393*A integrator. The GC conditions were: FID 300°C, injector 300°C, oven temperature initially 65°C, programmed to 200°C at 4°C/min, isothermal at 290°C (60 min). The gas chromatography-mass spectrometry (GC-MS) analyses were performed with a Finnigan *9610* GC (identical column with initial temperature 50°C, isothermal 6 min, programmed at 4°C/min to 310°C, isothermal 60 min) interfaced directly to a Finnigan *4021* quadrupole mass spectrometer (electron impact, emission current 0.45 mA, electron energy 70eV, scanned from 50 to 650 daltons). Data were acquired and processed with a Finnigan-INCOS Model *2300* data system.

Compound identification and quantification

Compound identification was based on comparison with the GC retention times and mass fragmentation patterns of standard reference materials and with the help of the National Institute of Standards and Technology (NIST) standard library (incorporated in the INCOS data system). Compound Identification was tabulated according to Rogge *et al.* (1993a) as follows: (a) *positive,* when the sample mass spectrum, authentic standard compound mass spectrum, and their retention times agreed well; (b) *probable,* same as above except no standards were available, but the sample mass spectrum agreed very well with the NIST standard library accessed by the INCOS data system; (c) *possible,* same as above except that the sample spectrum contained information from other compounds but with minor overlap; (d) *tentative,* when spectrum contained additional information

from possibly several compounds with overlap. The following standard mixtures were injected on both GC and GC-MS: (1) a series of *n*-alkanes ranging from C_{10} to C_{36}, and (2) regular isoprenoids as pristane and phytane. Quantification was based on the application of perdeuterated compounds, e.g., *n*-$C_{32}D_{66}$, as internal standards. In order to correct for detector response, sets of relative response factors were determined for the aliphatic fraction (C_{10} to C_{36}) from multiple injections.

Statistical analyses

Data for the aliphatic biomarkers was examined statistically in order to determine any significant environmental variations. All statistical analyses were performed using the SPSS/PC$^+$ statistical package (Norusis, 1986) as well as the statistical package provided on the SUN system of College of Oceanic and Atmospheric Sciences at OSU. These analysis include a measure of dispersion (standard deviation), a correlation analysis between variables, Q-mode cluster and factor analyses, and linear programming techniques. The objectives of the statistical analyses were to define the organic geochemical characteristics of the surficial sediments in the Alexandria region, examine the geochemical relationships between samples, and assess the sources and occurrence of the aliphatic biomarkers.

The principles of some of the statistical parameters, used for testing the organic geochemical data in the present study, are as follows:

a) Correlation analysis: In order to examine the interrelation between the analyzed samples, a linear correlation analysis is performed. Pearson correlation coefficients are calculated for every pair of variables in the data set. The significance level of compound associations are determined for correlation analysis at 99% and 99.9%, for both positively and negatively correlated variables, respectively.

b) Q-mode cluster analysis: The main purpose of using cluster analysis was to reduce the mass of data, without significant loss of information, to a tractable size, but in a way that emission patterns can be easily discerned. Cluster analysis is a numerical

technique for defining groups of related samples based on high similarity coefficients, computed between each pair of samples, which are then clustered. Thus, in most clustering procedures the nucleus of clusters (centroid) is formed by joining the samples with highest similarity and gradually admitting more samples as the similarity coefficient is lowered (Devillers *et al.*, 1988, Kaiser and Esterby, 1991).

During the steps of agglomeration in cluster analysis, all cases are first considered separate clusters; there are as many clusters as cases. At the second step, two of the cases are combined into a single cluster. At the third step, either a third case is added to the cluster already containing two cases, or two additional cases are merged into a new cluster. At every step, either individual cases are added to clusters or already existing clusters are combined. Once a cluster is formed, it cannot be split; it can only be combined with other clusters. Thus, clustering methods do not allow cases to separate from clusters to which they have been allocated (Norusis, 1986).

In the present study, the method of single linkage and complete linkage agglomerative (Q-mode) cluster analysis are used. In the single linkage method, the first two cases combined are those with the smallest distance (vertical lines) or greatest similarity between them (the distances are rescaled to fall in the range of 1 to 25). The distance between the new cluster and individual cases is then computed as the minimum distance between an individual case and a case in the cluster. At every step, the distances between two clusters is taken to be the distance between their two closest points. In the complete linkage method, the distance between two clusters is calculated as the distance between their two furthest points.

c) *Extended q-mode factor analysis and linear programming:* Factor analysis has recently been used in Environmental Chemistry (e.g. Thurston and Spengler, 1985; Massart *et al.*, 1988; Irwin and Meyer, 1989; Grant, 1990; Malinowski, 1991; Rapp, 1991; Tysklind *et al.*, 1992), but few studies have been reported for the Mediterranean region (El-Sayed *et al.*, 1988; Grimalt *et al.*, 1990, Aboul-Kassim *et al.*, 1992b, Aboul-Kassim and Simoneit, 1994a,b,c). Q-mode factor analysis is based on grouping a multivariate data

set based on the data structure defined by the similarity between samples. The measure of similarity used is the cosine theta matrix, i.e. the matrix whose elements are the cosine of the angles between all sample pairs (Imbrie and Purdy, 1962).

The goal of Q-mode factor analysis is analogous to geochemical partitioning models which seek to determine the absolute abundance of the dominant components in a sediment sample (Imbrie and Van Andel, 1964). It provides a description of the multivariate data set in terms of a few end members (factors, usually orthogonal), which account for the variance within the data set. The importance of each variable in each end member is represented by a factor score. The set of scores for all factors makes up the factor score matrix (Klovan and Imbrie, 1971). The relative importance of each end member factor in each sample is its factor loading value. The complete set of factor loadings describing each sample in terms of its end members is the factor loading matrix.

Factor analysis has not often been used to determine the actual composition of end member sources in geologic mixtures (Leinen and Pisias, 1984), because transformations of the original data variables during the analysis result in negative factor scores for some variables and negative concentrations of some variables in the end member. Thus, here we use the rotation technique proposed by Leinen and Pisias (1984) to determine the number of end members in the data set with an extended Q-mode factor analysis (Miesch, 1976) to identify the principal sources of variations in the data set (i.e., end members within the data set). This rotation scheme does not require the hypothesis of having sampled pure end members (Full *et al.*, 1981), assuming that the best known statistical parameter within a data set is the vector of mean composition, so that the true end members lie between the mean concentration and the varimax axes which contain negative values.

The end member compositions were found by rotating each varimax axis, one at a time, toward the mean vector until the composition of the rotated axis is reasonable (i.e., all variable concentrations are greater than or equal to zero). The criteria for choosing the number of end members used to model the data were: (1) at least 90% of the variance in the data set must be explained by the sums of squares of the end members, and (2) all end member factors that explained less than 2% of the total variance

were rejected. After identifying the end member composition using this objective approach, a linear programming technique (LPT) was used to determine the abundance of each end member in each sample (Dymond, 1981). This LPT utilized the inverse technique (Dymond, 1981) to calculate small corrections to the end member compositions and their abundances to better fit the observed multivariate data set. However, in order to determine the composition of end members in our data set, the extended Q-mode factor analysis was combined with the Leinen and Pisias (1984) new vector rotation scheme to obtain reasonable compositions for the end members as well as comparisons with some selected pure end members characteristic for the Alexandria environment.

RESULTS AND DISCUSSION

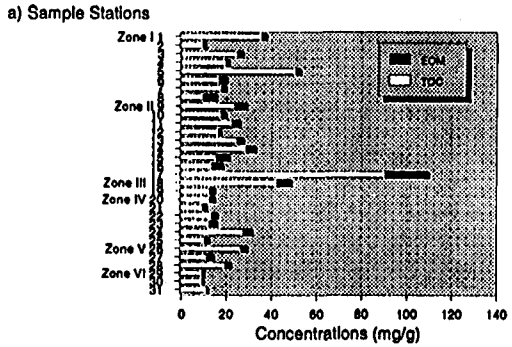
The sampling locations, sample grain sizes, total solvent extractable organic matter (EOM), total organic carbon (%TOC) contents, different *n*-alkane compositions as well as their biomarkers relative to both dry weight and TOC contents are given in Table V.2, while the organic geochemical ratios and parameters are presented in Table V.3. The average for each hydrocarbon in every zone of the Alexandria study area is given in Table V.4.

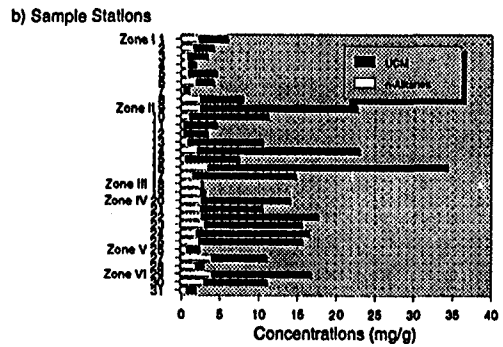
Sediment grain size and total yields

The sediment grain size technique indicates that the inclusive graphic mean (M_z) ranged between 1.32 ϕ and 4.32 ϕ with an average of $3.05\pm0.77\phi$ (Table V.2). The maximum values, i.e. the finest sediment grain sizes, were observed for stations 17, 26, 27, 30, 31 (sandy silt), while the minimum value was recorded for station 2 (coarse sand). Except for a few locations, the distribution of M_z for surficial sediments was homogeneous, which may be attributed to the general eastward coastal current in the Alexandria region, resulting in a homogeneous distribution of the bottom sediments.

The average EOM of the surficial sediments was high with a maximum of 19.1 mg/g dry sediment and a minimum of 0.4 mg/g (Figure V.2a, Table V.2), with an overall average characteristic for the Alexandria coastal area of 3.5 ± 3.3 mg/g. The high standard deviation most likely reflects variations in the sediment grain size and the quantity and

Figure V.2: Yields of: a) EOM and TOC (relative to dry sediment weight), b) total *n*-alkanes and UCM, and c) terrestrial wax *n*-alkanes, all relative to TOC in the study area.


a) Sample Stations
Zone I
Zone II
Zone III
Zone IV
Zone V
Zone VI
ECM
TPC
0
20
40
60
80
100
120
140
Concentrations (mg/g)


b) Sample Stations
Zone I
Zone II
Zone III
Zone IV
Zone V
Zone VI
LCM
n-Alkane
0
5
10
15
20
25
30
35
40
Concentrations (mg/g)

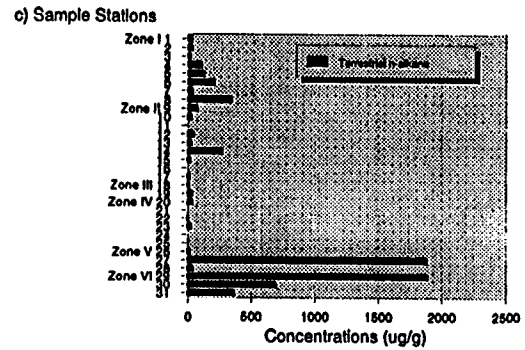

c) Sample Stations
Zone I
Zone II
Zone III
Zone IV
Zone V
Zone VI
Terrestrial n-alkane
0
500
1000
1500
2000
2500
Concentrations (ug/g)

Table V.2: Geochemical composition of the aliphatic hydrocarbons from the bottom sediments of the Alexandria coast*.

Zone Number	Sample Station	Grain size analysis: Mean size (ϕ)	Grain size analysis: Sediment type	TOC (%)	EOM mg/g	EOM/OC (%)	Σ Total n-alkanes: µg/g dry weight	Σ Total n-alkanes: mg/g TOC	Σ Total terrestrial n-alkanes[a] µg/g TOC	C_{range}	C_{max}	UCM[b]: µg/g dry weight	UCM[b]: mg/g TOC	Σ Total molecular biomarkers (relative to TOC): Isoprenoids[c] µg/g	Tricyclanes[d] ng/g	Tetracyclanes[e] ng/g	Pentacyclic Triterpanes[f] ng/g	Diasteranes[g] ng/g	Steranes[h] ng/g
I	1	2.81	sand	3.6	2.4	6.7	82.5	2.3	34.2	16-37	21	132.2	3.7	103.6	-	-	4066.7	33.3	983.2
	2	1.32-	sand	1.0	1.4	13.6	10.0	1.6	36.9	16-34	21,23	26.1	2.6	37.9	61.6	27.9-	3148.2	39.3	826.0
	3	1.74	sand	2.5	2.6	10.6	20.6	0.8	20.7	17-36	21	65.9	2.6	18.7-	122.4	53.7	2229.7	35.2	688.7
	4	1.92	sand	2.0	1.5	7.4	17.2	0.9	111.3	17-35	23	18.9	1.0	23.0	178.7	64.0	4257.6	31.4	648.7
	5	3.82	sand	5.1	2.3	4.6	45.0	0.9	133.1	16-35	21	184.5	3.7	61.0	234.9	74.3	3027.9	47.6	828.7
	6	2.10	sand	1.7	3.7	21.6	31.8	1.9	212.9	16-35	21,23	38.2	2.3	106.4	152.6	135.1	5609.4	17.5	950.9
	7	2.91	sand	1.8	2.3	12.5	7.8	0.4-	39.7	16-35	21,23	12.5	0.6	23.5	309.9	144.0	5462.6	75.2	1678.0
	8	3.11	sand	1.0-	6.2	38.5+	39.5	2.5	350.3	16-33	19,21	86.9	5.5	290.1	467.1	152.8	7313.7	132.8	2805.0+
II	9	3.22	sand	2.4	5.5	23.3	59.1	2.5	81.2	15-37	Ph,31	478.5	20.3	252.4	258.9	284.1	8681.1+	71.1	1710.8
	10	3.71	sand	1.8	2.3	1.3-	19.2	1.1	32.4	17-34	31	184.7	10.2	125.4	198.5	117.8	3819.7	31.5	762.4
	11	3.12	sand	2.3	3.5	15.4	8.0	0.4-	-	17-34	Ph,31	98.5	4.3	138.0	250.1	65.5	3389.0	22.9	654.2
	12	3.23	sand	1.7	1.0	5.8	7.1-	0.4-	53.1	17-35	31	53.6	3.1	133.0	189.8	75.5	4861.4	23.3	663.9
	13	3.71	sand	2.5	3.1	12.7	21.2	0.9	34.6	15-35	31	237.3	9.7	41.6	268.7	102.3	3405.2	25.8	624.4
	14	3.84	sand	2.9	4.5	15.7	60.8	2.1	280.4	16-34	Ph,21	602.1	21.0	249.7	314.8	238.7	7292.1	47.3	944.8
	15	3.33	sand	1.6	5.9	36.2	9.6	0.6	24.4	16-34	Ph,31	113.4	7.0	74.2	178.8	88.2	2083.5	17.2-	416.3
	16	3.31	sand	1.4	5.2	3.7	49.1	3.5	-	16-35	Ph,31	437.3	31.0+	494.2	154.7	297.8+	4681.1	76.6	1853.9
	17	4.10	sandy silt	9.1+	19.1+	21.0	142.8+	1.6	20.3	17-35	Ph,31	1213.5+	13.3	176.8	998.1+	161.8	5539.9	45.6	1103.6
III	18	2.91	sand	4.3	6.4	5.0	41.5	2.7	14.6	14-34	17	8.3-	0.2-	335.5	576.4	229.8	5110.5	61.1	1477.8
	19	2.19	sand	1.3	2.6	10.3	12.3	2.6	41.2	15-33	19	8.6	0.6	170.6	489.1	176.2	4106.2	50.7	1213.1
IV	20	2.63	sand	1.3	2.6	20.2	34.4	2.7	44.1	15-38	20	148.0	11.5	35.6	401.8	122.5	3101.9	40.2	948.2
	21	2.33	sand	1.0	2.0	20.4	24.9	2.6	-	15-37	21	77.2	8.0	21.3	299.0	83.3	2307.8	38.7	659.2
	22	2.94	sand	1.4	2.9	20.3	38.3	2.7	3.6-	15-37	21	218.1	15.1	37.8	448.5	130.1	3461.7	45.2	1080.1
	23	2.84	sand	1.3	3.6	28.0	39.6	3.1	31.2	16-37	23	102.2	12.6	31.3	401.8	117.7	3101.3	41.1	1120.3
	24	1.92	sand	2.8	4.2	15.3	54.7	2.1	-	16-38	21	399.3	14.5	58.2	859.7	180.3	5635.5	31.3	1195.5
	25	3.13	sand	1.1	2.1	18.6	27.3	2.4	-	15-38	21	152.9	13.4	45.6	355.1	155.2	3740.8	35.7	1180.3
V	26	4.12	sandy silt	2.7	2.9	9.9	22.4	0.8	23.0	15-34	21	47.0	1.7	101.5	57.7-	31.0	1125.5-	21.5	378.8-
	27	4.32+	sandy silt	1.2	3.1	25.4	50.1	4.1+	1889.3	19-36	31	85.3	7.0	368.9	478.5	162.8	3455.1	101.3	1354.1
	28	3.22	sand	2.0	2.7	13.4	39.2	2.0	49.3	14-28	17	19.6	1.0	327.4	268.7	101.0	5384.6	257.7+	2735.3
VI	29	2.70	sand	1.0-	1.0	9.9	43.1	4.1+	1896.2+	18-35	Ph,31	133.6	12.8	406.7	179.3	97.3	1394.3	113.7	813.6
	30	3.96	sandy silt	1.0-	0.7	6.7	31.2	3.1	702.0	16-34	23,31	81.1	8.1	1414.1+	83.6	110.9	1176.5	90.3	953.2
	31	4.10	sandy silt	1.2	0.4-	3.3	9.9	0.8	377.9	19-35	31	14.9	1.2	219.5	95.7	61.3	1291.4	81.7	756.8
Average		3.05		2.2	3.5	14.8	35.5	1.9	251.5			176.8	8.1	191.1	311.2	128.1	3976.2	57.5	1096.1
SD±		0.77		1.6	3.3	9.3	23.2	1.1	498.4			239.1	7.5	262.1	217.4	66.9	1849.8	46.4	573.2

* + = maximum, - = minimum.

[a]Terrestrial wax n-alkanes: calculated according to Simoneit et al. (1990) as: Wax n-C_n= [C_n] - 0.5 [$C_{(n+1)}$ + $C_{(n-1)}$].

[b]UCM: unresolved complex mixture of aliphatic hydrocarbons.

[c]Σ Isoprenoids = norpristane (when present) + pristane + phytane.

[d]Σ Tricyclanes = Σ [C_{19}+C_{20}+C_{21}+C_{23}+C_{24}+C_{25}+C_{26}(S+R)+C_{28}+C_{29}].

[e]Σ Tetracyclanes = Σ [C_{24}+C_{28}+C_{29}].

[f]Σ Pentacyclic triterpanes = Σ (C_{27}-C_{35})-αβ(22S+R)-hopanes, and gammacerane when present; no C_{28}-hopane, see Table 4 for complete compound class names.

[g]Σ Diasteranes = Σ C_{27}-αβ diasteranes (S+R), see Table 4 for complete compound class names.

[h]Σ Steranes = Σ [C_{27}-C_{29}][(ααα+αββ),(20S+R)] steranes, see Table 4 for complete compound class names.

Table V.3: Organic geochemical indices for source, maturity and biodegradation of biomarkers in the sediments of the Alexandria coast*.

Zone Location	Sample Station	Organic Geochemical Parameters** (I)	(II)	(III)	(IV)	(V)		(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)
		U/R	Pr/Ph	Pr/C_{17}	Ph/C_{18}	CPI_a	CPI_b	$TI/C_{30}\alpha\beta$	T_s/T_m	$\frac{C_{23}Tri}{C_{30}\alpha\beta}$	Triplet Ratio	$\frac{C_{29}\alpha\beta}{C_{30}\alpha\beta}$	$C_{31}\alpha\beta\left[\frac{S}{S+R}\right]$	$\frac{\alpha\beta DC_{27}}{\alpha\alpha\alpha C_{29}}$	$\alpha\alpha\alpha C_{29}\left[\frac{S}{S+R}\right]$
I	1	1.6	0.54	0.65	0.70	1.05	0.98	1.43	0.61	-	-	0.92	0.53	0.19	0.57
	2	2.6	0.34	0.56	0.63	1.17	1.06	0.55	0.67	0.04	-	0.87	0.52⁻	0.27	0.55
	3	3.2	-	-	0.64	0.94⁻	0.96	1.01	0.72	0.07	0.64⁻	0.82	0.53	0.35	0.52
	4	1.1	0.31	0.65	0.64	1.09	1.27	1.01	0.71	0.10	0.70	0.86	0.57	0.35	0.51
	5	4.1	0.62	0.57	0.58	1.21	1.28	9.47	0.69	0.12	0.75	0.90	0.61	0.34	0.50
	6	1.2	0.63	0.65	0.56	1.15	1.21	3.34	0.63	0.04	0.65	0.88	0.55	0.12⁻	0.39⁻
	7	1.6	0.59	0.67	0.63	1.08	1.16	2.93	0.63	0.06	0.68	0.91	0.57	0.16	0.45
	8	2.2	0.63	0.71	0.67	1.43	1.28	3.38	0.61⁻	0.08	0.70	0.94	0.59	0.30	0.51
II	9	8.1	0.54	3.03	5.42	1.35	1.33	1.10	0.81	0.13	1.61	0.81	0.63	0.31	0.61
	10	9.6	0.36	2.32	3.20	1.20	1.22	0.71	0.85	0.07	1.39	0.78	0.56	0.41	0.60
	11	12.3⁺	0.19⁻	3.64	11.54⁺	0.96	1.20	-	0.68	0.11	1.54	0.80	0.60	0.35	0.59
	12	7.5	0.41	2.79	2.18	1.14	1.09	0.82	0.73	0.07	2.27⁺	0.86	0.71⁺	0.43	0.67⁺
	13	1.2	0.55	2.13	3.35	1.17	1.07	1.31	0.78	0.06	1.33	0.78	0.67	0.22	0.59
	14	9.9	0.37	2.21	2.18	0.97	1.02	5.69	0.78	0.10	2.00	0.71	0.59	0.39	0.62
	15	11.8	0.35	3.00	4.78	1.25	1.37	0.91	0.61	0.08	1.67	0.94	0.59	0.30	0.51
	16	8.9	0.46	3.71	3.10	1.32	1.24	-	0.78	0.11	1.61	0.81	0.70	0.39	0.56
	17	8.5	0.40	3.81⁺	4.72	1.40	1.48	1.39	0.80	0.10	1.64	0.77	0.67	0.36	0.61
III	18	0.2⁻	0.41	0.68	0.48⁻	1.02	0.96	0.63	0.79	0.11	1.63	0.79	0.69	0.38	0.59
	19	0.7	0.68	0.63	0.56	1.23	1.05	0.61⁻	0.83	0.07	1.43	0.77	0.64	0.42	0.58
IV	20	4.3	0.90	0.50	0.55	1.52	1.39	0.83	0.87⁺	0.01⁻	1.23	0.79	0.58	0.45	0.56
	21	3.1	0.65	0.70	0.61	1.46	1.32	-	0.67	0.08	-	0.80	0.56	0.36	0.55
	22	5.7	0.71	0.56	0.50	1.50	1.42	0.61⁻	0.70	0.07	1.47	0.82	0.53	0.50⁺	0.52
	23	4.1	0.62	0.91	0.81	1.35	1.25	0.66	0.61	-	-	0.92	0.53	0.21	0.57
	24	7.3	0.38	1.40	0.71	0.94⁻	1.11	-	0.68	0.12	1.32	0.90	0.61	0.34	0.50
	25	5.6	0.70	0.78	0.82	1.10	0.99	-	0.63	0.05	1.35	0.88	0.55	0.14	0.39
V	26	2.1	0.79	0.70	0.74	1.11	1.01	2.87	0.78	-	0.8	1.00⁺	0.52	0.28	0.65
	27	1.7	0.32	-	-	3.79	2.77	30.32	0.61	0.12	0.75	0.93	0.53	0.34	0.51
	28	0.5	0.98⁺	0.20⁻	0.55	1.36	0.95⁻	1.01	0.87⁺	0.20⁺	-	0.79	0.58	0.45	0.56
VI	29	3.1	-	-	1.64	3.81⁺	2.76	67.32⁺	0.66	-	-	0.90	0.67	0.21	0.57
	30	2.6	0.40	1.95	2.42	2.21	1.52	30.81	0.79	0.13	0.91	0.91	0.63	0.34	0.59
	31	1.5	0.29	-	-	3.71	2.93⁺	16.23	0.81	-	0.87	0.71⁻	0.55	0.21	0.57
Average		4.5	0.52	1.49	1.93	1.48	1.34	7.19	0.72	0.09	1.24	0.85	0.59	0.32	0.55
SD±		3.5	0.19	1.16	2.36	0.79	0.52	14.82	0.09	0.04	0.46	0.07	0.06	0.10	0.07

* + = maximum, - = minimum.

** (I) U/R: unresolved complex mixture/resolved n-alkanes (Mazurek and Simoneit, 1983).

(II) Pr/Ph: pristane/phytane.

(III) Pr/C_{17}: pristane/n-C_{17} alkane.

(IV) Ph/C_{18}: phytane/n-C_{18} alkane.

(V) CPI: Carbon preference index.

(VI) $TI/C_{30}\alpha\beta$: Σ terrestrial indices (TI) calculated according to Simoneit et al. (1990)/C_{30}-17α(H),21β(H)-hopane.

(VII) T_s/T_m: 18α(H)-22,29,30-trisnorneohopane (T_s)/17α(H)-22,29,30-trisnorhopane.

(VIII) $C_{23}Tri/C_{30}\alpha\beta$: [$C_{23}$-tricyclic/17α(H),21β(H)-hopane].

(IX) Triplet ratio: [(C_{26}-tricyclic S + C_{26}-tricyclic R)/C_{24}-tetracyclic], calculated according to Kvenvolden *et al.* (1985).

(X) $C_{29}\alpha\beta/C_{30}\alpha\beta$: [17α(H),21β(H)-norhopane/17α(H),21β(H)-hopane].

(XI) $C_{31}\alpha\beta\left[\frac{S}{S+R}\right]$: homohopane index; ratio between the S and R epimer at C-22 for the extended 17α(H),21(H)-C_{31} homohopane.

(XII) $\alpha\beta DC_{27}/\alpha\alpha\alpha C_{29}$: $\alpha\beta C_{27}$-diasterane/$\alpha\alpha\alpha C_{29}$-sterane.

(XIII) $\alpha\alpha\alpha C_{29}\left[\frac{S}{S+R}\right]$: ratio between the S and R epimer at C-20 for $\alpha\alpha\alpha C_{29}$-sterane.

Table V.4: Mean aliphatic hydrocarbon composition relative to TOC for the sediments in the different zones of the Alexandria coast.

Table V.4: Continued.

Compound Class/Name	Formula	M.W.	Average Concentrations[a] Zones I	II	III	IV	V	VI	ID[b]
***n*-ALKANES (mg/g)**									
n-hexadecane	$C_{16}H_{34}$	226	0.01	0.01	bd	bd	0.02	0.02	a
n-heptadecane	$C_{17}H_{36}$	240	0.03	0.03	0.03	0.02	0.05	0.06	a
n-octadecane	$C_{18}H_{38}$	254	0.06	0.07	0.07	0.05	0.11	0.12	a
n-nonadecane	$C_{19}H_{40}$	268	0.08	0.08	0.10	0.07	0.12	0.15	a
n-eicosane	$C_{20}H_{42}$	282	0.11	0.12	0.15	0.10	0.18	0.21	a
n-heneicosane	$C_{21}H_{44}$	296	0.12	0.12	0.18	0.11	0.19	0.23	a
n-docosane	$C_{22}H_{46}$	310	0.13	0.01	0.20	0.13	0.02	0.22	a
n-tricosane	$C_{23}H_{48}$	324	0.12	0.10	0.21	0.14	0.15	0.21	a
n-tetracosane	$C_{24}H_{50}$	338	0.11	0.11	0.02	0.15	0.17	0.21	a
n-pentacosane	$C_{25}H_{52}$	352	0.11	0.10	0.23	0.15	0.15	0.15	a
n-hexacosane	$C_{26}H_{54}$	366	0.09	0.12	0.11	0.14	0.18	0.17	a
n-heptacosane	$C_{27}H_{56}$	380	0.08	0.09	0.22	0.14	0.14	0.19	a
n-octacosane	$C_{28}H_{58}$	394	0.07	0.08	0.18	0.12	0.12	0.14	a
n-nonacosane	$C_{29}H_{60}$	408	0.07	0.08	0.18	0.11	0.12	0.20	a
n-triacontane	$C_{30}H_{62}$	422	0.05	0.04	0.13	0.08	0.06	0.10	a
n-hentriacontane	$C_{31}H_{64}$	436	0.04	0.07	0.12	0.08	0.11	0.08	a
n-dotriacontane	$C_{32}H_{66}$	450	0.03	0.09	0.08	0.05	0.14	0.06	a
n-tritriacontane	$C_{33}H_{68}$	464	0.03	0.05	0.06	0.04	0.06	0.04	a
n-tetratriacontane	$C_{34}H_{70}$	478	0.02	0.03	0.03	0.02	0.05	0.04	a
n-pentatriacontane	$C_{35}H_{72}$	492	0.02	bd	0.03	0.02	0.01	0.04	a
n-hexatriacontane	$C_{36}H_{74}$	506	0.01	bd	0.02	0.02	0.02	0.02	a
n-heptatriacontane	$C_{37}H_{76}$	520	0.02	bd	0.02	0.01	bd	0.02	a
n-octatriacontane	$C_{38}H_{78}$	534	bd	bd	0.02	0.01	bd	bd	a
Isoprenoids (μg/g)									
2,6,10,14-tetramethylpentadecane (pristane)	$C_{19}H_{40}$	254	21.8	53.1	63.3	11.1	75.4	192.9	a
2,6,10,14-tetramethylhexadecane (phytane)	$C_{20}H_{42}$	268	61.2	144.3	189.8	26.1	204.9	524.1	a

Table V.4: Continued.

Compound Class/Name	Formula	M.W.	Average Concentrations[a] Zones I	II	III	IV	V	VI	ID[b]
Tricyclic Terpanes (ng/g)									
C_{19}-tricyclic	$C_{19}H_{34}$	262	4.8	7.3	5.6	4.9	2.9	2.6	b
C_{20}-tricyclic	$C_{20}H_{36}$	276	14.5	21.0	27.8	24.3	14.1	7.9	b
C_{21}-tricyclic	$C_{21}H_{38}$	290	4.8	7.0	13.1	9.7	15.6	2.6	b
C_{23}-tricyclic	$C_{23}H_{42}$	318	53.3	77.1	111.0	97.0	56.5	29.2	b
C_{24}-tricyclic	$C_{24}H_{44}$	332	36.4	52.7	138.8	118.5	59.0	19.9	b
C_{25}-tricyclic	$C_{25}H_{46}$	346	31.5	44.0	105.5	91.3	53.1	17.3	b
C_{26}-tricyclic (S)	$C_{26}H_{48}$	360	14.5	20.2	27.8	25.8	15.0	7.9	b
C_{26}-tricyclic (R)	$C_{26}H_{48}$	360	14.6	21.3	31.3	28.8	16.8	8.0	b
C_{28}-tricyclic	$C_{28}H_{50}$	388	17.0	24.4	33.3	30.1	17.5	9.3	c
C_{29}-tricyclic	$C_{29}H_{52}$	402	26.6	37.3	38.9	33.5	19.5	14.6	c
Tetracyclic terpanes (ng/g)									
C_{24}-tetracyclic	$C_{24}H_{42}$	330	54.4	94.9	101.5	67.4	50.4	53.6	b
C_{28}-tetracyclic	$C_{28}H_{50}$	386	18.4	31.7	57.8	33.5	25.0	17.9	b
C_{29}-tetracyclic	$C_{29}H_{52}$	400	18.2	32.4	43.5	30.6	22.9	18.3	b
Pentacyclic triterpanes (ng/g)									
18α(H)-22,29,30-trisnorneohopane (Ts)	$C_{27}H_{46}$	370	138.5	152.8	130.1	102.3	95.5	40.6	b
17α(H)-22,29,30-trisnorhopane (Tm)	$C_{27}H_{46}$	370	188.9	208.6	192.0	149.1	239.2	155.4	b
17α(H),21β(H)-29-norhopane	$C_{29}H_{50}$	398	847.0	938.7	922.9	715.6	468.0	248.4	b
17α(H),21β(H)-hopane	$C_{30}H_{52}$	412	1064.3	1179.8	1034.4	799.2	746.1	212.0	b
17α(H),21β(H)-homohopane (22S)	$C_{31}H_{54}$	426	481.8	532.7	489.3	381.9	456.5	141.1	b
17α(H),21β(H)-homohopane (22R)	$C_{31}H_{54}$	426	198.4	220.5	315.9	243.3	327.1	58.2	b
17α(H),21β(H)-bishomohopane (22S)	$C_{32}H_{56}$	440	343.2	380.9	346.9	268.2	150.4	70.7	b
17α(H),21β(H)-bishomohopane (22R)	$C_{32}H_{56}$	440	173.2	190.5	303.5	234.7	219.1	50.8	b
17α(H),21β(H)-trishomohopane (22S)	$C_{33}H_{58}$	454	277.1	305.3	216.8	169.2	158.0	81.3	b
17α(H),21β(H)-trishomohopane (22R)	$C_{33}H_{58}$	454	119.7	132.9	117.7	88.8	182.9	65.1	b
17α(H),21β(H)-tetrakishomohopane (22S)	$C_{34}H_{60}$	468	192.1	212.8	192.0	146.8	137.0	56.3	b
17α(H),21β(H)-tetrakishomohopane (22R)	$C_{34}H_{60}$	468	103.9	116.5	92.9	73.6	68.7	60.5	b

Table V.4: Continued.

Compound Class/Name	Formula	M.W.	Average Concentrations[a]						ID[b]
			Zones						
			I	II	III	IV	V	VI	
17α(H),21β(H)-pentakishomohopane (22S)	$C_{35}H_{62}$	482	201.5	221.9	154.9	120.5	112.5	59.1	b
17α(H),21β(H)-pentakishomohopane (22R)	$C_{35}H_{62}$	482	59.8	67.7	86.7	65.0	60.7	17.5	b
Diasteranes (ng/g)									
13α(H),17β(H)-diacholestane (20S)	$C_{27}H_{48}$	372	25.8	16.1	21.0	15.3	50.1	47.7	b,d
13α(H),17β(H)-diacholestane (20R)	$C_{27}H_{48}$	372	27.7	24.1	34.9	23.4	76.7	51.2	b,d
Steranes (ng/g)									
5α(H),14α(H),17α(H)-cholestane (20S)	$C_{27}H_{48}$	372	55.8	46.1	43.6	31.1	70.7	25.4	b
5α(H),14β(H),17β(H)-cholestane (20R)	$C_{27}H_{48}$	372	133.1	106.1	112.1	85.1	162.7	69.5	b
5α(H),14β(H),17β(H)-cholestane (20S)	$C_{27}H_{48}$	372	81.5	66.6	81.0	61.2	102.2	50.0	b
5α(H),14α(H),17α(H)-cholestane (20R)	$C_{27}H_{48}$	372	55.9	43.3	43.6	32.5	66.5	26.5	b
5α(H),14α(H),17α(H)-ergostane (20S)	$C_{28}H_{50}$	386	55.8	44.0	68.5	53.5	67.5	43.7	b
5α(H),14β(H),17β(H)-ergostane (20R)	$C_{28}H_{50}$	386	128.8	103.3	186.9	144.4	158.1	117.9	b
5α(H),14β(H),17β(H)-ergostane (20S)	$C_{28}H_{50}$	386	133.1	108.1	168.2	130.0	165.7	106.1	b
5α(H),14α(H),17α(H)-ergostane (20R)	$C_{28}H_{50}$	386	47.2	38.7	56.1	42.1	59.4	34.4	b
5α(H),14α(H),17α(H)-sitostane (20S)	$C_{29}H_{52}$	400	107.3	85.5	124.6	97.5	131.2	79.6	b
5α(H),14β(H),17β(H)-sitostane (20R)	$C_{29}H_{52}$	400	197.5	160.5	162.0	122.9	246.3	100.3	b
5α(H),14β(H),17β(H)-sitostane (20S)	$C_{29}H_{52}$	400	158.8	128.7	174.4	132.9	196.4	108.5	b
5α(H),14α(H),17α(H)-sitostane (20R)	$C_{29}H_{52}$	400	21.5	15.7	124.6	97.5	24.1	79.6	b,d

[a]A: concentration relative to organic carbon, bd: below detection limit.
[b]ID=compound identification, for more details see text.

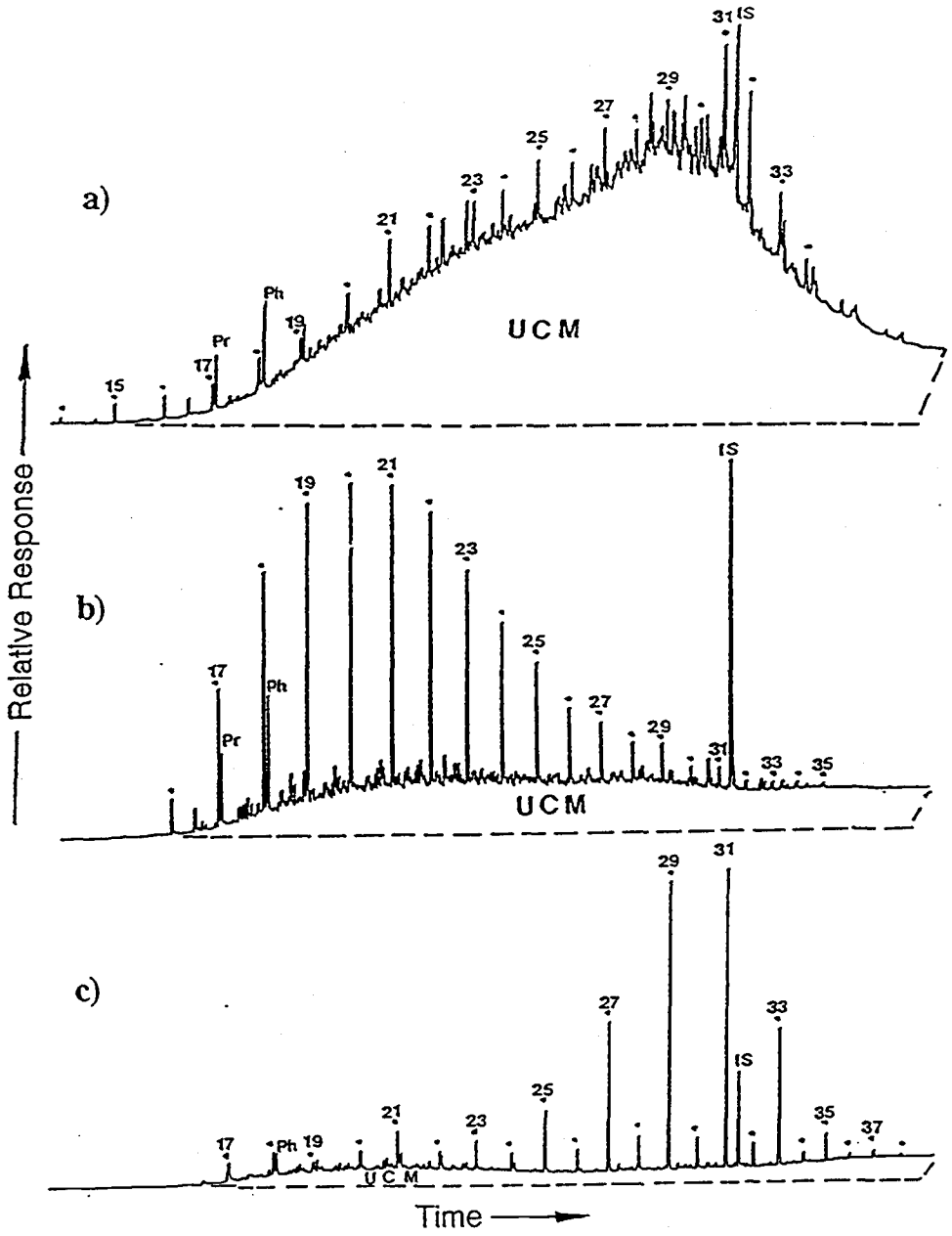
quality of the different organic matter sources. The EOM relative to TOC was a maximum of 38.5% for station 8, a low of 1.3% for station 10, and averaged 14.8%±9.3% (Table V.2). Significant direct correlations between TOC (mean 2.2%±1.6%) and EOM (mean 3.5±3.3 mg/g) with the M_z of the sediments (in ϕ) were found, indicating that organic matter increases with the decrease in sediment grain size.

Normal alkanes

Normal alkanes were present in all samples and ranged in carbon chain length from C_{15} - C_{38} (Table V.2). The *n*-alkane concentrations in the study area vary between 7.1-142.8 µg/g dry weight and 0.4-4.1 mg/g TOC, with overall averages of 35.5±23.2µg/g dry weight and 1.9±1.1 mg/g TOC, respectively (Figure V.2b, Table V.2). The positive correlation between bottom sediment grain sizes and total *n*-alkanes indicates that the *n*-alkane concentrations increase with decreasing grain sizes. Figure V.3 shows examples of GC traces of aliphatic hydrocarbon distributions representing the various zones in the Alexandria region, indicating that the hydrocarbon compositions have different contributions from both petrochemical and biogenic/terrestrial sources.

The identification of the homologous *n*-alkanes in the hydrocarbon fractions allowed the determination of both carbon preference index (CPI) and C_{max} for each sample set, which give supportive evidence for the relative incorporation of the different aliphatic hydrocarbon sources. The CPI, a measure of biologically synthesized *n*-alkanes (Simoneit, 1978; Simoneit *et al.*, 1991), indicates the relative contributions of *n*-alkanes from natural (biogenic/terrestrial; CPI>1) compared to anthropogenic (petroleum pollution; CPI≤1) sources. In the surficial bottom sediments from the Alexandria coast, two CPIs (CPI_a & CPI_b) were calculated (Table V.3). The CPI_a calculated according to Bray and Evans (1961), uses the same odd carbon number *n*-alkane concentrations in both ratios and the even carbon number concentrations in the denominator are shifted in one ratio versus the next:

Figure V.3: Examples of GC traces of the total aliphatic hydrocarbons (*n*-alkanes = dots over peaks, IS = internal standard) for surficial sediments from the Alexandria coast representing a) sewage, b) petroleum and c) terrestrial input sources.


a)
b)
c)
Relative Response
Time
UCM
UCM
UCM
Pr
Ph
IS
15
17
19
21
23
25
27
29
31
33
35
37

$$CPI_a = \frac{1}{2}\left(\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}}\right)$$

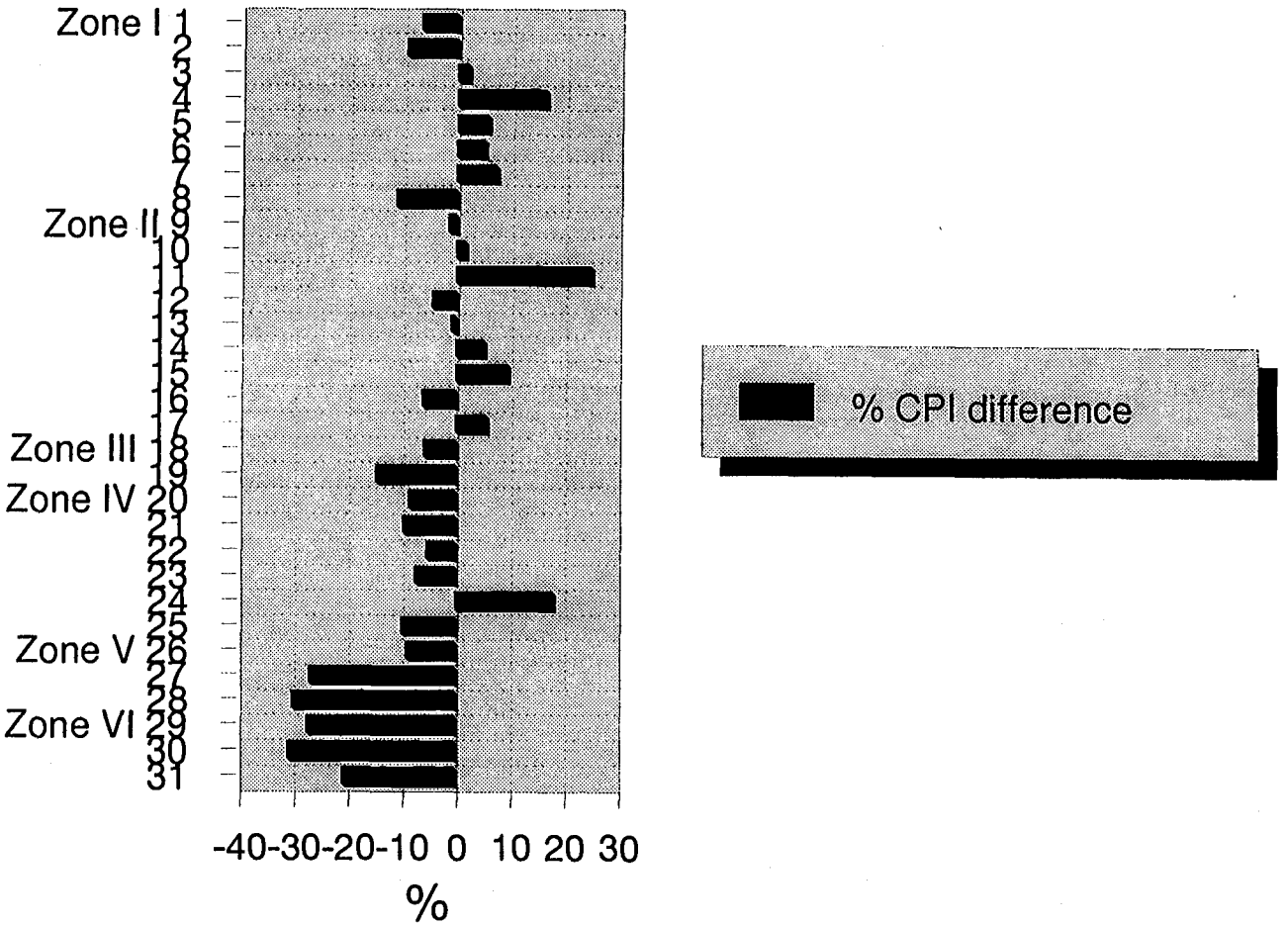
The CPI_a values characteristic for the bottom sediments of the Alexandria coast ranged between 0.94 and 3.81, with an average of 1.48±0.79 (Table V.3). The other formula proposed by Marzie *et al.* (1993) uses the odd and even carbon number concentrations in both the denominator and numerator, respectively:

$$CPI_b = \frac{\left(\sum_{i=n}^{m} C_{2i+1}\right) + \left(\sum_{i=n+1}^{m+1} C_{2i+1}\right)}{2\left(\sum_{i=n+1}^{m+1} C_{2i}\right)}$$

where n= starting *n*-alkane # divided by 2, m= ending *n*-alkane # divided by 2, i= index. The CPI_b values varied between 0.95 and 2.93, with an average of 1.34±0.52 (Table V.3). In general, the two CPI values are directly correlated with each other ($r=0.9704$, $p \leq 0.001$; $CPI_a = 1.4992\ CPI_b - 0.5307$, $n=31$), indicating the presence of severe petrochemical pollution as well as terrestrial/biogenic sources. In addition, the average CPI_a value is higher than that of CPI_b by 10.4%. This overestimation was reported by Marzie *et al.* (1993) who calculated a CPI of 1.22 for a recent oil sample using the CPI_a formula, which suggests a significant carbon number predominance. However, GC of the oil sample showed no obvious odd carbon predominance. This inconsistency was reported to be due to the fact that the largest carbon number peak height used in the calculation was very small, and if more than one denominator is used with small absolute values, there will be an asymptotic increase in the value of that term. As the denominator approaches zero, the term approaches infinity and dominates the overall relationship. Thus, the error will only be apparent if the peak height/area absolute values are small and the problem will be worse if there are fewer *n*-alkane peaks in the denominator. Thus, they reported that CPI_b is characterized by its equality to 1.00 for all linear derivations

Figure V.4: Differences (%) between the CPI_a and CPI_b values calculated for the sediment samples.

Sample Stations



(i.e. straight line envelope for *n*-alkanes will result in CPI_b=1) which is not true for CPI_a. In addition, the CPI_b formula gives consistent and more meaningful results, while CPI_a tends to overestimate odd and underestimate even carbon number predominances (Marzie *et al.*, 1993).

Figure V.4 indicates that CPI_a values overestimated most of the results for the samples, especially in zones IV, V and VI which receive significant terrestrial/biogenic input. This was supported by the low and high correlations between total terrestrial *n*-alkanes relative to TOC and both CPI_b ($r=0.7576$, $p\leq0.001$) and CPI_a ($r=0.8510$, $p\leq0.001$), respectively.

The determination of the C_{max} for every sample also gives an indication of the relative source input, where a $C_{max}\geq C_{25}$ for *n*-alkanes reflects the incorporation of higher plant wax and C_{max} at lower carbon numbers indicates a major input from microbial/petrochemical sources (Simoneit, 1978; 1982a; Mazurek and Simoneit, 1983). Generally, the dominant C_{max} determined for the *n*-alkanes of the Alexandria coastal sediment samples are $<C_{25}$ with a phytane predominance in some stations (Table V.2). This indicates a petroleum source, with some values $>C_{25}$ supporting the interpretation of a terrestrial contribution to the bottom sediments, while various C_{max} values may result from regional differences in source strengths.

Since mixtures of *n*-alkanes from petroleum and terrestrial sources were detected at most stations, a substraction of the corresponding *n*-alkane concentrations was carried out to determine the distribution signatures of the residual plant wax alkanes. Thus, the terrestrial higher plant wax *n*-alkane signature was calculated by subtracting the average of the next higher and lower even carbon numbered homolog (Simoneit *et al.*, 1990) as follows: Wax $n\text{-}C_n = [C_n] - 0.5[C_{(n+1)}+C_{(n-1)}]$, where negative values of C_n were taken as zero. The total terrestrial *n*-alkanes (TI) recorded an average value of 251.5 ± 498.4 µg/g TOC (Figure V.2c, Table V.2), representing 13% of the total *n*-alkane concentrations. The significant direct correlation ($r=0.9088$, $p\leq0.001$) between the $TI/C_{30}\alpha\beta$-hopane (Table V.3, parameter VI) and the terrestrial *n*-alkane concentrations relative to TOC indicates

the usefulness of that ratio in determining and tracking the terrestrial source input in surficial bottom sediments.

Unresolved complex mixture

Besides the chromatographically resolved compounds, an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons eluting between *n*-C_{16} and *n*-C_{33} is present in all samples (e.g., Figure V.3). This UCM has a maximum concentrations of 31 mg/g TOC for station 16 and a minimum of 0.2 mg/g for station 18 (Table V.2), confirming a petroleum origin (Mazurek and Simoneit, 1983; Kennicutt II *et al.,* 1994). The UCM/resolved hydrocarbon (U/R, Mazurek and Simoneit, 1983) ratio (Table V.3, parameter I) is higher for samples in direct contact with sewage/petrochemical input and can be confirmed by the characterization of petroleum biomarkers (Seifert and Moldowan, 1979; Simoneit and Kaplan, 1980; Simoneit *et al.,* 1980; Simoneit, 1978, 1986a; Peters and Moldowan, 1993). The observed linear correlation between both *n*-alkanes (C_{15}-C_{38}) and UCM ($r=0.4714$, $p \leq 0.01$) indicates a common (petrochemical) origin of these aliphatic hydrocarbons. Also, the U/R ratio (Table V.3) correlates well with the UCM concentrations ($r=0.5733$, $p \leq 0.01$) implying its usefulness as a UCM (i.e. petroleum/biodegradation) source parameter.

Biomarkers

Molecular biomarkers, i.e. organic compounds detected in the geosphere with structures suggesting an unambiguous link with known contemporary natural products, are specific indicator compounds (found in geological and environmental sample extracts) that can be utilized for genetic source correlations (Simoneit and Mazurek, 1982; Simoneit, 1984; 1986a,b). Such molecules are characterized by their restricted occurrence, source specificity, molecular stability, and suitable concentration for analytical detection (Simoneit, 1984). Biomarkers have wide spread applications in organic matter source identification in both recent and ancient sediments as well as fossil fuels (e.g., Curiale, 1993; Hedges and Prahl, 1993; Philp, 1993; Zumberge, 1993). The biomarker suites examined in this study are the isoprenoids, tri- and tetracyclic terpanes, hopanes, steranes,

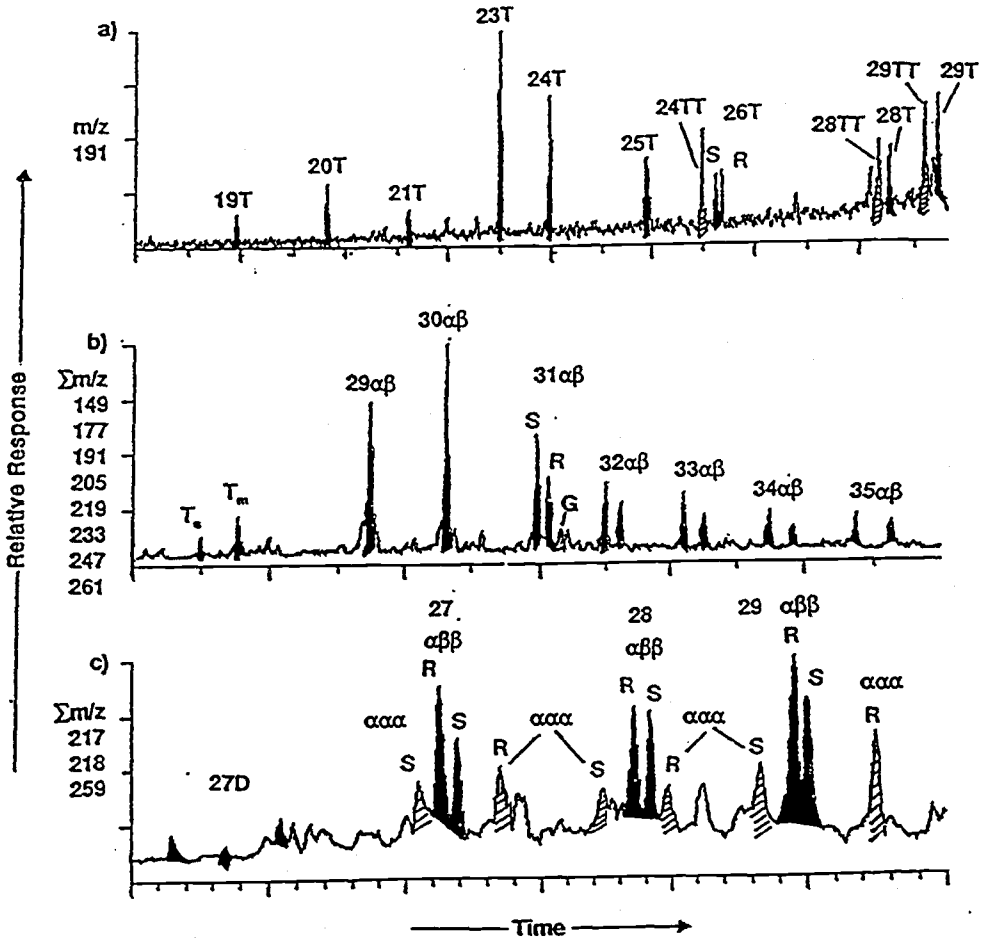
and diasteranes. The following will examine these biomarkers both qualitatively and quantitatively. A typical example of the distributions of the tri- and tetracyclic terpanes (key ion m/z 191), hopanes (∑m/z 149, 177, 191, 205, 219, 233, 247, 261) and steranes/diasteranes (∑m/z 217, 218, 259) is shown in Figure V.5.

Pristane (2,6,10,14-tetramethylpentadecane), phytane (2,6,10,14-tetramethylhexadecane) and lower molecular weight homologs are geologic alteration products of phytol and are not primary constituents of most terrestrial biota (Didyk *et al.,* 1978; Rowland, 1990; Peters and Moldowan, 1993). Isoprenoid hydrocarbons were present in all samples mainly as norpristane, pristane and phytane (average 191.1±262.1 µg/g TOC, Table V.2), which confirms the petroleum related origin of the *n*-alkanes and UCM (Figure V.3; e.g., Simoneit, 1978, 1982a,b; Albaigés and Albrecht, 1979; Simoneit and Kaplan, 1980; Farran *et al.,* 1987; Peters and Moldowan, 1993). The distribution of these isoprenoids and their ratios (Table V.3, parameters II to IV) for all samples points to a common petrochemical source in the Alexandria environment.

Tricyclic terpanes (Structure I, cf. Appendix I), important geochemical tracers occurring in most crude oils, range from $C_{19}H_{34}$ to $C_{45}H_{86}$ (Aquino Neto *et al.*, 1982, 1983; Moldowan *et al.,* 1983; Peters and Moldowan, 1993). The tricyclic terpane series (key ion m/z 191) is present in all the surficial bottom sediments of the Alexandria coast and ranges from $C_{19}H_{42}$ to $C_{29}H_{52}$, no C_{22}, with a C_{23} predominance (Figure V.5a, Table V.4): The highest concentration of the tricyclic series occurred for station 17 (998.1 ng/g TOC) and lowest for station 26 (57.7 ng/g TOC), with an average of 311.2±217.4 ng/g TOC (Table V.2). The occurrence and variation in the relative distribution of the homologs of this series, as determined by GC-MS, in these samples makes them useful tracers for petroleum source identification.

Tetracyclic terpanes, another group of biomarkers detected in these sediments, are derivatives of the hopanes (Aquino Neto *et al.*, 1983). Both 17,21- and 8,14-*seco*-hopanes (Structures II & III) are found in fossil fuels. The 17,21-*seco*-hopanes were proposed to be derived from either thermocatalytic degradation of hopane precursors during geological maturation, microbial ring opening of hopanoids during early diagenesis, or cyclization

Figure V.5: Typical mass fragmentograms representing a) tri- and tetracyclic terpanes (m/z 191), b) hopanes (summed m/z 149, 177, 191, 205, 219, 233, 247, 261), and c) steranes/diasteranes (summed m/z 217, 219, 259) representing the petrochemical biomarkers in the sediment samples [T= tricyclane, TT= tetracyclane, T_s= 18α(H)-22,29,30-trisnorneohopane, T_m= 17α(H)-22,29,30-trisnorhopane, αβ= 17α(H),21β(H)-hopanes (R&S at C-22), G= gammacerane, αββ= 5α(H),14β(H),17β(H)-steranes (R&S at C-20), ααα=5α(H),4α(H),17α(H)-steranes (R&S at C-20), αβD=13β(H),17α(H)-diasteranes (R & S at C-20)].


a)
m/z
191
19T
20T
21T
23T
24T
25T
24TT
S
R
26T
28TT
28T
29TT
29T
b)
Σm/z
149
177
191
205
219
233
247
261
T_s
T_m
29αβ
30αβ
31αβ
S
R
G
32αβ
33αβ
34αβ
35αβ
c)
Σm/z
217
218
259
27D
27 αββ
28 αββ
29 αββ
αααS
αααR
Relative Response
Time

of squalene to ring-D (Trendel *et al.*, 1982). The 8,14-*seco*-hopanes have ring-C opened hopane structures (Peter and Moldowan, 1993). The tetracyclic terpanes in the study area are comprised of a C_{24}-(17,21-*seco*-hopane, i.e. E-norhopane, II) and C_{28} and C_{29}-(8,14-*seco*-hopanes, III) (Figure V.5a, Table V.4). The total tetracyclic terpanes in the study area ranged from 27.9 to 297.8 ng/g TOC, with an average of 128.1±66.9 ng/g TOC (Table V.2).

Pentacyclic triterpane hydrocarbons from petroleum found in the bottom sediments are the 17α(H),21β(H)-hopanes (Structure IV, Simoneit, 1986b). The identification of these compounds is based primarily on their mass spectra and GC retention time in the key ion fragmentogram (Philp, 1985). The predominant analog in these samples (e.g., Figure V.5b) is 17α(H),21β(H)-hopane, with subordinate amounts of 18α(H)-22,29,30-trisnorneohopane (Ts), 17α(H)-22,29,30-trisnorhopane (Tm), 17α(H),21β(H)-29-norhopane, and minor concentrations of the 17β(H), 21α(H)-hopanes and the extended 17α(H),21β(H)-hopanes (>C_{31}). The distributions of the 17α(H)-hopane series (Figure V.5b) and the trace presence of gammacerane (V) are as found for petroleum confirming that major input to Alexandria coastal sediments. The total hopane concentrations for the sediments ranged from 1.1-8.7 µg/g TOC, with an average of 4.0±1.9 µg/g TOC (Table V.2). In typical petroleums, the extended 17α(H),21β(H)-hopane homologs >C_{31} have the epimers at C-22 at an equilibrium ratio {S/(S+R)} of 0.6 (homohopane index; Seifert and Moldowan, 1978). The homohopane index (Table V.3, parameter XI) for these sediments varies from 0.52 to 0.71.

Steranes and diasteranes (VI-VIII) present in fossil fuels are useful biomarker indicators for petroleum pollution in urban coastal areas (e.g., Albaigés, 1980; Albaigés and Cuberes, 1980; Grimalt *et al.*, 1984, 1986, 1990). These biomarkers were detected (e.g., Figure V.5c) and quantified (Table V.2&V.4) in the surficial bottom sediments of the Alexandria coastal area. The steranes have mainly the 5α(H),14β(H),17β(H)-configuration (VI), and a minor amount of the 5α(H),14α(H),17α(H)-configuration (VIII), with traces of 13α(H),17β(H)-diasteranes (VI; 5.2%, Table V.2). The total sterane concentrations in the study area ranged between 0.38 and 2.81 µg/g TOC (average 1.10±0.57 µg/g TOC, Table V.2). The epimerization ratio at C-20 of the C_{29} sterane

(Table V.3, parameter XIII) is high, indicating full maturity of the petroleum residues in the bottom sediments.

Organic geochemical ratios

Several biodegradation/source/maturity indicators for the biomarkers (Mackenzie, 1984) are considered (Table V.3). The {S/(S+R)} ratios of the C_{31}-αβ hopanes are essentially equal and fully mature (average 0.59±0.06) for these sediments. The ratios of the trisnorhopanes, T_s/T_m, which in this case may have maturity and/or source implications have a narrow range of 0.61-0.87 with no observable trend between samples, indicating probably a common petrochemical source in the area. The {S/(S+R)} ratios of the 5α(H),14α(H),17α(H)-C_{29} steranes show a significant range (0.39-0.67), indicating maturity (0.5 at equilibrium) where some changes in the ratio are due to biodegradation (e.g., Chosson *et al.*, 1992). In addition, the variations of the values of the C_{23}-tricyclic terpane/C_{30}-hopane (range 0.01-0.20) and of the C_{27}-αβ diasterane /C_{29}-ααα sterane (range 0.12-0.50) ratios show systematic trends among the samples.

Biodegradation was observed in most of these sediment samples, where the petroleum pollution enhanced microbial activity as inferred from the biodegradation indices (Table V.3). The main characteristic feature of biodegradation is the strong depletion or total absence of *n*-alkanes, resulting in GC signatures with a prominent UCM (Figure V.3; Bailey *et al.*, 1973a,b; Connan *et al.*, 1980). This feature appeared especially in GC traces for stations located in the main two harbors of Alexandria and for stations in direct contact with sewage outfalls. This is inferred from the high U/R, Pr/C_{17} and Ph/C_{18} (>1) ratios and low Pr/Ph (<1) ratio (Table V.3). The lack of *n*-alkane depletion for some stations may be explained by the strong terrestrial signal over the anthropogenic input. Aboul-Kassim and Simoneit (1994b) report that biodegradation in the Eastern Harbor of Alexandria is relatively high, even with a selective microbial attack on αβ-homohopanes in the order $C_{35}>C_{34}>C_{33}>C_{32}>C_{31}$ and 22R>22S. For ααα20R sterane epimers, preferential degradation, like the 22R αβ-homohopanes, appeared to reflect enzymatic specificity in the bacteria for the biological over the geological stereochemistry. Although microorganisms typically degrade petroleum by utilizing the less complex

hydrocarbon compounds first (Seifert and Moldowan, 1979; Zhang *et al.*, 1988), biodegradation is considered to be quasi-sequential (Peters and Moldowan, 1991) in that more resistant compound classes can be attacked prior to complete utilization of less resistant classes. Kvenvolden *et al.*(1985) used the triplet ratio of the two C_{26} tricyclanes to the C_{24} tetracyclane (Table V.3, parameter IX) to evaluate oil biodegradation, where a ratio of 2.0-2.2 indicated heavy biodegraded petroleum. For the bottom sediments of the Alexandria coast, the triplet ratio ranged from 0.6 to 2.3 (Table V.3), suggesting commencement of biodegradation for some samples. This is also inferred statistically from the significant direct correlations ($p \leq 0.001$) between U/R and Pr/C_{17} ($r=0.7961$), Ph/C_{18} ($r=0.7077$) and the triplet ($r=0.6613$) ratios.

Thus, coupling CPI, C_{max}, UCM, and wax *n*-alkane values with quantitation of biomarkers, as well as the organic geochemical parameters allowed the definition of the main sources of the aliphatic hydrocarbons (biogenic vs. anthropogenic) characteristic for Alexandria coastal region. However, these analyses presented only the assessments of the different sources of lipids in the bottom sediments and not their source strengths (cf. the statistical part).

Data interpretation and source confirmation

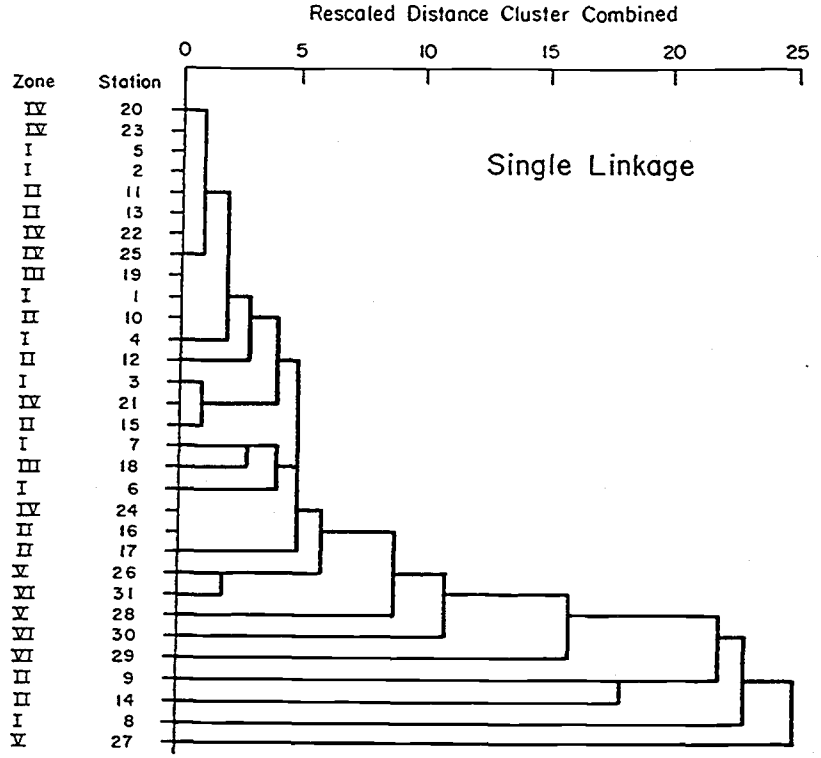
The OTPESEM multi-tracer model for the Alexandria region generated a large amount of data, necessitating the use of univariate/multivariate statistical techniques to group the data into significant clusters and reduce them into a number of factors (end members or sources), which represent in an organic geochemical sense, the combined effect of several geochemical processes or factors. These methods included correlation, cluster, and factor analyses and linear programming techniques.

Cluster analysis

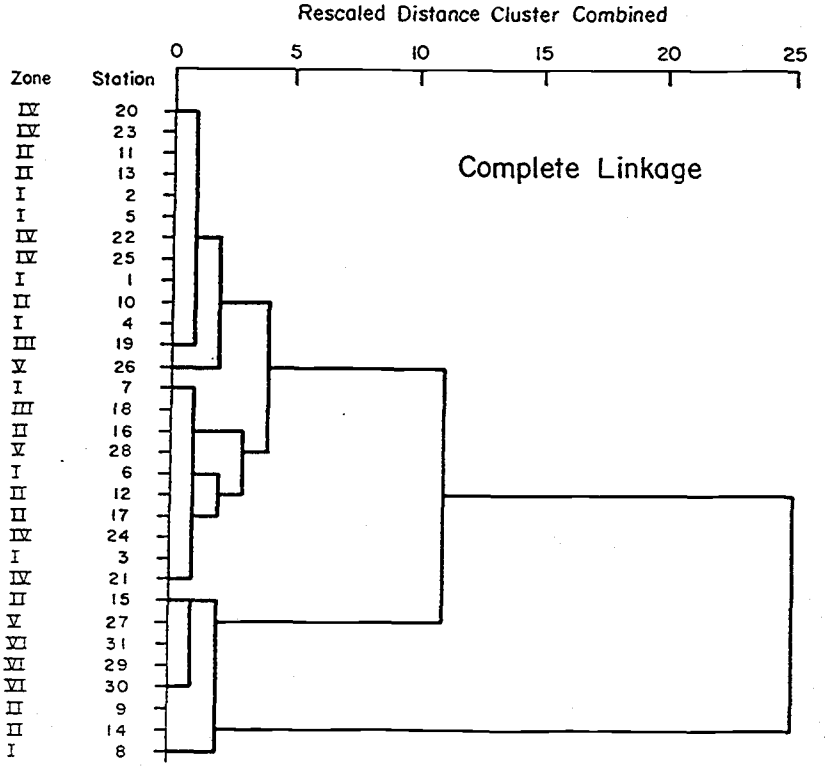
Q-mode cluster analysis was employed here to classify the study area into specific regions, each having definite characteristics. The whole set of organic geochemical data for the aliphatic hydrocarbons was subjected to this analysis. The single linkage method (Figure 6a) indicated that stations as 20, 23, 5 and 2 (zones I & IV) were combined first

Figure V.6: Q-mode cluster analysis showing the a) simple linkage and b) complete linkage techniques based on the organic geochemical information (concentrations and ratios) for the coastal sediments of the Alexandria region.

a)


Rescaled Distance Cluster Combined
0
5
10
15
20
25
Zone
Station
20
23
5
2
11
13
22
25
19
1
10
4
12
3
21
15
7
18
6
24
16
17
26
31
28
30
29
9
14
8
27
Single Linkage

b)


Rescaled Distance Cluster Combined
0
5
10
15
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25
Zone
Station
20
23
11
13
2
5
22
25
1
10
4
19
26
7
18
16
28
6
12
17
24
3
21
15
27
31
29
30
9
14
8
Complete Linkage

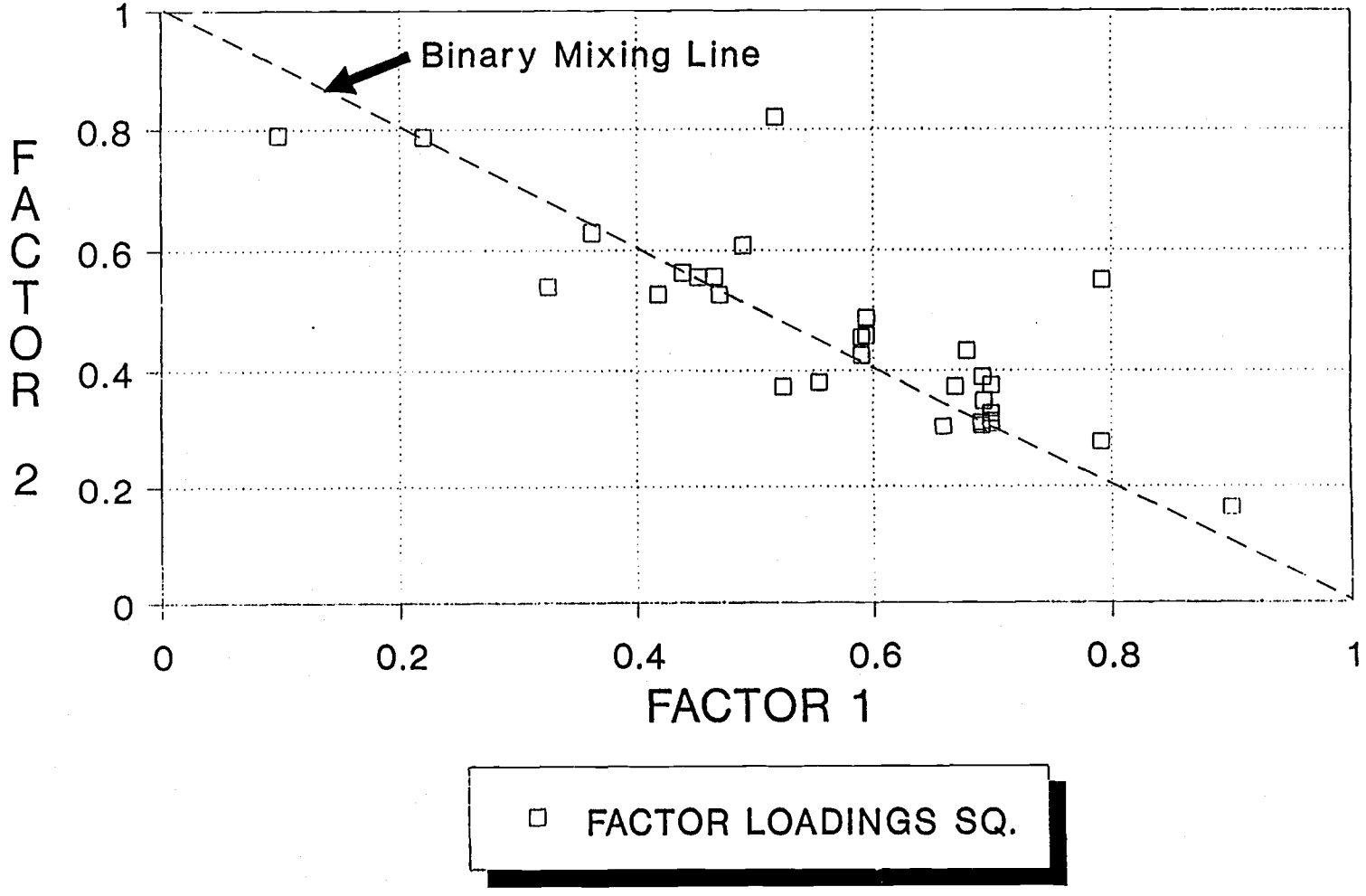
with the smallest distance (or greatest similarity) between them. The combining distance then increases to stations 11, 13, 22 and 25 until it reaches stations 30, 29 and 27 (zones V & VI). These stations show the greatest dissimilarity to the former stations. In the complete linkage method dendrograms (Figure V.6b), and based on the organic geochemical parameters for the sediments, two main groups were distinguished, the distance between them shows their great dissimilarity. The first cluster group (CG I) includes samples mainly located in zones I, II, III, IV and V (sample #28), while the second cluster group (CG II) consists of samples located in zones V and VI (Figure V.6b). All samples within the two main cluster groups (CG I & CG II) were combined at short distances showing great similarity among these samples.

Despite the different statistical approach of cluster analysis, dendrograms a and b coincide with each other and differentiate the study area into two main regions without any indication for the existence of other subregions. In general, the CG I (larger group) corresponds to samples characterized by relatively high *n*-alkane, EOM, UCM, tricyclane, tetracyclane and diasterane concentrations (Table V.2). These features define zones affected mainly by high levels of petroleum pollution from either ship traffic (zones II & III), sewage disposal (zones I, II & IV) or atmospheric fallouts (Aboul-Kassim and Simoneit, 1994a). The CG II consists of samples from the western side of Alexandria (Figure V.6b). These samples (the smaller group) are characterized by high ϕ values (i.e., the finest grain size), high terrestrial *n*-alkanes and isoprenoids (Table V.2), with high CPI and TI/$C_{30}\alpha\beta$-hopane values (Table V.3).

Q-mode factor analysis and linear programming

In the case of Q-mode factor analysis of the data, the first result yields two significant principal factor loading scores, providing information about sample variation of about 88.93% and 3.96%, respectively (maximum cumulative information 92.89%). When individual compounds of this factor loading matrix are squared, the sum of the squared loadings for all factors of a particular sample equals 1.00 (i.e. communality; which is the proportion of the total variance in a particular sample that is explained by those factors). The individual squared loading of one factor represents the fraction of the

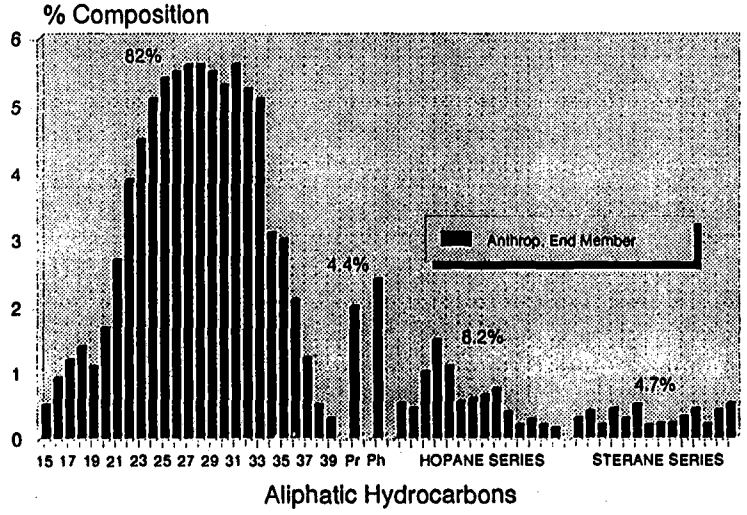
Figure V.7: Factor loadings squared.


Binary Mixing Line
FACTOR 2
FACTOR 1
0
0.2
0.4
0.6
0.8
1
FACTOR LOADINGS SQ.

sample which that factor contributes to the sample (e.g., if a sample has a factor 1 loading of 0.4 then $(0.4)^2$=0.16 or 16% of the sample is from factor 1). Thus the distribution of the various factors in each sample was obtained. A plot is used to observe associations (SAS, 1991, Rapp, 1991) between samples (groupings; Figure V.7). Most samples plot near the binary mixing line (a line from factor 1=1.00, factor 2=0 to factor 1=0, factor 2=1.00), indicating that two main factors can explain the majority of the composition of the samples. The second result is from squaring individual elements of the factor score matrix yielding the sum for a particular factor equal to 1.00. The proportion which an individual lipid class contributes to the total composition of an end member is determined by dividing the absolute values of all lipid fraction scores for that factor by the sum of the absolute values of all the scores for that factor.

After using both the rotation proposed by Leinen and Pisias (1984) and linear programming techniques, the two end member (EM I & EM II) compositions were obtained (Figure V.8). In order to assign the origin (source) of the observed factors, we used both the statistical and biomarker approaches. EM I (Figure V.8a) is dominated mainly by *n*-alkanes (82%), regular isoprenoid hydrocarbons (i.e. pristane and phytane, 4.4%), the hopane series (8.2%) with a predominance of 17α(H),21β(H)-hopane and both C-22 S/R configurations for the homologs $>C_{31}$, and the diasterane/sterane series (4.7%). The EM II (Figure V.8b) is dominated mainly by *n*-alkanes of a terrestrial origin and traces of isoprenoids (0.5%), hopanes (1.2%) and diasteranes/steranes (0.5%). Thus, based on the statistical findings, these two end members can be compared with the compositions of known sources (e.g., sewage/petroleum and terrestrial and marine sources, Aboul-Kassim and Simoneit, 1993; Figure V.9). It is obvious that the origins (sources) of the lipids in the surficial sediments of the Alexandria coastal region are mainly petroleum pollution (anthropogenic) from ships and waste waters (end member 1), followed by secondary terrestrial input represented by EM II.

Figure V.8: End member compositions (after q-mode factor analysis and linear programming technique) of the surficial bottom sediments of the Alexandria coast, a) anthropogenic end member, and b) terrestrial end member.


% Composition
6
5
4
3
2
1
0
82%
4.4%
6.2%
4.7%
Anthrop. End Member
15 17 19 21 23 25 27 29 31 33 35 37 39 Pr Ph
HOPANE SERIES
STERANE SERIES
Aliphatic Hydrocarbons

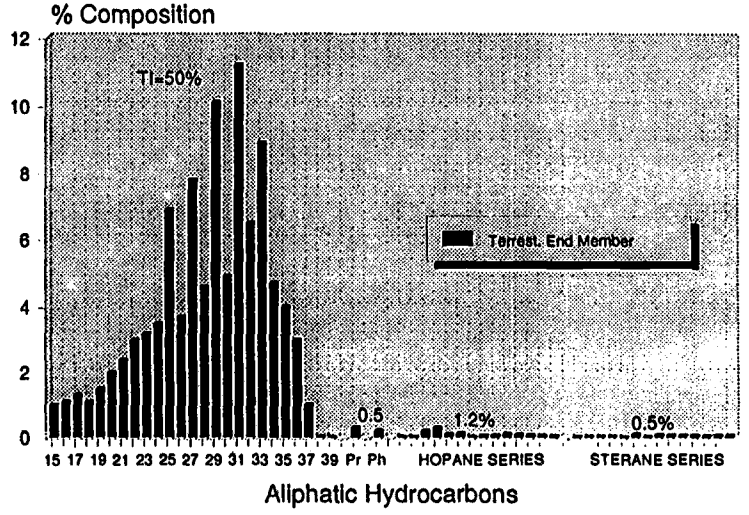
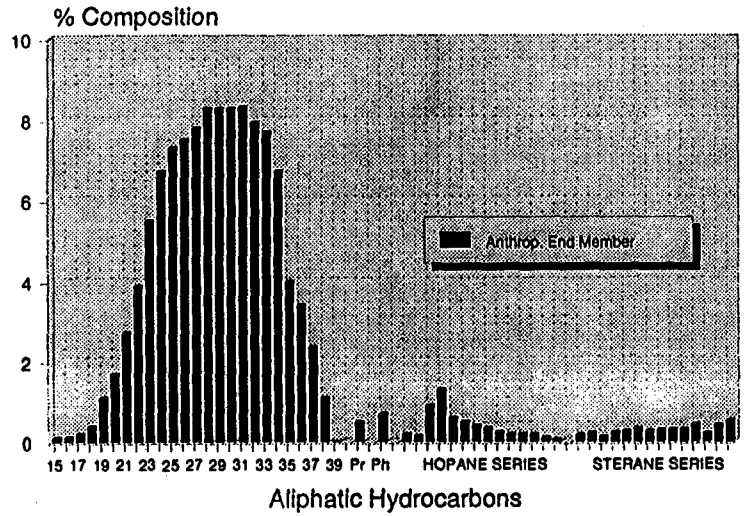
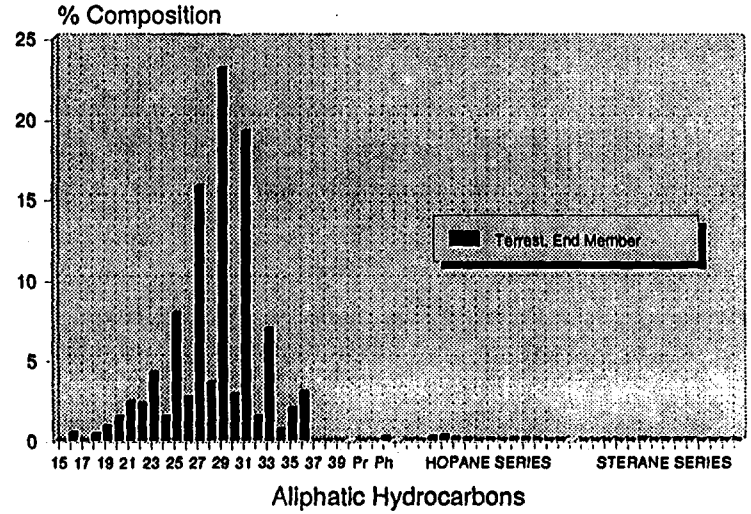

% Composition
12
10
8
6
4
2
0
TI=50%
0.5
1.2%
0.5%
Terrest. End Member
15 17 19 21 23 25 27 29 31 33 35 37 39 Pr Ph
HOPANE SERIES
STERANE SERIES
Aliphatic Hydrocarbons

Figure V.9: Source end members representing: a) anthropogenic, and b) terrestrial sources (Aboul-Kassim and Simoneit, 1993b).


% Composition
10
8
6
4
2
0
Anthrop. End Member
15 17 19 21 23 25 27 29 31 33 35 37 39 Pr Ph
HOPANE SERIES
STERANE SERIES
Aliphatic Hydrocarbons


% Composition
25
20
15
10
5
0
Terrest. End Member
15 17 19 21 23 25 27 29 31 33 35 37 39 Pr Ph
HOPANE SERIES
STERANE SERIES
Aliphatic Hydrocarbons

CONCLUSION

This initial characterization of the aliphatic hydrocarbons in the surficial sediments of the Alexandria coastal area has confirmed the presence of biomarkers which are emission source specific as terrestrial and oil pollution indicators. Petrochemical residues comprised the anthropogenic component and were confirmed by the UCM, U/R, pristane, phytane, CPI, C_{max}, tricyclic (C_{19} - C_{29}) and tetracyclic (C_{24}, C_{28} and C_{29}) terpanes, αβ-hopanes, steranes (αββ-, with minor ααα-configuration), and traces of diasteranes. The terrestrial components consisted of wax *n*-alkanes with C_{25}, C_{27}, C_{29} or C_{31} predominances, recording the contemporary biogenic input to the area.

Statistical analyses of the hydrocarbon data proved to be useful in clustering and partitioning the surficial bottom sediments. Q-mode cluster analysis differentiated the study area into two main regions without any evidence for the existence of other subregions. The first cluster group defined mainly the eastern zones of Alexandria which are impacted by anthropogenic pollution, while the second cluster group represented the natural terrestrial sources in the western Alexandria zones. Both extended Q-mode factor analysis and linear programming technique reduced the hydrocarbon data set into two significant end members (sources), explaining 92.89% of the variation among the sediment samples. These multivariate techniques confirmed the end members as representing petrochemical (88.93%) and terrestrial (3.96%) sources.

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CHAPTER VI

CONCLUSIONS

The lack of information about the environmental quality of the coastal environment of Alexandria (Egypt) and the need for environmental protection, particularly from various forms of pollution, initiated this multi-tracer biomarker study. The composition of extractable organic matter was determined for different environmental compartments (i.e., atmospheric particulate fallout, untreated sewage and waste water discharge, surficial bottom sediments). Then, both hydrocarbon biomarkers and statistical analysis techniques were used to trace anthropogenic and biogenic inputs as well as possible sediment movement.

The characterization of aliphatic hydrocarbons in the Alexandria environment has confirmed source specific tracers (but with different emission strengths in the various compartments) as oil pollution and terrestrial indicators. Petrochemical residues comprised the anthropogenic component and were confirmed by the UCM, U/R,CPI, and C_{max} parameters, and by the pristane, phytane, tricyclic (C_{19} - C_{29}) and tetracyclic (C_{24}, C_{28} and C_{29}) terpane, αβ-hopane, sterane (αββ-, with minor ααα-configuration), and traces of diasterane biomarkers. The terrestrial components consisted of wax *n*-alkanes with C_{25}, C_{27}, C_{29} or C_{31} predominances, recording the contemporary biogenic input to the area.

Statistical analyses were useful for reducing the data set as well as clustering and partitioning the samples into meaningful end members representing the Alexandria environment.

1) The analysis of variance indicated statistically significant differences in lipid concentrations for all environmental samples, except for the Σketone+ aldehyde+ester fractions of both the atmospheric fallout and waste water samples. It also indicated significant variations in lipid compositions between sample sites and temporal variations in lipid compounds in the sediments.
2) Q-mode cluster analysis differentiated the surficial sediments of the Alexandria coast into two main regions, eastern and western; without any evidence for the existence of other subregions. It defined the major anthropogenic pollution and the minor natural terrestrial sources in the area.

3) Extended Q-mode factor analysis and linear programming technique were implemented to reduce the data set into statistically significant end members specific for the environment of Alexandria, as well as to assess their contributions to each sample. For the quantitative data, multivariate analysis indicated the presence of two significant end members, which were further confirmed by using biomarker characterization. This explained 93.2% of the data for the sediments from the Alexandria urban area. The anthropogenic end member for the particulate fallout samples (PFS) represented 80% as a petrochemical source. For the surficial bottom sediments along the Alexandria coast, the end member were represented by both petrochemical (88.93%) and terrestrial (3.96%) sources.

In addition, the multi-tracer biomarker and statistical approaches were useful to differentiate between sewage and petroleum sources (anthropogenic end member) and to assess suspended sediment particulate matter or transport in the harbor area using the gradient change in factor loading values. Petrochemicals were detected in all the input sources of Alexandria environment, with a minor natural background source of terrestrial plant wax (marine components were not detectable due to the high dilution). Because this study is preliminary for that area, future research for pollution risk assessment should consider the determination of all possible input sources of organic pollutants to the region, with complete compositional analyses for these sources.

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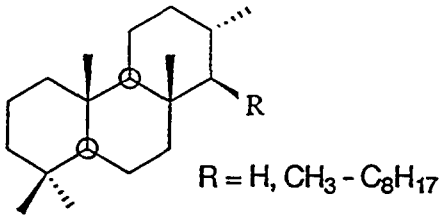
APPENDIX

Chemical Structures Cited



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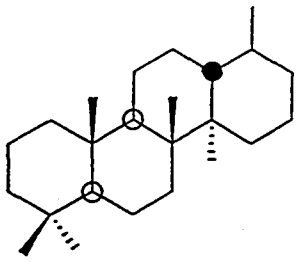
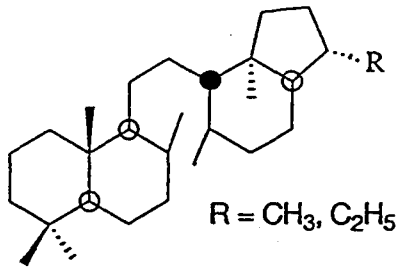
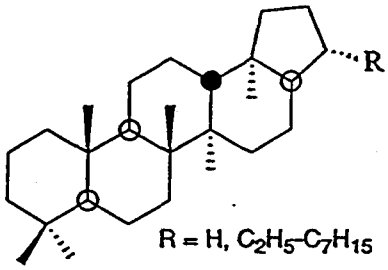


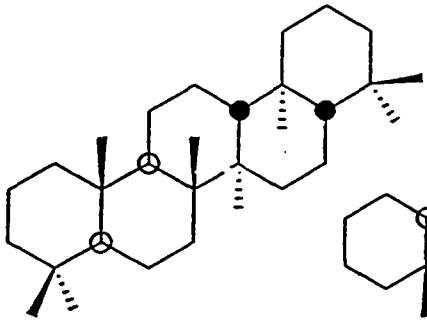
II. E-norhopane (C_{24})



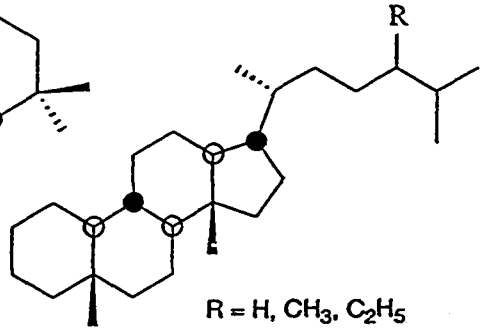
III. 8,14-*seco*-Hopanes



IV. α-Hopanes



V. Gammacerane



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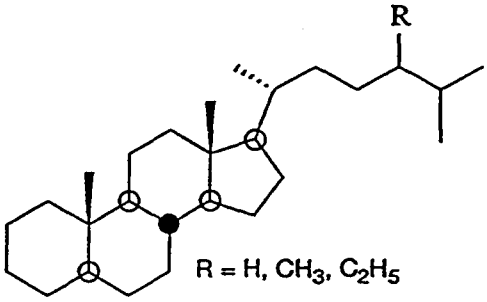

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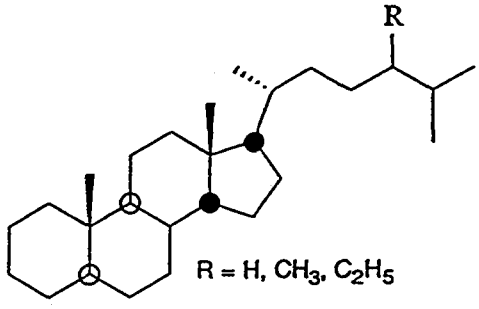

VIII. αββ-Steranes