EGYPTIAN JOURNAL OF AQUATIC RESEARCH 1687-4285
VOL. 31 NO. 2, 2005: 166-182.

FORENSIC ANALYSIS AND SOURCE PARTITIONING OF ALIPHATIC HYDROCARBON CONTAMINATION IN LAKE MARUIT AQUATIC SEDIMENTS

TAREK A. KASSIM

Department of Civil, Construction and Environmental Engineering
College of Engineering, Oregon State University
202 Apperson Hall, Corvallis, Oregon 97331, USA

Keywords: Aliphatic hydrocarbons, forensic analysis, bottom sediments, Lake Maruit

ABSTRACT

Investigations of natural and/or engineered environmental systems require achieving a comprehensive characterization and identification of contaminants of concern. The differentiation of contaminant molecular markers (MMs) that originate from various sources is difficult when simply based only on their chemical compositions. Thus, a comprehensive forensic analysis coupled with source partitioning modeling is needed for characterizing contaminant compositions, predicting their possible transport, and discriminating their main sources.

The lack of information about the organic contamination of Lake Maruit (Egypt) and the impact of various anthropogenic sources in the area have initiated an extensive research project to study the various *trace* organic contaminants of concern in both natural and engineered environmental systems. The present paper, the first in a series, is an attempt to characterize the major sources of aliphatic hydrocarbon contamination in Lake Maruit sediments. Various surficial bottom sediments were sampled and analyzed for organic molecular 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. A multivariate statistical approach, including both q-mode factor analysis and linear programming technique, was used to determine the end member compositions and evaluate sediment partitioning in the study area.

INTRODUCTION

Environmental forensic analysis (EFA) is a scientific methodology developed for analyzing and identifying contamination-related environmental contaminants, and for determining their sources. It combines experimental analytical procedures with scientific principles derived from several science- and engineering-disciplines (Kassim and Simoneit, 2001; Kassim and Williamson, 2003). It can also provide a valuable tool for obtaining scientifically proven data when applied to investigations of environmental contamination. An accurate and defensible forensic analysis approach requires answering the following key questions (Kassim and Williamson, 2003): (a) What are the current chemical composition (qualitative and quantitative) present due to contamination? (b) What are the potential sources of contamination?, and (c) Can these potential sources be linked to their original sources? Answers to these questions require the use of sophisticated contaminant-specific methods of *trace* chemical analysis together

E-mail: Tarek_kassim@yahoo.com

with advanced data examination, statistical/mathematical modeling and visualization techniques (Kassim and Williamson, 2003). The selection of appropriate molecular marker (MM) compounds, which will differentiate contaminant sources, is central to designing an analytical program. Because aliphatic hydrocarbons, for instance, have a variety of sources, the most important objective in analytical selection is to identify specific markers for both the released hydrocarbon mixture and other potential sources. MMs must have the attributes of uniquely identifying the released contaminants from other sources and resistance to alteration (i.e., weathering) over time. Most often, the appropriate markers are not known at the start of a forensic investigation, but are identified during the characterization processes. Successful contamination fingerprinting usually requires analysis of more than one target analyte group.

Although a major element in an environmental forensics investigation is the chemical fingerprinting that is designed to identify contaminants; however, fingerprinting alone is not sufficient enough to provide answers to questions of source location and legal responsibility (Kassim and Simoneit, 2001). Accordingly, incorporation of chemometrics (i.e., the numerical analysis of chemical data) to a forensic analysis data set would synthesize all the complex information to make it easily visualized (Kassim, 1998; Kassim and Simoneit, 2001; Kassim and Williamson, 2003).

This paper, the first presentation of a series of companion studies, aims to demonstrate a unique forensic analysis and genetic source partitioning model for analyzing the aliphatic hydrocarbon composition in Lake Maruit bottom sediments (Figure 1). It is hoped that the characterization of the extent of aliphatic hydrocarbon contamination would help build up an ultimate sampling scheme to be adopted by the Egyptian Environmental Affairs Agency to aid in the final phase of feasibility study and remedial investigation of the impacted region.

THE STUDY AREA

Lake Maruit, one of the Nile Delta lakes, is located on the Mediterranean coastal area of Egypt, southeast of the highly populated and industrialized Alexandria City (Figure 1). The lake receives the strongest human impact among the Egyptian lakes, as its water body is intensively used for urbanization, reclamation, sewage discharge and highway construction. Such impacts have altered its aquatic environment, and reduced its water body to a surface area of 68 Km^2, representing about 50% of its original area measured 35 years ago. The current remaining area of the lake has been artificially divided into four main regions (Figure 1), namely: Main, Northwest, Southwest and Fisheries Basins. All basins are shallow with an average depth of approximately 1 m, where various types and amounts of Alexandria wastewaters are being discharged. In addition, considerable amounts of ground waters enter the lake with unequal flows depending mainly on the variable bedrock features of the region.

Vegetative masses, principally phragmites and hyacinths, occupy significant portions of the surface area of these basins. The hyacinths, and some of the phragmites, are free-floating and driven by wind and currents. Most of the phragmites are fixed in place, either by roots or by attachment to traps set by fishermen. In addition, there are areas (primarily in the Northwest Basin) where the bottom is covered with submerged aquatic vegetation (Figure 1).

Ongoing dredging operations in the Main Basin and the Fisheries Basin are producing a pattern of 1 m deep regions and piles of dredged materials. In the Main Basin (Figure 1), recent construction activities have produced a base for a new road on the northern shore. Inflow of sediment and the buildup of solids in the water column have

resulted in the encroachment of the shoreline along the northern and eastern boundaries. The fixed masses consist of both clumps of vegetation and soil. In addition, there are remnants of a dike extending from the Kalaa Drain to the Nubaria Canal in the Main Basin. This dike forms on side of a path referred to as the cross channel. As a result of recent dredging operations, two parallel channels, approximately 500 m apart run from the Desert Road to the cross channel and a third is being under construction.

The Omoum Drain (Figure 1) has an average depth of 3.5 m upstream of Desert Road. Between Desert Road and the siphon, the bottom rises resulting in a depth of 2 m at the siphon. This shallow depth continues for the next 500 m downstream of the siphon. The bottom slopes downward in the direction of El Mex reaching a depth of 5 m. The drain has a general "U" shape with a width ranging from 40 to 50 m. Beginning at a point 1100 m upstream of Desert Road, the Nubaria Canal (Figure 1) has a centerline depth of 3 m. This depth decreases to 2.5 m at Desert Road, and between Desert Road and the Sea Locks, the depth varies between 2.5 and 3 m. the upper end of the canal has a "V" shape with a width of 60 to 80 m. Beginning at a point approximately 3,000 m downstream of Desert Road, the width of the canal increases to over 200 m.

A number of sources have fed the Eastern (Main) Basin of Lake Maruit. These include current sources (Kalaa Drain, Omoum Drain, Nubaria Canal) and former outfalls to the lake which are now included with the West Treatment Plant outfall after primary treatment (Kabbary Drain, Gheit El-Enab Drain, Industrial Drain).

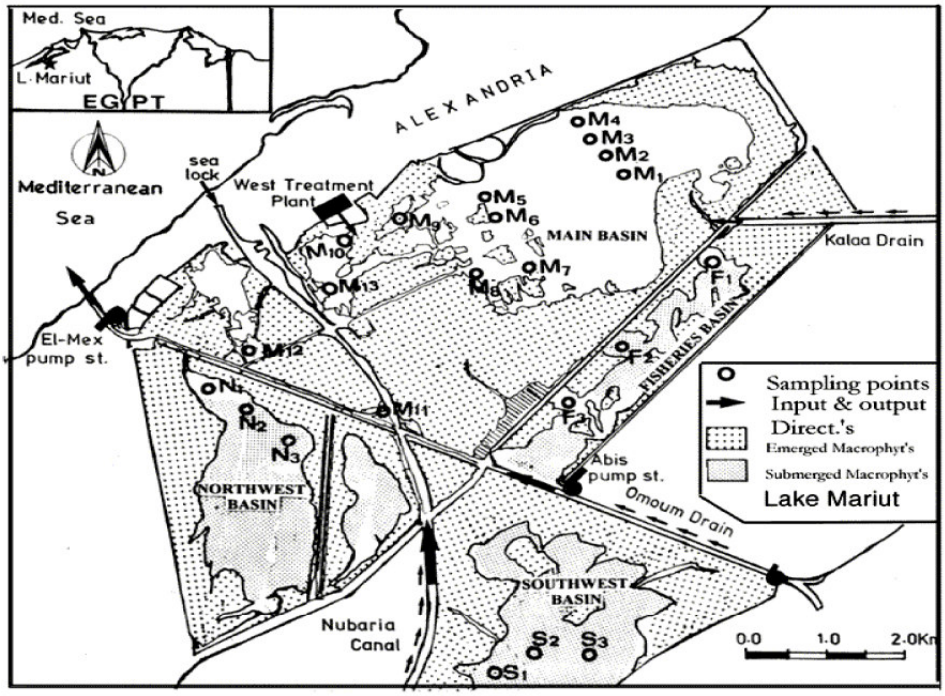

Figure 1: Lake Maruit, Egypt.

EXPERIMENTAL DESIGN

Sampling

Surficial bottom sediment samples were collected from the Main Basin (stations M1-M13), Northwest Basin (N1-N3), Southwest Basin (S1-S3), and the Fisheries Basin (F1-F3) of Lake Maruit (Figure 1) with a grab sampler. Sediment samples were removed from the middle of the grab, wrapped in aluminum foil and stored frozen at -20°C. Before extraction, sediment samples were dried and sieved to pass through 250 µm.

Pure end member sources from engineered sources (e.g., wastewater influents, effluents and sludge representing several outfalls) and tarry surficial sediment samples, believed to contain solely petroleum residues, were collected from Lake Maruit (Figure 1). These samples were also kept frozen at -20°C to prevent organic matter alteration.

Forensic Analysis

The following sections summarize the extraction, analysis, instrumental detection, identification and quantification of molecular markers in Lake Maruit's natural and engineered environmental samples, as follow:

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 each 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 interference.

An extraction protocol was designed for qualitative and quantitative MM forensic analyses from all stations in Lake Maruit basins, both natural and engineered (Kassim and Simoneit, 2001; Kassim and Williamson, 2003). For aqueous samples (influents and effluents), liquid/liquid extractions were performed in separatory funnels using *n*-hexane followed by chloroform ($CHCl_3$). The solid phase samples (e.g., sediment, sewage sludge) were extracted in a Soxhlet apparatus with methylene chloride-methanol (2:1v/v). These extracts are a measure of the amount of extractable organic matter (EOM) present in any sample. All the extracts (i.e. 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 (4x30 ml), the latter after acidification (pH 2) with 6*N* HCl.

The acidic fractions, previously reduced to 0.5 ml, were esterified by refluxing overnight with 15 ml of 10% BF_3/methanol. The BF_3/methanol complex was destroyed with 15 ml of water, and the methyl esters were recovered by extraction with 4x30 ml of *n*-hexane.

The neutrals were fractionated by long column chromatography. A column (50x1.2 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-mass spectrometric (GC-MS) analysis for further qualitative molecular examination by silylation with bis(trimethylsilyl)- trifluoroacetamide.

Here, the results of fraction 1 are only presented that represent the aliphatic hydrocarbons composition of natural and engineered samples (aqueous and solid). A recovery experiment for the long column chromatography was carried out using *n*-$C_{32}D_{66}$ and a series of 35 *n*-alkane standards.

Instrumental analyses

The gas chromatography-mass spectrometry (GC-MS) analyses were performed using an HP GC (initial temperature 50°C, isothermal 6 min, programmed at 4°C/min to 310°C, isothermal 60 min) interfaced directly to an HP-MSD quadrupole mass spectrometer (electron impact, emission current 0.45 mA, electron energy 70eV, scanned from 50 to 650 daltons).

Compounds identification and quantification

Compounds identification was based on comparison with the retention times and/or mass fragmentation patterns of standard reference materials. With the help of the Library, MM identification was tabulated 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 are available, but the sample mass spectrum agreed very well with the standard library; (c) *Possible,* same as above except that the sample spectrum contained information from other compounds but with minor overlap; and (d) *Tentative,* when spectrum contained additional information from possibly several compounds with overlap. Identification and response factors of pollutants were determined using a suite of standard compounds.

Compounds quantification was based on the application of a perdeuterated compound (e.g. *n*-$C_{32}D_{66}$) as an internal standard. In order to correct for detector response, a sets of relative response factors were determined for the aliphatic hydrocarbon fraction from multiple injections.

Organic Carbon Analysis

Organic carbon analyses were carried out for all aqueous and solid phase samples using a Carlo Erba NA-1500 CNS analyzer. Solid samples (e.g., sediments, sewage sludge) were combusted at 1000°C in an oxygen-rich medium to CO_2. The CO_2 gas was separated chromatographically, detected with a thermal conductivity detector, and the resulting signals were digitized, integrated, and mathematically processed along with results based on standards. For aqueous samples (influent and effluent), dissolved organic carbon (DOC) was determined using a Hitachi DOC analyzer and calculated by the difference between the measured total carbon (TC) and inorganic carbon (IC) content of the samples. Concentrations of aliphatic hydrocarbon MMs in all samples were calculated relative to the organic carbon content (TOC or DOC).

Source Partitioning Model

The quantitative composition of the aliphatic hydrocarbon fractions relative to TOC, as well as the molecular marker (MM) biodegradation ratios, were submitted to extended Q-mode factor analysis and linear programming technique (LPT). This source partitioning model is well described elsewhere (Kassim and Simoneit, 2001, Kassim and Williamson, 2003).

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 (Kassim and Simoneit, 2001, Kassim and Williamson, 2003). 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 (Kassim and Simoneit, 2001, the "new rotation" technique proposed by Kassim and Simoneit (2001) and Kassim and Williamson (2003) which corrects the negative values and does not necessarily require the assumption of having sampled pure end members. However, both the new rotation technique as well as sampling pure end member sources (Kassim and Simoneit, 2001) were used in the present study.

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 (Kassim and Simoneit, 2001).

RESULTS AND DISCUSSION

The average aliphatic hydrocarbon (e.g., *n*-alkane compositions as well as their molecular markers) contents of Lake Maruit 4 main basins are given in Table 1, while the organic geochemical ratios/parameters are presented in Table 2.

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-MS traces (Figure 2). The *n*-alkanes ranged in chain length from C_{13} - C_{35} with a carbon number predominance near unity (Table 2). 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 2; e.g., Kassim and Simoneit, 2001; Kassim and Williamson, 2003; 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 Lake Maruit bottom sediments.

Because mixtures of *n*-alkanes from petroleum and terrestrial origins were detected in many stations, a substraction of the corresponding *n*-alkane concentrations with a CPI=1 was carried out to determine the distribution signatures of the residual plant wax alkanes (Table 1). 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}.

Besides the chromatographically resolved compounds, an UCM of hydrocarbons eluting between *n*-C_{16} and *n*-C_{33} is present in all samples (Figure 2; Table 1). The U/R ratio (Table 2) for most samples is high, that 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 molecular markers (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 lake environment.

A typical example of the distributions of the tri- and tetracyclic terpanes (key ion m/z 191), hopanes (Σm/z 149, 177, 191, 205, 219, 233, 247, 261) and steranes/diasteranes (Σm/z 217, 218, 259) is shown in Figure 2. The tricyclic terpane series is present in all surficial bottom sediments ranging from C_{19} to C_{29}, with no C_{22} & C_{27}, and a C_{23} predominance (Figure 2, Table 12; 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 2, Table 1; 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 oil biodegradation, where a ratio of 2.0-2.2 indicated heavy biodegraded petroleum. For Lake Maruit bottom sediments, the triplet ratio ranged from 1.1 to 2.5, 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 (Tables 1 and 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 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 molecular markers are considered (Table 2) in this study. The S/R ratios of the C_{31}-αβ hopanes are equal and fully mature (Table 2). The ratios of the trisnorhopanes, T_s/T_m (Table 2), which in this case may have maturity and/or source implications, have an average of 0.833 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 (Table 2) 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. 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 1 and 2) allow the confirmation of one dominant end member of a petrochemical origin.

The aliphatic hydrocarbon compositions of the surficial sediments indicate a predominance of petrochemicals which can be compared with two possible end members, i.e., untreated sewage/waste water and petroleum hydrocarbons. Since heavy petroleum pollution 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, resulting in GC-MS 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 in Lake Maruit is rather unusual and may be explained by a recent input of petroleum products. Peters and Moldowan (1991) reported 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: ααα20R(C_{27}-C_{29}) > ααα20S C_{27} > ααα20S C_{28} > ααα20S C_{29} $\geq$ αββ(20S+20R)C_{27}-C_{29} (Chosson *et al.,* 1992; Peters and Moldowan, 1993). Preferential degradation of the ααα20R 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, molecular marker (MM) biodegradation indices were calculated for these samples. Based on the information about MM biodegradation ratios, 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, 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 biodegradation rate for the sewage end member. In the case of the homohopane indices (Table 2, 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 (Table 2), 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 (Table 2) indicate a higher biodegradation rate for sewage than for the petrochemicals.

The main result from q-mode factor analysis and linear programming on these samples yields two significant principal factor loading scores, providing information about sample variations of 55.9% and 37.3% (maximum cumulative information 93.2%), 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 derived from untreated sewage (end member #1) and from direct input (end member #2). In addition, a minor insignificant end member, describing 0.137% of the sample variations, was characterized with a predominance of the C_{25}, C_{29} and C_{31} alkanes, representing the terrestrial plant wax input to the lake area.

CONCLUSION

Aliphatic hydrocarbons from petrochemical sources have been identified in natural and engineered samples representing Lake Maruit. The petroleum origin was indicated by the pristane/phytane ratio, UCM signal, low carbon preference index, and the presence of petroleum molecular markers such as tri-, tetra-, and pentacyclic terpanes and steranes/diasteranes. Biodegradation parameters were used to differentiate between petroleum hydrocarbons derived from discharge of 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 in the area.

ACKNOWLEDGMENT

The author wishes to thank the staff of the Wastewater Treatment Plant in Alexandria for sample collection, F.G. Prahl for TOC analyses and Nicklas G. Pisias for extended Q-mode factor analysis and linear programming software and useful suggestions for improvement of the manuscript.

Table 1: Mean aliphatic hydrocarbon compositions relative to total organic carbon of the surficial bottom sediments from Lake Maruit.

Compound Class/Name	Formula	M.W.	Average Concentrations[a] Basins				ID[b]
			Main	Northwest	Southwest	Fisheries	
***n*- ALKANES (µg/g)**							
n- hexadecane	$C_{16}H_{34}$	226	3.2	4.7	bd	bd	a
n -heptadecane	$C_{17}H_{36}$	240	9.6	14.1	4.5	3.8	a
n -octadecane	$C_{18}H_{38}$	254	19.2	32.9	10.5	9.5	a
n -nonadecane	$C_{19}H_{40}$	268	25.6	37.6	15	13.3	a
n -eicosane	$C_{20}H_{42}$	282	35.2	56.4	22.5	19	a
n -heneicosane	$C_{21}H_{44}$	296	38.4	56.4	27	20.9	a
n -docosane	$C_{22}H_{46}$	310	41.6	4.7	30	24.7	a
n -tricosane	$C_{23}H_{48}$	324	38.4	47	31.5	26.6	a
n -tetracosane	$C_{24}H_{50}$	338	35.2	51.7	3	28.5	a
n -pentacosane	$C_{25}H_{52}$	352	35.2	47	34.5	28.5	a
n -hexacosane	$C_{26}H_{54}$	366	28.8	56.4	16.5	26.6	a
n -heptacosane	$C_{27}H_{56}$	380	25.6	42.3	33	26.6	a
n -octacosane	$C_{28}H_{58}$	394	22.4	37.6	27	22.8	a
n -nonacosane	$C_{29}H_{60}$	408	22.4	37.6	27	20.9	a
n -triacontane	$C_{30}H_{62}$	422	16	18.8	19.5	15.2	a
n -hentriacontane	$C_{31}H_{64}$	436	12.8	32.9	18	15.2	a
n -dotriacontane	$C_{32}H_{66}$	450	9.6	42.3	12	9.5	a
n -tritriacontane	$C_{33}H_{68}$	464	9.6	23.5	9	7.6	a
n -tetratriacontane	$C_{34}H_{70}$	478	6.4	14.1	4.5	3.8	a
n -pentatriacontane	$C_{35}H_{72}$	492	6.4	bd	4.5	3.8	a
n -hexatriacontane	$C_{36}H_{74}$	506	3.2	bd	3	3.8	a
n -heptatriacontane	$C_{37}H_{76}$	520	6.4	bd	3	1.9	a
n -octatriacontane	$C_{38}H_{78}$	534	bd	bd	3	1.9	a
Isoprenoids (µg/g)							
2,6,10,14-tetramethylpentadecane (pristane)	$C_{19}H_{40}$	254	6.976	24.957	9.495	2.109	a
2,6,10,14-tetramethylhexadecane (phytane)	$C_{20}H_{42}$	268	19.58	67.821	28.47	4.959	a
Tricyclic Terpanes (ng/g)							
C_{19}-tricyclic	$C_{19}H_{34}$	262	1.536	3.431	0.84	0.931	b
C_{20}-tricyclic	$C_{20}H_{36}$	276	4.64	9.87	4.17	4.617	b
C_{21}-tricyclic	$C_{21}H_{38}$	290	1.536	3.29	1.965	1.843	b
C_{23}-tricyclic	$C_{23}H_{42}$	318	17.06	36.237	16.65	18.43	b
C_{24}-tricyclic	$C_{24}H_{44}$	332	11.65	24.769	20.82	22.515	b
C_{25}-tricyclic	$C_{25}H_{46}$	346	10.08	20.68	15.825	17.347	b
C_{26}-tricyclic (S)	$C_{26}H_{48}$	360	4.64	9.494	4.17	4.902	b
C_{26}-tricyclic (R)	$C_{26}H_{48}$	360	4.672	10.011	4.695	5.472	b
C_{28}-tricyclic	$C_{28}H_{50}$	388	5.44	11.468	4.995	5.719	c
C_{29}-tricyclic	$C_{29}H_{52}$	402	8.512	17.531	5.835	6.365	c
Tetracyclic terpanes (ng/g)							
C_{24}-tetracyclic	$C_{24}H_{42}$	330	17.41	44.603	15.225	12.806	b
C_{28}-tetracyclic	$C_{28}H_{50}$	386	5.888	14.899	8.67	6.365	b
C_{29}-tetracyclic	$C_{29}H_{52}$	400	5.824	15.228	6.525	5.814	b

Cont. (Table 1)

Pentacyclic triterpanes (ng/g)							
18a(H)-22,29,30-trisnorneohopane (Ts)	$C_{27}H_{46}$	370	44.32	71.816	19.515	19.437	b
17a(H)-22,29,30-trisnorhopane (Tm)	$C_{27}H_{46}$	370	60.45	98.042	28.8	28.329	b
17a(H),21ß(H)-29-norhopane	$C_{29}H_{50}$	398	271	441.189	138.435	135.964	b
17a(H),21ß(H)-hopane	$C_{30}H_{52}$	412	340.6	554.506	155.16	151.848	b
17a(H),21ß(H)-homohopane (22S)	$C_{31}H_{54}$	426	154.2	250.369	73.395	72.561	b
17a(H),21ß(H)-homohopane (22R)	$C_{31}H_{54}$	426	63.49	103.635	47.385	46.227	b
17a(H),21ß(H)-bishomohopane (22S)	$C_{32}H_{56}$	440	109.8	179.023	52.035	50.958	b
17a(H),21ß(H)-bishomohopane (22R)	$C_{32}H_{56}$	440	55.42	89.535	45.525	44.593	b
17a(H),21ß(H)-trishomohopane (22S)	$C_{33}H_{58}$	454	88.67	143.491	32.52	32.148	b
17a(H),21ß(H)-trishomohopane (22R)	$C_{33}H_{58}$	454	38.3	62.463	17.655	16.872	b
17a(H),21ß(H)-tetrakishomohopane (22S)	$C_{34}H_{60}$	468	61.47	100.016	28.8	27.892	b
17a(H),21ß(H)-tetrakishomohopane (22R)	$C_{34}H_{60}$	468	33.25	54.755	13.935	13.984	b
17a(H),21ß(H)-pentakishomohopane (22S)	$C_{35}H_{62}$	482	64.48	104.293	23.235	22.895	b
17a(H),21ß(H)-pentakishomohopane (22R)	$C_{35}H_{62}$	482	19.14	31.819	13.005	12.35	b
Diasteranes (ng/g)							
13a(H),17ß(H)-diacholestane (20S)	$C_{27}H_{48}$	372	8.256	7.567	3.15	2.907	b,d
13a(H),17ß(H)-diacholestane (20R)	$C_{27}H_{48}$	372	8.864	11.327	5.235	4.446	b,d
Steranes (ng/g)							
5a(H),14a(H),17a(H)-cholestane (20S)	$C_{27}H_{48}$	372	17.86	21.667	6.54	5.909	b
5a(H),14ß(H),17ß(H)-cholestane (20R)	$C_{27}H_{48}$	372	42.59	49.867	16.815	16.169	b
5a(H),14ß(H),17ß(H)-cholestane (20S)	$C_{27}H_{48}$	372	26.08	31.302	12.15	11.628	b
5a(H),14a(H),17a(H)-cholestane (20R)	$C_{27}H_{48}$	372	17.89	20.351	6.54	6.175	b
5a(H),14a(H),17a(H)-ergostane (20S)	$C_{28}H_{50}$	386	17.86	20.68	10.275	10.165	b
5a(H),14ß(H),17ß(H)-ergostane (20R)	$C_{28}H_{50}$	386	41.22	48.551	28.035	27.436	b
5a(H),14ß(H),17ß(H)-ergostane (20S)	$C_{28}H_{50}$	386	42.59	50.807	25.23	24.7	b
5a(H),14a(H),17a(H)-ergostane (20R)	$C_{28}H_{50}$	386	15.1	18.189	8.415	7.999	b
5a(H),14a(H),17a(H)-sitostane (20S)	$C_{29}H_{52}$	400	34.34	40.185	18.69	18.525	b
5a(H),14ß(H),17ß(H)-sitostane (20R)	$C_{29}H_{52}$	400	63.2	75.435	24.3	23.351	b
5a(H),14ß(H),17ß(H)-sitostane (20S)	$C_{29}H_{52}$	400	50.82	60.489	26.16	25.251	b
5a(H),14a(H),17a(H)-sitostane (20R)	$C_{29}H_{52}$	400	6.88	7.379	18.69	18.525	b,d

[a]A: concentration relative to organic carbon, bd: below detection limit.

[b]ID = compound identification, for more details see text.

Table 2: Average molecular marker ratios specific for Lake Maruit Bottom Sediments

#	Molecular Marker Ratios*	Value
1	CPI_a (odd/even)	0.89
2	U/RHC	8.16
	U/RMM	0.58
3	Pr/Ph	0.490
4	Pr/C_{17}	0.430
5	Ph/C_{18}	1.351
6	C_{max}	27
7	Ts/Tm	0.833
8	Triplet Ratio	0.560
9	C23Tri/C30αβ	0.060
10	C29αβ/C30αβ	0.787
	Homohopane Index (HHI) for:	
11	C31	0.712
12	C32	0.645
13	C33	0.670
14	C34	0.612
15	C35	0.792
	Sterane epimerization	
16	αααC29[S/(S+R)]	0.610
17	αββC29[S/(S+R)]	0.682

*Abbreviations stand for the following ratios:

- #1. CPI_a = Carbon preference index
- #2. U/RHC = concentration of unresolved complex mixture (UCM)/concentration of Σ resolved Hydrocarbon peaks; U/RMM = concentration of unresolved complex mixture (UCM)/concentration of Σ resolved molecular marker peaks
- #3. Pr/Ph = 2,6,10,14-tetramethylpentadecane (pristane)/2,6,10,14-tetramethylhexadecane (phytane)
- #4. Pr/C_{17} = pristane to C_{17}
- #5. Ph/C_{18} = phytane to C_{18}
- #6. C_{max} = the highest *n*-alkane peak
- #7. Ts/Tm = 18α(H)-22,29,30-trisnorneohopane (Ts)/ 17α(H)-22,29,30-trisnorhopane (Tm).
- #8. Triplet ratio
- #9. C23Tri/C30αβ
- #10. C29αβ/C30αβ
- #11-15. 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}) = [22S/(22S+22R)]
- #16-17. Sterane epimerization parameter at C-20 is calculated for C_{29} for 5α(H),14α(H),17α(H)-C_{29}-sterane and 5α(H),14β (H),17β (H)-C_{29}-sterane as: [(20S)/(20S+20R)]

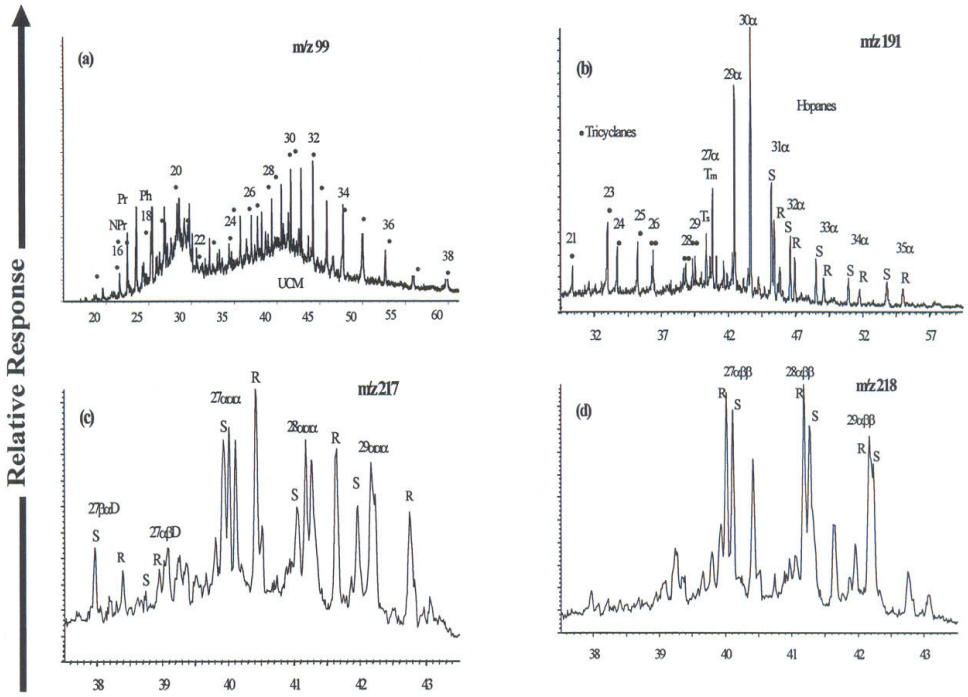

Figure 2: Typical GC-MS fingerprints for: (a) *n*-alkanes, m/z 99 (Pr = pristane, Ph = phytane, Npr = norpristane, UCM = unresolved complex mixture, numbers over peaks indicate carbon numbers); (b) tri- and tetracyclic terpanes "hopane series", m/z 191; (c) ααα sterane series, m/z 217; and (d) αββ sterane series, m/z 218

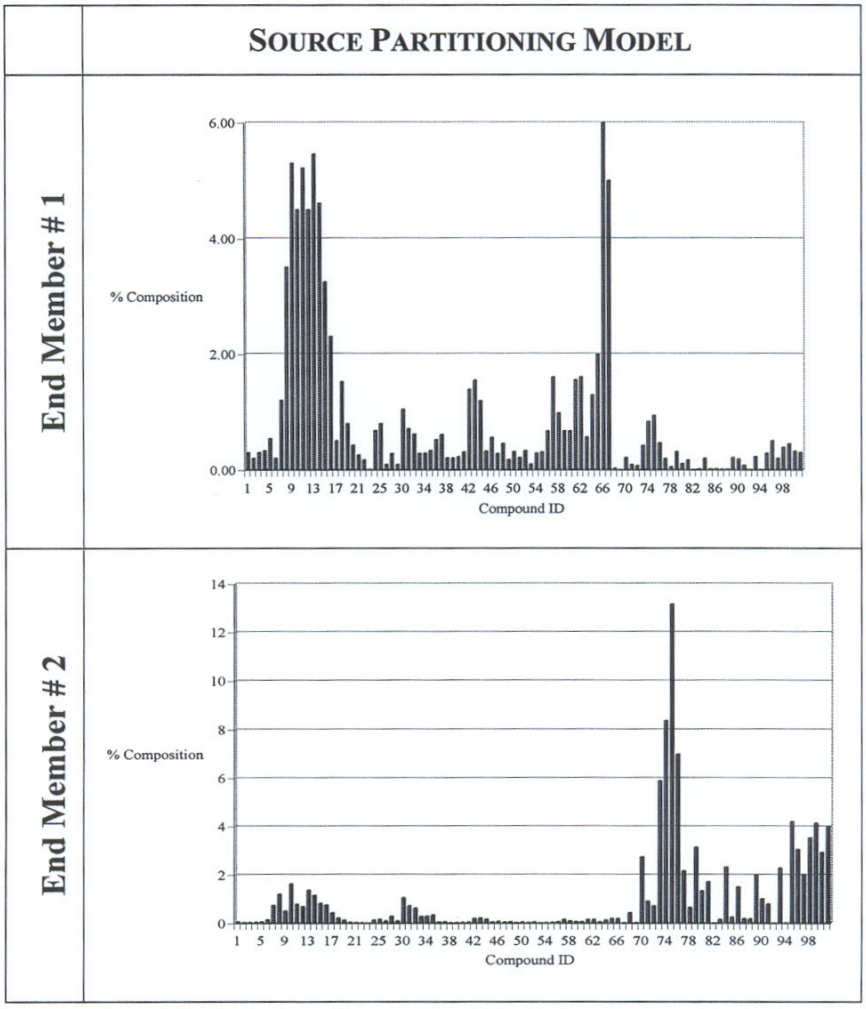

Figure 3: End member compositions (after q-mode factor analysis and linear programming technique) of Lake Maruit bottom sediments.

REFERENCES

Aquino Neto, F.R., Trendel, J.M., Restle, A.,Connan, J. & Albrecht, P.A. (1983). Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum. In *Advances in Organic Geochemistry 1981* (Bjorøy *et al.,* eds.), pp. 695-676. Wiley and Sons, Chichester.

Bailey, N.J.L., Jobson, A.M. & Rogers, M.A. (1973a). Bacterial degradation of crude oil: Comparison of field and experimental data. *Chem. Geol.* 11, 203-221.

Bailey, N.J.L., Krouse, H.R., Evans, C.R., & Rogers, M.A. (1973b). Alteration of crude oil by waters and bacteria-evidence from geochemical and isotope studies. *Amer. Assoc. Petrol. Geol. Bull.* 57, 1276-1290.

Chosson, P., Connan, J., Dessort, D. & Lanau, C. (1992). In vitro biodegradation of steranes and terpanes: A clue to understanding geological situations. In *Biological Markers in Sediments and Petroleum* (J.M. Moldowan, P. Albrecht & R.P. Philp, eds.), pp. 320-349. Prentice Hall, Englewood Cliffs, NJ.

Kassim, T.A. (1998). Characterization, chemodynamics and environmental impact assessment of organic leachates from complex mixtures. Ph.D. Dissertation, College of Engineering, Department of Civil, Construction and Environmental Engineering, Oregon State University, Corvallis, Oregon.

Kassim, T.A. and Simoneit, B.R.T. (2001). *Pollutant-Solid Phase Interactions: Mechanisms, Chemistry and Modeling.* The Handbook of Environmental Chemistry, Water Pollution Series, Volume 5/Part E, Springer-Verlag, Berlin-Heidelberg, pp. 430.

Kassim, T.A. and Williamson K.J. (2003). Environmental Analysis and Impact Assessment of Portland Harbor Contaminated Sediments. *Journal of Environmental Informatics*. 1(1), 58-75

Kvenvolden, K.A., Rapp, J.B. and Bourell, J.H. (1985). Comparison of molecular markers in crude oils and rocks from the north slope of Alaska. *In: Alaska North Slope Oil/Rock Correlation Study, (Magoon, L. B. and Claypool, G. E., Eds.,* American Association of Petroleum Geologists, Tulsa, OK, Study in Geology, No. 20, 593-617.

Peters, K.E. & Moldowan, J.M. (1991). Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. *Org. Geochem.* 17, 47-61.

Peters, K.E. and Moldowan, J.M. (1993). *The Biomarker Guide. Interpreting Molecular Fossils in Petroleum and Ancient Sediments,* Prentice Hall, Englewood Cliffs, NJ, pp. 363.

Philp, R. P. (1985). *Fossil Fuel Biomarkers: Applications and Spectra (Methods in Geochemistry and Geophysics)*. 294pp, Elsevier Science Publishers, Amsterdam.

Prince, R.C., Elmendorf, D.L., Lute, J.R., Hsu, C.S., Haith, C.E., Senlus, J.D., Dechert, G.J., Douglas, G.S. & Butler, E.L. (1994). 17α(H),21β(H)-hopane as a conserved internal marker for estimating the biodegradation of crude oil. *Environ. Sci. Technol.* 28, 142-145.

Seifert, W. K. & Moldowan, J. M. (1979). The effect of biodegradation on steranes and terpanes in crude oils. *Geochim. Cosmochim. Acta* 43, 111-126.

Seifert, W.K. and Moldowan, J.M. (1993). Applications of steranes, terpanes, and monoaromatics to the maturation, migration, and source of crude oils. *Geochim. Cosmochim. Acta*., 42, 77-95.

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

Simoneit, B. R. T. (1986). Cyclic terpenoids of the geosphere. In: *Biological Markers in*

the Sedimentary Record (R.B. Johns, ed.), pp. 43-99. Elsevier, New York.

Simoneit, B. R. T., Mazurek, M. A. & Cahill, T. A. (1980). Contamination of the Lake Tahoe air basin by high molecular weight petroleum residues. *Amer. Pollut. Contr. Assoc. J.* 30, 387-390.

Simoneit, B.R.T. & Kaplan. I.R. (1980). Triterpenoids as molecular indicators of paleoseepage in recent sediments of the southern California Bight. *Mar. Environ. Res.* 3, 113-128.

Simoneit, B.R.T. (1982a). Composition, sources and transport of organic matter to marine sediments - The organic geochemical approach. In *Marine Chemistry into the Eighties* (J.A.J. Thompson & W.D. Jamieson, eds.), pp. 82-112. National Research Council of Canada, Ottawa.

Simoneit, B.R.T. (1982b). Some applications of computerized GC-MS to the determination of biogenic and anthropogenic organic matter in the environment. *Intern. J. Environ. Anal. Chem.* 12, 177-193.

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

Simoneit, B.R.T., Cardoso, J.N. & Robinson, N. (1990). An assessment of the origin and composition of higher weight organic matter in aerosols over Amazonia. *Chemosphere*. 21, 1285-1301.