Project OTPESEM: the fate of organic pollutants in the environment. Extractable organic matter

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Project OTPESEM (Organic Tracers of Pollution in the Environment of the South-Eastern Mediterranean) is a new non-traditional research project in the South-Eastern Mediterranean. The aim of the project is to: (1) identify specific organic molecular markers (hydrocarbons and PAHs) in aerosols, water and sediments; (2) assess fecal sterols and sterones as indicators of urban sewage inputs to Alexandria (Egypt) coastal waters; (3) provide preliminary data on the levels and distributions of indicator microorganisms in domestic sewage-impacted areas for confirmation of pollution; (4) study the distributions, concentrations and fluxes of linear alkylbenzene sulfonates (LAS); and (5) carry out complete statistical analyses of the data in order to evaluate the transport pathways, the regions of concentration, the annual fluxes of selected organic pollution tracers, and to conceptually model the environment. The lack of information about the organic geochemistry of the Alexandria coastal environment initiated this extensive study of organic pollution tracers in the Alexandria metropolitan area. In this paper, our objectives are to report the impact of sewage disposal on the percent and composition of total solvent soluble organic matter. In addition, identification of statistically significant end members, representative of the study area and a conceptual model of the environment of Alexandria are also presented. Alexandria is the principal summer resort of Egypt. It is one of the densely populated regions of the Eastern Mediterranean. The problem of organic pollution of the Alexandria coastal environment has been and is still discussed on a national and multinational scale. The problem is identified as industrial versus agricultural pollution on one hand and sewage pollution on the other. The domination of either depends mainly on the disposal location. The study area (Fig. I) lies off Alexandria between 31°08'-31°26'N and 29°47-30°04'E, extending for about 38 km from El-Agami to Abo-Qir headland. According to the type of regional impact, the coastal waters can be divided into six main zones (Fig. 1). Zone I (beaches) receives a significant amount of untreated sewage ($36x10^6$ m^3/yr); zones II (Eastern Harbor) and III (Western Harbor), the main trading and fishing harbors of the city, receive waste water and untreated sewage ($35x10^6$ m3/yr); zone IV (Kayet Bey) receives domestic sewage from the main metropolitanpumping station ($112x10^6$ m^3); zone V (El-Mex Bay) receives various industrial waters from several outfalls: agricultural ($2200x10^6$ m^3/yr) and chlor-alkali plant ($13x10^6$ m^3/yr); and zone VI (El-Agami) is regarded as the reference area receiving little local discharge.

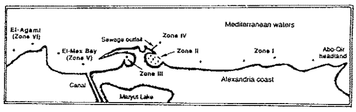

Figure 1: The study area of Alexandria City

Surficial bottom sediments were collected from the study area using a modified Ekman grab, and frozen until analysis. Air dried, sieved samples were Soxhlet extracted with methylene chloride-methanol. This extract after water washing is a measure of the amount of extractable organic matter in the sample (%EOM). The extracts (EOM) were concentrated, hydrolyzed, separated into acidic and neutral fractions, esterified and fractionated by column chromatography. The following fractions were collected: F1 alkanes and alkenes, F2 monoaromatic hydrocarbons, F3 PAHs, F4 esters and ketones, F5 ketones, and F6 alcohols. Assessment of hydrocarbon pollution in a contaminated aqueous environment is generally not conclusive because of changes in waste water discharges, variation in the predominance of certain sources and/or irregular local emissions. The application of the concept that aquatic sediments act as pollutant sinks may overcome this drawback because sediments provide an integrated picture of the events taking place in the water column. For this reason, surficial sediment samples have been analyzed from the Alexandria environment. The %EOM in the area is high compared with other contaminated coastal environments. The HC content the EOM ranges between 18% in the reference area to 66% in zone V. The concentrations of the different extract fractions indicate that alcohols represent about 40, 55 and 28% in zones I, IV and VI, respectively. PAHs represent about 41% of HC in zone V, while alkanes & alkenes represent about 56% in zone II & III.

Table 1: Extractable Organic Matter Composition in the Different Zones of Alexandria

				EXTRACT FRACTIONS (µg/g dry weight)					
ZONE	%O.C.	%EOM	% HC/EOM	F1	F2	F3	F4	F5	F6
I	2.08	0.4112	32.5	312	214	189	291	318	876
II & III	3.07	0.5565	48.3	509	228	176	266	217	494
IV	3.60	0.7811	30.1	417	298	312	241	274	1871
V	4.10	0.8910	56.5	321	301	431	328	228	256
VI	1.50	0.0701	18.0	78	12	50	212	203	212

According to HAMILTON-TAYLOR (1979), a way to convert the sedimentation rate to a weight basis is to use the following formula: **Bulk sedimentation rate (F)=R (1-p)d**, where R= sedimentation rate, p= porosity and R= density. According to ABOUL-DAHAB *et al.* (1990), the sedimentation rate in El-Mex Bay is 0.85 cm/yr, and the average density and porosity of sediments in the bay are 2.6 g/cm^3 and 0.75%, respectively. So, F will be equal to 0.6 $g/cm^2/y$ or 15 $g/m^2/d$. Using the average hydrocarbon concentration in the sediments of El-Max Bay (1053 µg/g, Table 1), and given the surface area of the bay ($19.4x10^6/m^2$), the hydrocarbon sedimentary flux for the whole bay would be: $(15)x(19x10^6)x(1053$ µg/g$)$=300 kg/d. In other words, the sedimentary flux for the different fractions of the extract in El-Mex Bay were: 92, 86, 123, 94, 65 and 73 kg/d for F1 to F6, respectively. Q-mode factor analysis is based on grouping a multivariate data set based on the data structure defined by the similarity between samples. By applying this technique to our data, two significant principal factor loading scores were obtained, giving information about the sample variation of about 93.2% and 4.96%, respectively. The factor loading matrix represented the sample representation in the model and indicated the importance of each of the factors or end members in each sample. After varimax rotation of the composition scores, two significant end members resulted, dominated by the variables as fraction I (alkanes and alkenes) and fraction 6 (alcohols), respectively. Because the transfer of the original data variables during the analysis results in negative factor scores for some variables and negative concentrations of some variables in the end members, the use of a non-orthogonal rotation of end member vectors, toward the mean vector was used to bring the end members into positive vector space. By using a linear programming technique (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, so that they are close to the true compositions. The alkanes and alkenes as the first end member is representative of the Alexandria environment, polluted with oil from ships in both its harbors and El-Mex Bay as well as waste water disposal. The importance of the second end member (alcohols) comes from the dominance of coprostanol (5ß-cholestan-3ß-ol) which is used as a fecal pollution indicator. In conclusion, a significant fraction (20%) of the total solvent extractable matter consists of inorganic salts which should be taken into consideration in quantitative analysis of HC. The reference zone is obviously different than the other polluted zones with varying levels HC. By applying factor analysis to these data, two significant end members were defined as alkanes & alkenes and alcohols, respectively. Future work concerning the molecular composition of the different fractions, qualitatively and quantitatively, will be useful in constructing the Alexandria environmental organic tracers model.