# EVOLUTION OF TRACE METAL LEVELS AND MAGNETIC PROPERTIES IN SEDIMENTS OF THE ELEFSIS GULF, GREECE

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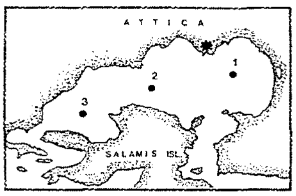


The small (68 km$^2$) and shallow (max depth 33 m) Gulf of Elefsis (Fig. 1) located in the northern part of the Saronikos Gulf, close to Athens and Pireaus, has received particular attention due to its scientific and ecological importance and its relation to the economy of the country. It is connected to the rest of the Saronikos Gulf with two natural narrow and shallow channels and receives considerable amounts of industrial effluents from crude oil refineries, shipyards, steel works, cement, food, electroplating and chemical industries, mainly in its eastern part where the town and the port of Elefsis are located. In this study an attempt is made to trace any trend in the pollution of the area which is continously studied from our laboratory since 1974 (SCOULLOS *et al.*, 1979; SCOULLOS *et al.*, 1986; FOUFA, 1993) by using a combination of chemical partitioning of trace metals and measurements of some magnetic parameters in the sediments for two sampling periods (1988 and 1992). Sea bottom sediments were collected from three sampling stations during two oceanographic cruises on May 1988 and May 1992, using a van Veen box corer. Sediment samples were wet sieved through a 61 μm nylon net, dried at 40°C and subjected to sequential extraction. The reagents used for this procedure were (TESSIER *et al.*, 1979) : **1** : $MgCl_2$ 1M, pH7; **2** : $CH_3COONa$, 1M, pH 5; **3** : $NH_2OH.HCl$ 0.04M, $CH_3COOH$ 25%; **4** : $H_2O_2$ 30%, 0.02M $HNO_3$, 85%; **5** : HF-$HNO_3$-$HClO_4$ 120°C. The sediment fractions extracted respectively broadly correspond to A : Easily exchangable, B : Carbonates, C : Fe-Mn oxides, D : Organics, E : Detrital silicates. Metal concentrations were measured with a Perkin Elmer 2380 AAS system. The magnetic parameters measured were the following (SCOULLOS & ZERI, 1993) :

- 1. Magnetic susceptibility x represents the ease with wich a material can be magnetized. It was measured using a Bartington susceptibility meter at 0.1T and 0.47kHz.
- 2. Saturation isothermal remanent magnetization (SIRM), represents the magnetic content and is measured in a fluxgate magnetometer (Minispin, Molspin Ltd) after placing the sample in a strong d.c. magnetic field (1000 mT) at 24°C temperature
- 3. Frequency depended susceptibility xFd%, defined by the ratio $[(x_1-x_h)/x_1]*100$, ($x_1$:0.1T, 0.47kHz - $x_h$: 1T, 0.47kHz). It helps in idenifying very fine grains (< 0.03 μm).

| Pb-1988 | % | | | | | total |
|---|---|---|---|---|---|---|
| Station | A | B | C | D | E | ug/g |
| 1 | 15 | 10 | 62 | 6 | 7 | 274 |
| 2 | 12 | 12 | 62 | 6 | 8 | 191 |
| 3 | 11 | 11 | 62 | 7 | 9 | 169 |
| Pb-1992 | | | | | | |
| 1 | 19 | 14 | 52 | 10 | 5 | 264 |
| 2 | 19 | 15 | 50 | 10 | 6 | 230 |
| 3 | 20 | 15 | 49 | 10 | 6 | 216 |

| Cu-1988 | % | | | | | total |
|---|---|---|---|---|---|---|
| Station | A | B | C | D | E | ug/g |
| 1 | 2 | 4 | 52 | 34 | 8 | 188 |
| 2 | 3 | 5 | 46 | 36 | 10 | 111 |
| 3 | 2 | 4 | 48 | 34 | 12 | 105 |
| Cu-1992 | | | | | | |
| 1 | 2 | 3 | 54 | 32 | 9 | 178 |
| 2 | 3 | 4 | 48 | 33 | 12 | 123 |
| 3 | 2 | 3 | 51 | 34 | 10 | 121 |

| Zn-1988 | % | | | | | total |
|---|---|---|---|---|---|---|
| Station | A | B | C | D | E | ug/g |
| 1 | 4 | 5 | 55 | 27 | 27 | 632 |
| 2 | 2 | 6 | 46 | 31 | 31 | 332 |
| 3 | 3 | 6 | 40 | 23 | 23 | 181 |
| Zn-1992 | | | | | | |
| 1 | 3 | 5 | 57 | 26 | 9 | 606 |
| 2 | 3 | 3 | 59 | 20 | 15 | 346 |
| 3 | 3 | 5 | 44 | 23 | 25 | 206 |

| Mn-1988 | % | | | | | total |
|---|---|---|---|---|---|---|
| Station | A | B | C | D | E | ug/g |
| 1 | 1 | 21 | 62 | 9 | 7 | 1223 |
| 2 | 1 | 22 | 58 | 9 | 10 | 734 |
| 3 | 1 | 25 | 53 | 0 | 12 | 701 |
| Mn-1992 | | | | | | |
| 1 | 1 | 19 | 63 | 9 | 8 | 1100 |
| 2 | 1 | 20 | 59 | 10 | 10 | 776 |
| 3 | 0.1 | 19 | 59 | 10 | 12 | 655 |

Fig.2. Fractionation of trace metals in surface sediments

The total metal content of the sediments (Fig. 2) reveals that the sediments of the eastern part of the Gulf (st. 1) are enriched in trace metals. Increased concentrations of magnetic particles of anthropogenic origin were also observed at the same station during the 1988 sampling as it becomes clear from the high SIRM and x and the low xFd% values. The SIRM and x values at station 1 were found reduced at the 1992 sampling to the levels of stations 2 and 3 (Fig. 2). This may indicate a reduction of anthropogenic inputs in the area during the period 1988-92, due to the cease of some industrial activities (such as production of iron and steel). Metal concentration levels were similar in the two sampling periods but a slight decrease of total values was observed at station 1 followed by a clear increase at stations 2 and 3. This is probably caused by remobilization and/or transport of metals from particles and sediments of the eastern part of the gulf to the western part. That means that the eastern part acts now not only as a sink but also as secondary pollution source. The sequential extraction procedure for trace metals revealed that the main fraction of the examined metals was connected with Fe-Mn oxides (Fig. 1). High proportion of Cu and Zn was found in the organic fraction whereas elevated percentage of Mn and Pb was connected with carbonates. The percentage of metals held into the alumino-silicate lattice was rather limited and only for Zn exceeded 20%. Significant differentiations in metal partitioning between the two samplings were not observed. From Fig. 3 becomes clear that the variations of SIRM and x were similar with the corresponding variations of trace metal concentrations.

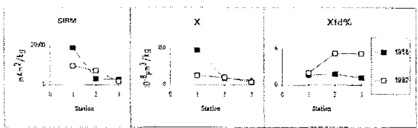


Fig.3. Magnetic measurements in surface sediments

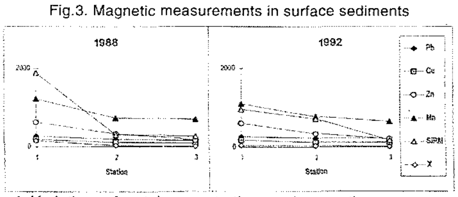


Fig.4. Variations of metal concentrations and magnetic measurements

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M.I. SCOULLOS & C. ZERI, 1993. *Oceanol. Acta*, 16,1 : 53-61.

# POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN THE NEARSHORE SUPERFICIAL SEDIMENT OF BOUISMAIL'S BAY (ALGERIA)

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The stability of the sedimentary phase and its important role in the accumulation of chemicals makes it interesting for monitoring purposes of PAHs. In order to check their concentrations, twenty six stations were sampled in the Bouismail's bay (fig. 1) during the summer 1992. This bay is surrounded by small touristic and/or urban settlements where agriculture is the main activity. Four marinas and fishing ports are present in the area and three important rivers discharge their waters in the bay : Mazafran, Nador and Beni-messous.

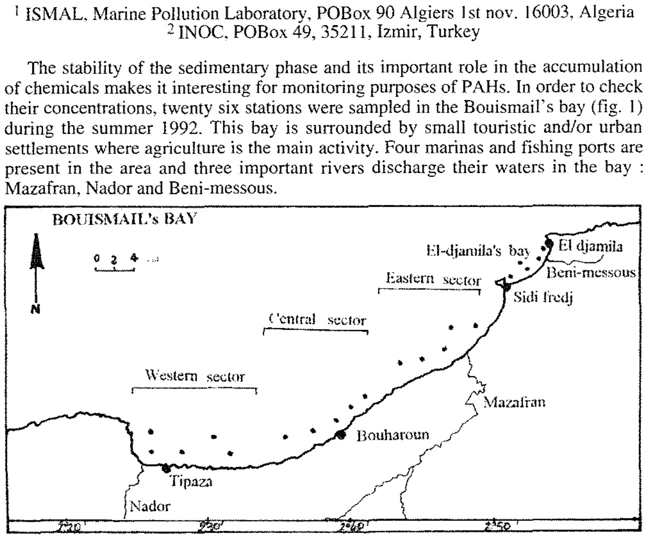


Fig. 1: Bouismail's bay : sampling stations

Sediments were collected with a Van-Veen grab and stored in glass flasks at - 18°C. The analysis was held using UVSF according to the IOC (1982) protocole. Results are expressed in μg/g dry weight (chrysene equivalents). Intercalibration exercises were carried out on a lyophilised material coded SDK 1 (IAEA, Monaco). In order to estimate the percentage of PAHs in accordance with the number of aromatic rings, the synchronous spectra technique, as described by LLYOD (1971), is used. The data in table 1 are given by having divided Bouismail's bay into three major sectors. Following a decreased PAHs concentrations diagram : western, central and eastern sectors; El-djamila's bay can be integrated into what we defined as the eastern sector. Standard deviations are high : this is due to the heterogenous distribution of PAHs in each sector. Petroleum products inputs are important at all stations : 2, 3 and 4 rings PAHs are present in elevated proportions (> 70 %); diagenic and / or pyrolytic compounds are also present in all samples : they range from 12 to 34 %.

| SECTOR | | PAHs μg/g | 2 rings (%) | 3-4 rings (%) | 5 & + rings (%) |
|---|---|---|---|---|---|
| El djamila | range | 0.11 - 1.18 | 23.6 - 33.4 | 27.5 - 47.8 | 12.7 - 22 |
| Bay. | mean | 0.72 | 30.7 | 40.1 | 18.8 |
| n = 5 | S D | 0.49 | 2.9 | 7.5 | 3.7 |
| Eastern | range | 0.26 - 1.24 | 21.9 - 38.5 | 30.4 - 45.2 | 14.6 -32.1 |
| sector | mean | 0.69 | 33.3 | 37.8 | 19.1 |
| n = 5 | S D | 0.39 | 6.8 | 5.3 | 7.3 |
| Central | range | 0.46 - 3.06 | 17.2 - 30.2 | 35.4 - 45.2 | 21.1 - 34.3 |
| sector | mean | 1.46 | 25.5 | 41.4 | 26.4 |
| n = 5 | S D | 0.99 | 5.4 | 3.4 | 4.8 |
| Western | range | 0.72 - 4.23 | 32.1 - 40.2 | 37.0 - 45.2 | 11.7 - 21.2 |
| sector | mean | 2.22 | 36.1 | 40.8 | 16.3 |
| n = 5 | S D | 1.37 | 3.6 | 3.3 | 3.6 |
| Sidi fredj | n = 2 | 8.6 | 49.2 | 28.9 | 14.2 |
| port | | 13 | 19.7 | 51 | 24.1 |
| Bouharoun | n = 2 | 3.9 | 33.1 | 41.3 | 21.5 |
| port | | 8.7 | 47.9 | 24.4 | 12.9 |
| El djamila port | n = 1 | 3.4 | 35.8 | 39.4 | 16.6 |
| Tipaza port | n = 1 | 7.8 | 21.5 | 40.5 | 34.1 |

Table 1 : PAHs concentrations in the superficial sediment of Bouismail's bay.

Harbour levels appear high : these particular sites are influenced by touristic and fishing activities which increase during the summer.

A part from the ports, the arithmetic means indicate that Bouismail's bay is only moderately polluted in comparison with other regions of the Algerian coastline, where PAHs concentrations range from 1.2 to 36 (μg/g) in Algiers' bay, and from 1.9 to 28.8 (μg/g) in Arzew's gulf (SELLALI *et al.*, 1993). Compared with data given for Habibas islands (0.087 μg/g), a site considered as a reference sector (SELLALI *et al.*, 1992), the studied area appears to be contaminated by PAHs.

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