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POLLUTION STUDIES OF TRACE ELEMENTS IN SEDIMENTS FROM THE UPPER SARONIKOS GULF, GREECE

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Seventeen trace elements (As, Ce, Co, Cr, Cs, Eu, Fe, Hg, Hf, La Lu, Rb, Sb, Sc, Sm, Yb and Zn) have been determined by Instrumental Neutron Activation Analysis in sediments from the upper Saronikos Gulf, Greece. It was found that the discharge of industrial and domestic wastes in the Keratsini and Elefsis bays of the upper Saronikos Gulf had led to elevated concentrations of all toxic and other trace elements determined over at least 100 km^2 of seafloor. Increases above natural level range from 2 fold for rare earths to 200 fold for arsenic.

Introduction

Several trace elements are known to be essential, non-essential or toxic for animal life.[1–8] However, all elements in high concentrations may become toxic to organisms.[9] Monitoring of the marine environment should therefore include as many trace elements as possible.

Several investigators[10–24] have found high trace element concentrations in estuarine and coastal sediments where high anthropogenic activity occurs.

The untreated domestic and industrial waste water for most of the greater Athens Greece area is discharged into relatively shallow water of Keratsini and Elefsis bays at the upper end of semi-enclosed Saronikos Gulf. Keratsini bay is the discharge point of the Athens sewage outfall. Most of the industries of the city also discharge via this outfall. Keratsini bay also receives waste water from a fertilizer factory and other industries outside Piraeus harbor. Elefsis bay is surrounded by at least 25 large industries which discharge effluents to the bay. Such discharges usually contain harmfull substances including toxic trace elements.

Heavy metals and other pollutants when discharged to the marine environment will be transported by prevailing currents and removed by either physical, chemical

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or biological processes. Either through adsorption, ion exchange, complexing or chelation trace elements are picked up by particulate or organic matter and settle on the bottom. Although circulation patterns may change seasonally and even over much shorter periods, the bottom sediments are continually accumulating on the sea floor and are, therefore, a record of the long term input, dispersal and settling processes in the overlying waters.

In a previous work elevated concentrations of 7 heavy metals were found by Instrumental Neutron Activation Analysis (INAA) in sediments collected near the Athens sewage outfall area.[25]

In this work a more intensive multielement study of sediments from Elefsis and Keratsini bays was made applying INAA. The 17 trace elements selected are: As, Hg, Cr, Zn, Sb, Ce, Co, Cs, Eu, Fe, Hf, La, Lu, Rb, Sc, Sm and Yb. The aim of this investigation is (1) to examine a wider sea floor which is polluted with trace elements by waste water discharges in the upper Saronikos Gulf, (2) to outline the extent of pollution areas, (3) to delineate more accurately the trace element dispersal patterns and pin-point individual sources and (4) to determine a greater number of toxic and non toxic trace elements by practical INAA (30 min irradiation – 60 min counting).

Experimental

Sampling

At the beginning of 1975, 84 sediment samples have been collected from Elefsis, Keratsini and Piraeus harbor sea floor areas with a snapper grab sampler of ~20 cm maximum penetration. Elefsis and Keratsini bays of the upper Saronikos Gulf with sample locations are shown in Fig. 1. On board of the research vessel, care was taken to select a subsample from each collected sediment sample corresponding to the upper 5 cm of sediments and to avoid metal contamination from the grab sampler itself. Subsamples of sediments were placed in plastic bags. On shore the samples were frozen until ready for analysis.

Preparation of samples and standards for irradiation

Sediment samples were thawed and then centrifuged with a Sorvall RC-2 automatic centrifuge at 9000 g for 30 min to remove excess sea water. They were then air-dried at about 25 °C for 3–4 days (until less than 5% moisture retained) and subsequently homogenized by grinding. Approximately 0.5 g of each sample were placed in polyethylene vials (10 X 30 mm); Synthetic standard mixtures of the elements Ag, As, Co, Cr, Cs, Fe, Hg, Rb, Sc, Sb and Zn were prepared. Standard so-

lutions were placed in quartz tubes (10 X 30 mm). A standard pottery sample[26] – kindly offered to us by Prof. I. PERLMAN – was also used for calibration as well as for rare earths, Hf and Ta determination. Pottery standards, weighing ~0.25 g each, were placed in plastic vials as well.

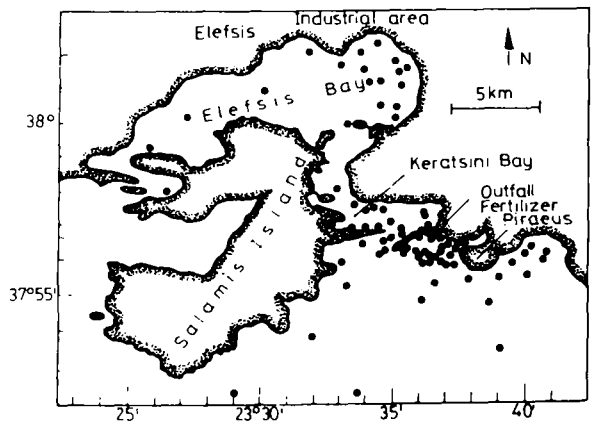

Fig. 1. Elefsis and Keratsini bays of the upper Saronikos Gulf with sample locations

Irradiation

The plastic and quartz tubes were heat-sealed and irradiated for 30 min in the "Demokritos" swimming pool Reactor of the Nuclear Research Center of Greece using the rotation system (thermal neutron flux density $2.2 \cdot 10^{13}$ n · cm^{-2} · sec^{-1}).

Gamma-ray spectrometry

Gamma-ray spectrometry was carried out with a 37 cm^3 ORTEC Ge(Li) detector connected to a 4000 channel Intertechnique analyser. The system was adjusted so that every channel corresponded to 1 keV. System resolution was about 4 keV and the peak to Compton ratio was about 20 : 1 for the 1332 keV peak of ^{60}Co. The efficiency of the Ge(Li) detector was about 5%. The analyser was coupled with an Ampex magnetic tape memory system. The magnetic tape output was fed to the CDC 3300 Computer of the Demokritos Center. The data were processed using the routine activation analysis Computer program of our Laboratory "ACT-ANAL 6".[27]

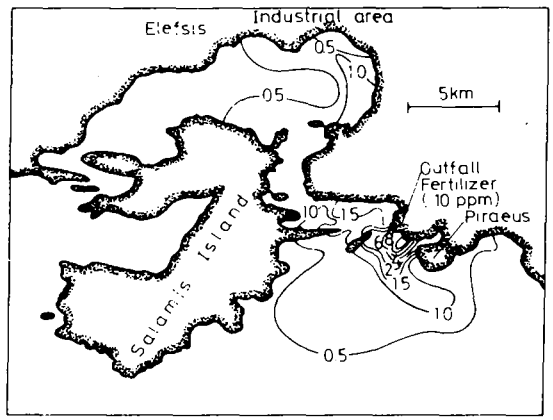

Fig. 2. Distribution of mercury (ppm) in sediments from the upper Saronikos Gulf

Measurements

After irradiation the samples and standards were counted for one hour on the Ge(Li) detector twice. Once they were measured after a cooling period of one week to allow most of the ^{24}Na activity to decay to a negligible amount. This analysis was performed for radionuclides with half lives ranging from 1–7 days in order to get results for As, Hg, La, Lu, Sm and Yb. After the first counting the areas under the photopeaks corresponding to the γ-rays[28] of ^{197}Hg at 78 keV, ^{153}Sm at 103 keV, ^{177}Lu at 208 keV, ^{175}Yb at 396 keV, ^{76}As at 559 keV and ^{140}La at 1595 keV of samples and standards were compared.

The second counting of samples was made after a cooling period of 2 weeks for radioactive species with half lives greater than 7 day to obtain data for Ce, Co, Cr, Cs, Eu, Hf, Fe, Rb, Sb, Sc, Zn. After counting the area under the photopeaks corresponding to the γ-rays[28] of ^{141}Ce at 145 keV, ^{51}Cr at 320 keV, ^{181}Hf at 482 keV, ^{134}Cs at 796 keV, ^{46}Sc at 889 keV, ^{86}Rb at 1077 keV, ^{59}Fe at 1099 keV and/or at 1291 keV, ^{65}Zn at 1115 keV, ^{60}Co at 1173 keV and/or at 1332 keV, ^{152}Eu at 1408 keV and ^{124}Sb at 1691 keV of samples and standards were compared.

Results and discussion

Distribution of trace elements in the sediments of the upper Saronikos Gulf

The results (in ppm dry weight) of Hg, As, Sb, Cr and Zn in sediments throughout the upper Saronikos Gulf are plotted in Figs 2–6.

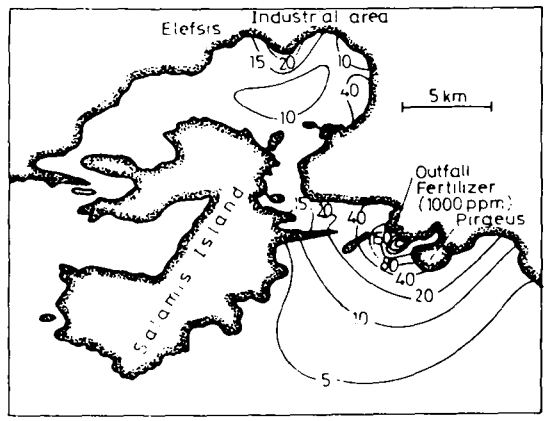

Fig. 3. Distribution of arsenic (ppm) in sediments from the upper Saronikos Gulf

Mercury

The distribution of Hg in the sediments from the upper Saronikos Gulf is shown in Fig. 2. Concentrations range from 0.5–10 ppm, a 20 fold increase over natural or background levels. The highest values of 9 to 10 ppm Hg are found at the entrance of Piraeus Harbor. Mercury levels at sewage outfall are 2 to 3 ppm about 6 times higher than natural levels. The whole of Keratsini bay has concentrations 2 to 4 times above background. The dominant dispersal path for Hg from the Piraeus Harbor area is to the southeast down-coast around Piraeus and southwest into Keratsini bay along Salamis island. Central Elefsis bay has natural levels of Hg whereas concentrations are 2 times higher in the far eastern end. Approximately 20 km^2 of the upper Saronikos Gulf seafloor has Hg values 2 times higher than background levels.

Arsenic

Fig. 3 shows the concentrations of As in the sediments from the upper Saronikos Gulf. The patterns of As distribution are similar to those of Hg. However a greater seafloor area of the upper Saronikos Gulf is affected by As pollution. Arsenic values show the greatest increase – 200 fold – above natural or background levels of any of the trace elements determined in this study. The highest values of about 1000 ppm As are found just outside Piraeus Harbor in the red muds which occur offshore from the fertilizer factory. Levels of As around the sewage outfall were found to be 20 times higher than those of natural levels. Elefsis bay has As values 2 to 8 times higher than background, with the highest levels in the easter basin.

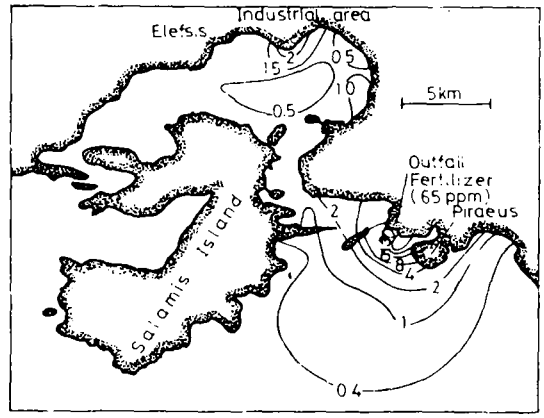

Fig. 4. Distribution of antimony (ppm) in sediments from the upper Saronikos Gulf

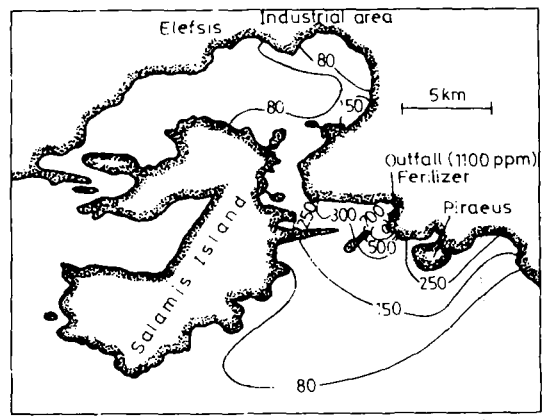

Fig. 5. Distribution of chromium (ppm) in sediments from the upper Saronikos Gulf

Antimony

Fig. 4 shows the concentrations of Sb in the sediments from the upper Saronikos Gulf. The patterns of Sb distribution are very similar to those of As, but Sb concentrations are approximately an order of magnitude lower than those of As. Antimony values in the polluted areas of the upper Saronikos are about 160 times greater than natural levels. Peak values of 65 ppm Sb are found in the entrace to Piraeus Harbor. Levels of Sb around the sewage outfall are 40 times higher than natural levels. Values of Sb 2–5 times above background were found in the northern and eastern part of Elefsis bay.

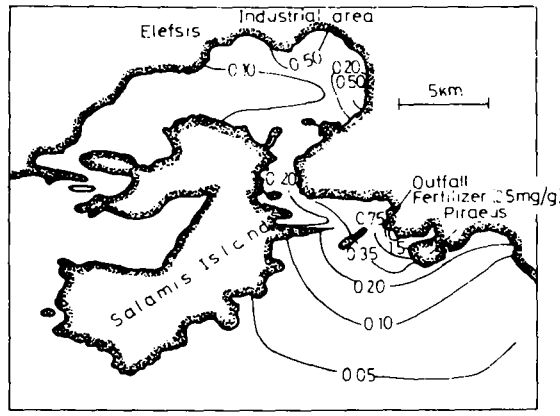

Fig. 6. Distribution of zinc (mg/g) in sediments from the upper Saronikos Gulf

Chromium

The concentrations of Cr in the sediments from the upper Saronikos Gulf are shown in Fig. 5. The distribution patterns of Cr are different than those of Hg, As and Sb. Background levels of Cr in sediments are about 80 ppm which increase to 1100 ppm around the sewage outfall. Values around the outfall are 5 times higher than those off Piraeus Harbor. The outfall is apparently the chief source of this micropollutant. The seafloor entrance of the Piraeus Harbor has about 250 ppm of Cr and these values extend southeast around Piraeus and southwest along Salamis island. Elefsis bay sediments have natural levels of Cr whereas concentrations 2 times higher than background are found in the far eastern basin.

Zinc

The concentrations of Zn in the sediments from the upper Saronikos Gulf are shown in Fig. 6. Background levels of Zn in sediments of Keratsini and Elefsis bays are about 50 ppm. Peak values are 30–50 times higher than natural levels around the outfall and off Piraeus Harbor. Zinc values in Elefsis bay sediments are again lower than those of outfall – Piraeus Harbor seafloor, but about 2 to 10 times higher than natural levels.

Micropollutant index of Hg, As, Sb, Cr and Zn

In a previous work[25] in an attempt to combine or average out the distribution patterns of the individual toxic trace elements, a micropollutant index was introduced. This index combines the concentration values for each element into a single

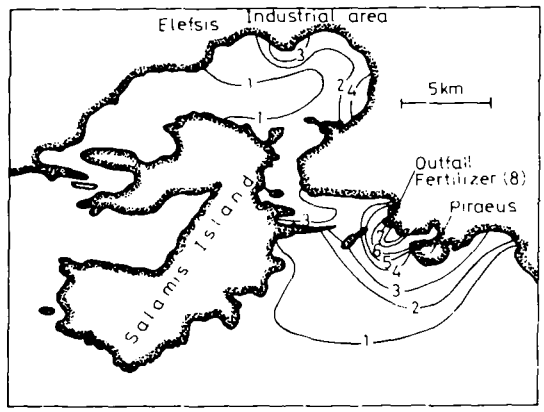

Fig. 7. The micropollutant index

$$\lg \frac{As \cdot Cr \cdot Hg \cdot Sb \cdot Zn}{As_0 \cdot Cr_0 \cdot Hg_0 \cdot Sb_0 \cdot Zn_0}$$

in sediments from the upper Saronikos Gulf

parameter, defined as the logarithm of the ratio of the product of the concentration of the elements at each station, relative to a reference station (the station farthest from the polluted area). The micropollutant index of Hg, As, Sb, Cr and Zn in sediments from the upper Saronikos Gulf is shown in Fig. 7. This index indicates in Keratsini bay maximum pollution near the outfall and outside Piraeus Harbor. In Elefsis bay maximum pollution of the 5 toxic trace elements in sediments was found in the northern and eastern part of the bay. At least 100 km^2 of seafloor in the Elefsis–Keratsini upper Saronikos Gulf area has elevated Hg, As, Cr, Sb, Zn concentration. The dispersal paths from the Piraeus Harbor Athens outfall area extends southeast along Piraeus, west into Keratsini bay and southwest along the Salamis island.

Rare earths

The six rare earths (Ce, Eu, La, Lu, Sm, Yb) determined in this study follow similar distribution patterns with those of Hg, As and Sb. Peak values are found near the entrance of Piraeus Harbor ranging 8–30 times higher than natural levels. Increased concentrations of rare earths 2–5 times higher and 1.3–3 times higher than background levels were also found in sediments of the Athens sewage outfall and in Elefsis bay, respectively. The micropollutant index of Ce, Eu, La, Lu, Sm and Yb is shown in Fig. 8. Dispersal pattern is somewhat similar with those of the 5 toxic trace elements (Hg, As, Sb, Cr, Zn) in this study. However, it is less widespreaded and limited along the southwest towards the Salamis island.

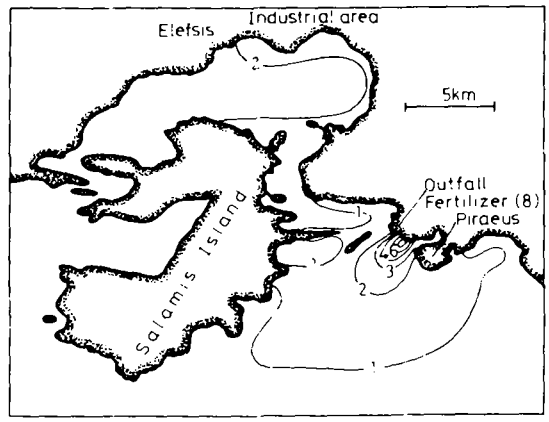

Fig. 8. The micropollutant index

$$\lg \frac{Ce \cdot Eu \cdot La \cdot Lu \cdot Sm \cdot Yb}{Ce_0 \cdot Eu_0 \cdot La_0 \cdot Lu_0 \cdot Sm_0 \cdot Yb_0}$$

in sediments from the upper Saronikos Gulf

Cobalt-hafnium-iron

These 3 elements follow the distribution pattern of the rare earths. Peak values for iron, however, from Piraeus Harbor area sediments are 10 times higher than those of sewage outfall and Elefsis bay sediments.

Cesium-rubidium-scandium

Concentrations of Cs, increased to the same extent, are found in sediments in the entrance of Piraeus Harbor, near the Athens sewage outfall and in Elefsis bay. Rubidium does not follow a distinct dispersal pattern, while Sc does not show any significantly elevated concentrations in the examined areas of seafloor of the two bays.

Lower and upper limit values of trace element concentrations in sediments of the upper Saronikos Gulf

Table 1 presents maximum trace element concentrations in sediments taken from very polluted parts of seafloor of Piraeus Harbor, Athens outfall and Elefsis bay, as well as minimum trace element concentrations in sediments collected from seafloor which appears to be unpolluted. Values given are means of at least 3 different sediment samples. Maximum concentration of Cr was found in the vicinity of the Athens sewage outfall. Maximum concentration of all the other trace ele-

Table 1
Low and upper limit values of trace element concentrations in sediments of Saronikos Gulf

Element	Minimum concentration Bg level, ppm	Maximum concentration		
		Piraeus Harbor, ppm	Athens outfall, ppm	Elefsis bay, ppm
As	5	1 000	100	40
Cr	80	250	1 100	150
Hg	0.5	10	3	1
Sb	0.4	65	15	2
Zn	50	2 500	1 800	500
Fe	10 000	400 000	40 000	40 000
Co	5	140	18	13
Cs	0.7	4	4	4
Rb	100	700	150	200
Sc	5	6	6	7
Ce	30	300	60	60
Eu	1	11	1.5	1.5
Hf	1.5	10	3	3
La	10	300	50	30
Lu	0.2	4	0.4	0.3
Sm	2.5	20	7	5
Yb	0.7	18	2.5	2

ments were found outside Piraeus Harbor. Elefsis bay is also polluted with toxic and other trace elements but less than Keratsini bay. Maximum increases of trace element concentrations above average natural level in the sediments of the industrial area of the Elefsis bay seafloor range from about 2X for Hg and Cr to 10X for Zn; of the Athens sewage outfall from about 3X for rare earth elements to about 40X for Sb and Zn; and of Piraeus Harbor area from about 6X for Cs to 200X for As.

Precision of the INAA method

In order to check the precision of the proposed INAA method 14 samples were taken from the same sediment sample and analyzed by this method. The overall relative standard deviations per cent (SD%) found are as follows: ±3.2 for Sm, ±3.8 for Sc, ±4.2 for Cs, ±4.3 for As, ±4.4 for La, ±4.8 for Hf, ±5.1 for Co, ±6.6 for Yb, ±6.8 for Cs, ±7.3 for Eu, ±8.3 for Fe, ±9.0 for Cr, ±9.8 for Zn, ±12.7 for Sb, ±14.9 for Hg and ±18.1 for Lu. These SD% are considered satis-

factory because they also include errors originating from the inhomogeneity of the samples belonging to the same sediment sample.

Accuracy

The accuracy of the proposed INAA method for As, Co, Cr, Cs, Fe, Rb, Sb, Sc and Zn was checked by analyzing the pottery standard[26] simultaneously with the sediment samples and standards.

Possible loss of trace elements during irradiation

A set of duplicate sediment samples were irradiated in polyethylene and quartz tubes under exactly the same conditions. No appreciable loss of any trace element was observed in the case of polyethylene tubes.

Interferences

Zinc. The 1115 keV peak of ^{65}Zn was used for the determination of Zn. Interference occurs from the 1120 keV peak of ^{46}Sc. To avoid this, the computer takes the left half of ^{65}Zn photopeak for calculation.

Chromium. Chromium-51 also arises from the irradiation of Fe due to the reaction ^{54}Fe(n, α)^{51}Cr. It was calculated that under our experimental conditions even with sediment samples with maximum Fe concentration (400 000 ppm) this interference is less than 6%.

Arsenic. The 559 keV peak of ^{76}As was used for the determination of As. The main interference is from ^{82}Br 554 keV and ^{122}Sb 564 keV γ-rays. To avoid this, the computer locates the ^{76}As 559 keV photopeak. It sums the peak channel plus one below and one above the peak. For background the computer skips 12 channels above and 18 channels below the peak; it takes 4 channels in each size, sums them and normalizes to the number of channels summed in the peak.

Conclusions

Seventeen trace elements have been determined by INAA in sediments from the upper Saronikos Gulf, Greece. It was found that the discharge of industrial and domestic wastes in the Keratsini and Elefsis bays of the upper Saronikos Gulf has led to elevated concentrations of all toxic and other trace elements determined over at least 100 km^2 of seafloor. Increases above natural level range from 2 fold for rare earths to 200 fold for As. The principal source areas for the trace elements appear to be (1) The industrial plants at the entrance of Piraeus Harbor,

(2) The Athens sewage outfall and (3) The industries in the northern and eastern Elefsis bay. Principal dispersal or transport paths for the trace elements from the Piraeus Harbor-Athens outfall area, where maximum pollution exists, are (1) Southeast along Piraeus and (2) Southwest into Keratsini bay and along the Salamis island.

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