

ZINC IN SEAWATER AND SEDIMENTS

(of the Gulf of Elefsis, Greece)

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Abstract. Dissolved and particulate Zn were measured in the sea water of the small Gulf of Elefsis, near Athens, Greece, for one year and as a function of depth. Particulate Zn was correlated with magnetic properties. Total Zn distribution in surface and subsurface sea bottom sediments and the partitioning of Zn among various sediment fractions were studied on a number of cores. The results for the Gulf of Elefsis are compared to recent results from other areas.

1. Introduction

Zinc in nature is well studied because of its involvement in enzymic reactions; production of radioactive pollutant, Zn-65; accumulation in certain marine minerals; and enrichment in the tissues of marine organisms (Bernhard *et al.*, 1975; Vinogradov, 1953; Goldberg, 1965). Some authors reported that its content generally decreases when going up the food chain (Jernolöv, 1974) and in some cases for older organisms (Papadopoulou *et al.*, 1978). Zinc is a common pollutant found in industrial effluents, such as from textile mills, basic chemicals, electroplating and motors (Bryan, 1971). However, practically nothing is known about Zn contamination in the open sea (Jernolöv, 1974) and relatively little is known about its chemistry in coastal areas, particularly in the eastern Mediterranean which is a region of international environmental concern. Bruland *et al.* (1978) suggested that most of the data reported about Zn in the marine environment are inaccurate, due to gross contamination from faulty sampling and analytical procedures.

In the present paper an attempt was made to systematically study the distribution of Zn in sea water and sea bottom sediments, using clean sampling and analytical techniques. Dissolved and particulate Zn was measured on a monthly basis, over a period of one year in sea water as a function of depth. Total Zn and Zn partitioning among various sediment fractions were also measured in a number of sediment cores.

Preliminary results of the high concentrations of Zn found in the Gulf of Elefsis and the dissolved and particulate distributions have been presented recently by Scoullos (1980a, b).

2. The Area Studied

The Gulf or Bay of Elefsis (both terms are used widely for the same area) (Figure 1) is a small (ca. 68 km²) shallow (maximum depth 33 m) embayment in the northern part of the Saronikos Gulf, close to Athens and Piraeus. It is naturally divided into two parts and is connected to the rest of the Saronikos Gulf by two natural narrow and

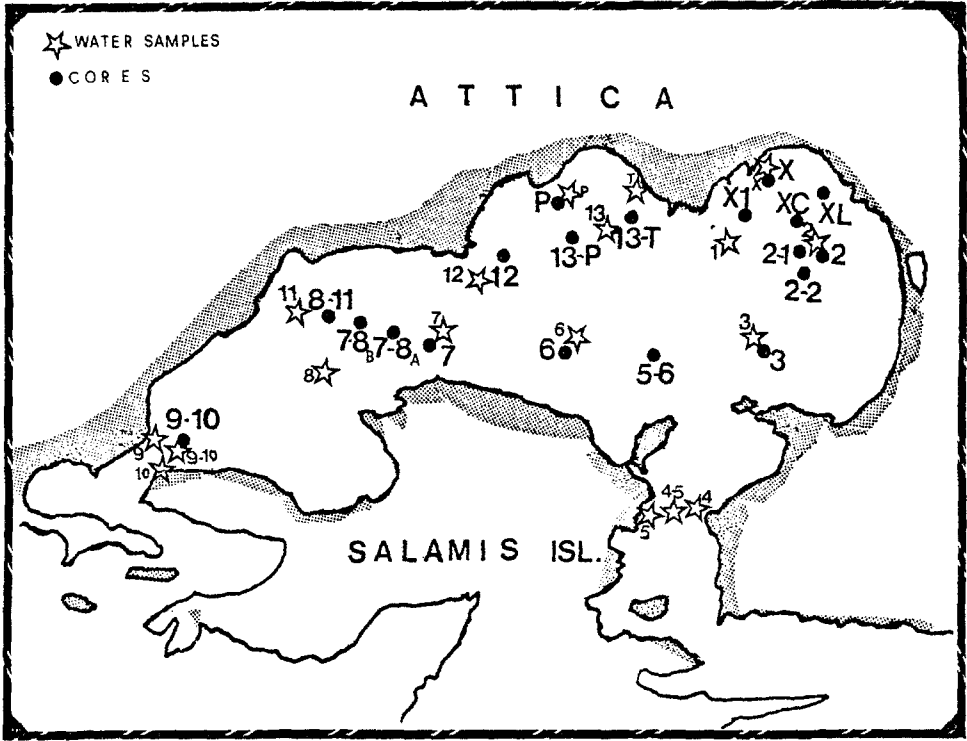


Fig. 1. The grids of the stations sampled in the Gulf of Elefsis (a) for sea water, and (b) for sediments.

shallow channels. It receives considerable amounts of effluents from ~40 industries (crude oil refineries, shipyards, steel works, cement, food, electroplating and chemical factories, etc.) located on its eastern section where the town and the Port of Elefsis are located. The water circulation pattern (Scoullos and Riley, 1978) is mainly clockwise, thermohaline and restricted by shallow sills at the channels.

The water column is well mixed during winter but highly stratified and anoxic at the bottom during summer. Therefore the Gulf is excellent for the study of pollution in combination with redox reactions.

3. Sampling and Analysis

Figure 1 shows the permanent stations (numbered 1 to 13) and some of the stations sampled periodically (M, T, X).

3.1. SEA WATER SAMPLES

Sea water samples were collected monthly at standard depths of 0 (~0.20), 10, 20, and 30 m using 1.25 l and 7.3 l IOS polypropylene sampling bottles and plastic coated

steel wire. For a comparison, surface sea water samples were collected (24 to 28th March 1980) from twelve stations of the Eastern Aegean Sea (between 39° 35' N and 36° 37' N and between 24° 58' E and 27° 17' E).

Accurately measured volumes (usually ~ 5 l) of sea water were filtered through carefully prewashed and preweighed 0.45 µm Nulflow-Oxoid membrane filters and the filtrates were passed through columns containing Chelex-100 resin following the method described by Riley and Taylor (1968). The metal retained by the columns was eluted into polyethylene bottles with three 7 to 10 ml aliquots of 2 M redistilled nitric acid. Additional hydrochloric and ammonia eluates were also collected and analyzed in order to determine the efficiency of the columns. The particulates retained on the filters were dried at 50 °C to constant weight and they were leached at ca. 90 °C with 25 ml of 2 M redistilled nitric acid in covered PTFE beakers for ~ 6 h. Addition of few drops of nitric and hydrochloric acid and repeated leaching was often necessary. The acidic solution was then centrifuged at 3000 r.p.m. and the supernatant was retransferred to the PTFE beaker. After evaporation to almost dryness it was redissolved in 25 ml of 0.1 M redistilled nitric acid.

3.2. SEDIMENT SAMPLES

Sea bottom sediments were collected from seventeen localities (see Figure 1) from which sediment cores up to 1 m long were taken using a pneumatic Mackereth (1969) corer and transparent Perspex core tubes. This method of sediment sampling normally eliminates the metal contamination of the samples and preserves an undisturbed water-sediment interface. Each core was sliced horizontally into subsamples of either 1 or 2 cm depth range. The slices were dried at 50 °C to a constant weight and they were treated repeatedly with HF/HNO₃ in PTFE beakers in order to extract the total Zn content of the sediment. Selected sediment samples were examined for the partitioning of Zn between the different sediment components and the fractions of various sizes.

Three physical procedures were used:

(A) Grinding of total homogenized dried section after manual removal of stones and shells;

(B) Wet sieving through a 560 µm nylon net;

(C) Wet sieving through a 61 µm nylon net; and

(AC) Procedure A followed by procedure C.

The chemical partitioning was conducted using a combination of reagents proposed by Hirst and Nicholls (1958), Lynn and Bonatti (1965), Chester and Hughes (1967) and Gibbs (1973) in a sequence similar to that suggested by Chester (1978) and Scoullos (1979).

3.3. ANALYSIS

A double beam Instrumentation Laboratory 351 Atomic Absorption Spectrophotometer (AAS) was employed for the analysis of all Elefsis Gulf samples, using an

air-acetylene flame at 213.9 nm. The precision/reproducibility of the measurements is given as standard deviation

$$\left(\sigma = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n - 1}} \right),$$

where x is the mean of $n = 8$ measurements and as coefficient of variation (c.v. = $[\sigma \times 100]/x$). The values are $\sigma = 0.0585$ and c.v. = 5.2 for the suspended solids and $\sigma = 3.2$ and c.v. = 3.45 for the sediments respectively. The evaluation of accuracy of the AAS method was made by analysing three USGS rock standards as follows: AGV1: (1) 88, (2) 112, (3) 64–304; BCR1: (1) 161, (2) 132, (3) 94–278; G-2: (1) 69, (2) 75, (3) 42–138; where (1) is the mean of three analyses, (2) is the USGS mean and (3) the range of the results given by other workers using a variety of methods. All measurements are given in $\mu\text{g g}^{-1}$.

3.4. MAGNETIC MEASUREMENTS

The filters holding the suspended solids were measured for saturation isothermal remnant magnetization (SIRM) – which is also roughly proportional to the magnetic susceptibility. The measurements were conducted by first placing the samples in a ‘saturating’ magnetic field, of 1 T (10 kOe) at room temperature and then measuring the magnetic moment induced in and retained by the sample after removal to zero field. A computerised slow speed spinner magnetometer was used. Further description of the method is given by Scoullos *et al.* (1979).

4. Results and Discussion

4.1. DISSOLVED AND PARTICULATE ZINC IN THE SEA WATER

Selected monthly surface isocontours of Zn dissolved (Zn_d) and particulate (in suspended solids (Zn_{ss})) are given in Figure 2. From the distributions it is apparent that the highest concentrations were found in the NE section of the Gulf and along the eastern bank of the eastern channel. The latter observation supports the circulation proposed by Scoullos and Riley (1978), according to which a ‘tongue’ of heavily polluted water, originating from the nearby Athens sewage outfall, enters the Gulf through the channel, particularly when S or SE winds prevail.

The monthly averaged dissolved Zn concentrations (Table I) are high, ranging between 9.3 and 29.2 $\mu\text{g l}^{-1}$. Some of the individual concentrations in the bottom waters or near the point sources are, however, considerably higher (70 to 85 $\mu\text{g l}^{-1}$). The mean annual concentration is nearly 4 times higher than that (5.6 $\mu\text{g l}^{-1}$) found in the open ‘unpolluted’ Aegean Sea (Table II) which is similar to that reported for the same area by Fukai and Huynh-Ngoc (1976a, b) (5.3 $\mu\text{g l}^{-1}$), but significantly lower than that found by Aubert *et al.* (1980) (20 to 40 $\mu\text{g l}^{-1}$) who used anodic voltammetry at pH 4.5.

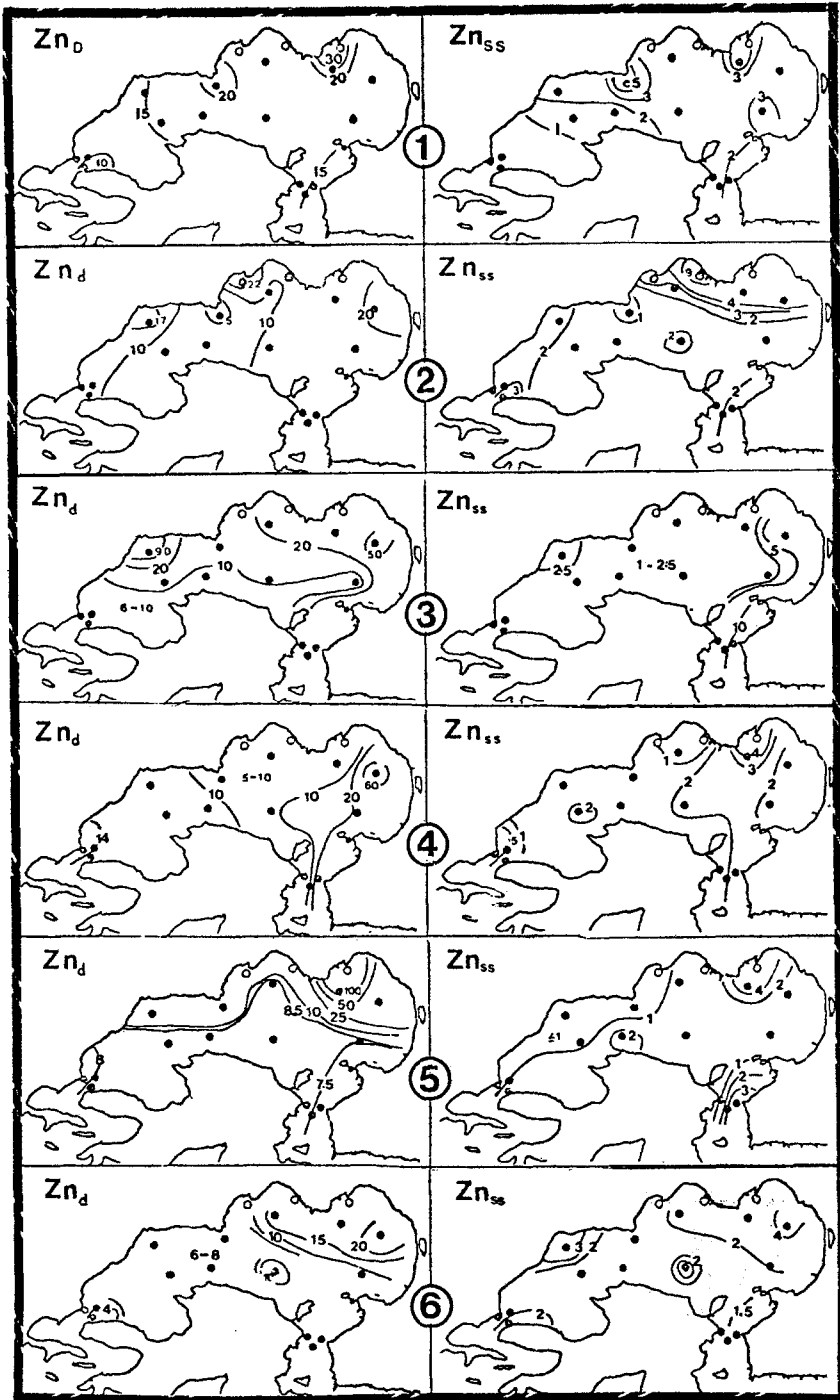


Fig. 2. Surface distributions of zinc dissolved (Zn_d) and in suspended solids (Zn_{ss}) ($\mu g l^{-1}$) for selected cruises: (1) March 1977; (2) April 1977; (3) May 1977; (4) August 1977; (5) January 1978; (6) February 1978.

Zinc in the dissolved form exceeds 80% of the total Zn content. Such a high percentage may be taken as a sign of pollution. Increased dissolved Zn concentrations have been reported also for other polluted regions (Bloom, 1976) and they are partly attributed to the formation of soluble humic and fulvic acid complexes or fine colloids of lipids etc. with Zn. High 'ionic Zn' concentrations were also found in contaminated areas, such as near the shipyards of the Gulf of La Spezia (Bernhard *et al.*, 1975) or the coast of Alexandria, where Zn is thought to be released from the anodic protection plates of ships and the ship paints of which it is an active ingredient (El-Sayed and El-Sayed, 1980).

The monthly averaged concentration of particulate Zn varied between 1.7 and 4 $\mu\text{g l}^{-1}$. The mean annual value (Table I) is also considerably higher than that of the Aegean Sea (Table II) whereas the average Zn content of the particulates (600 $\mu\text{g l}^{-1}$) can be compared only with that of heavily polluted regions and is very similar to the average content of the surface sea bottom sediments. The 'enrichment' of the particulate matter in Zn and other metals is due to the low content of clay and other metal-poor minerals in the sea water because of the absence of rivers in the area.

TABLE I
Monthly average concentrations of Zn ($\mu\text{g l}^{-1}$) in the Gulf of Elefsis

Month	Dissolved	Particulate	Total	Ratio particulate to total (% wt.)
March 1977	24.5	2.1	26.6	7.9
April 1977	20.8	2.2	23.0	9.6
May 1977	26.5	4.0	30.5	13.1
July 1977	29.2	2.7	31.9	8.4
August 1977	13.9	2.6	16.5	15.8
September 1977	11.9	3.2	15.1	21.0
November 1977	11.0	2.0	13.0	15.4
January 1978	17.8	1.7	19.5	8.7
February 1978	9.3	1.7	11.0	15.4
Mean annual	18.3	2.4	20.7	12.8

The elevated concentration of Zn in the Gulf, seems to affect the levels of the metal in the zooplankton. Zafiroopoulos and Grimanis (1977) reported that Elefsis Gulf copepod *Acartia clausi* had Zn concentrations ranging between 800 and 2500 $\mu\text{g g}^{-1}$ whereas the values reported by Martin (1970) and Martin and Knauer (1973) for copepods from 'unpolluted' seas are in the range 50 to 1200 $\mu\text{g g}^{-1}$.

The observed marked seasonal and areal fluctuation of the concentration of Zn is not surprising because of the intensive planktonic activity, the significant variations in the direct input from the industrial and sewage outfalls and the runoff, the differences in the circulation pattern and the redox reactions which are taking place near the bottom during summer and autumn. During August, for example, the water stratifi-

TABLE II
A comparison of the concentrations of Zn found in the Gulf of Elefsis with concentrations reported in other seas

Region	Zn dissolved ($\mu\text{g l}^{-1}$)		Range	Zn particulate		Reference
	Mean			$\mu\text{g l}^{-1}$	$\mu\text{g g}^{-1}$	
World Ocean	3		1-50			Brewer (1975)
World Ocean	5					Riley and Chester (1971)
Atlantic Ocean	3					Preston (1973)
N.W. Atlantic Ocean	4.2					Spencer and Brewer (1969)
North Atlantic	1.5		0.1-16.5		159	Chester and Stoner (1974)
South Atlantic	0.9		2.8-14.6		260	Chester and Stoner (1974)
Gulf of Mexico	9.7		0.7-35			Noshkin (1972)
Beaufort N.C.	1.6		0.8-12.0**			Chipman <i>et al.</i> (1958)
Monterey Bay	6.3*					Knauer and Martin (1973)
North Sea						*Dutton <i>et al.</i> (1974)
						**Bowen (1974)
Eastern Irish Sea	26.6					Preston (1973)
Conway Bay (Wales)	8.8					Elderfield <i>et al.</i> (1971)
1) February 1970		9.0			264	Elderfield <i>et al.</i> (1971)
2) June 1970		2.4			64	Elderfield <i>et al.</i> (1971)
Liverpool Bay	11.86		2.3-47.6			Abdullah <i>et al.</i> (1972)
Cardigan Bay	7.46		3.63-19.7			Abdullah <i>et al.</i> (1972)
Bristol Channel	9.98		3.57-21.4			Abdullah <i>et al.</i> (1972)
1) April 1971					337-370	Abdullah and Royle (1974)
2) June 1971					315-708	Abdullah and Royle (1974)
Severn Estuary	25.8					Butterworth <i>et al.</i> (1972)
Severn Estuary	22.2					Preston (1973)
Tyne - Tees	11.7					Preston (1973)
Clyde (Hunterston)	6.2					Preston (1973)
Firth of Clyde	18					Halorow <i>et al.</i> (1973)
Inners Oslofjord	57.9					Anderson <i>et al.</i> (1975)
Dutch Wadden Sea			7-35.5		310-890	Duinker <i>et al.</i> (1974)
Seine Estuary			6-20			Guegueniat and Gandon (1972)
Escaut Estuary	4.9					Peeters <i>et al.</i> (1973)

Table II (cont.)

Region	Zn dissolved ($\mu\text{g l}^{-1}$)		Zn particulate		Reference
	Mean	Range	$\mu\text{g l}^{-1}$	$\mu\text{g g}^{-1}$	
N.E. Pacific	2.0	0.8-3.4			Knauer and Martin (1973)
China Sea	2.4				Chester and Stoner (1974)
Indian Ocean				231	Chester and Stoner (1974)
Hong Kong waters	92	330 max			Chan <i>et al.</i> (1974)
Cape of Good Hope			0.9 (max)		Van As <i>et al.</i> (1973)
Marion Bay (Australia)			0.41		Ayling (1974)
Derwent Estuary (Australia)	1500				Bloom (1976)
1) Surface, high area			53	2,980	Bloom (1976)
2) Surface, control area			6.4	667	Bloom (1976)
Tasmania					
1) N.W. Coast (high S.S. waters)			10.1	2,850	Anonymous (1974)
2) N.W. Coast (low S.S. waters)			2.5	2,320	Anonymous (1974)
Black Sea	1.9	0.21-12.4			Spencer and Brewer (1969)
Mediterranean	2.3	0.1-7.9			Fukai and Huynh-Ngoc (1976a, b)
N.W. Mediterranean	3.0	0.5-7.9			Fukai and Huynh-Ngoc (1976a, b)
Golfe de Fos (surface)	46.3	6.0-120			Benon <i>et al.</i> (1978)
(bottom)	48.5	3.2-400			Benon <i>et al.</i> (1978)
S.W. Mediterranean	1.4	0.1-4.1			Fukai and Huynh-Ngoc (1976a, b)
Tyrrhenian Sea	10	0.2-2.3			Fukai and Huynh-Ngoc (1976a, b)
Ionian Sea	1.4	0.7-2.4			Fukai and Huynh-Ngoc (1976a, b)
Cretan Sea	1.5				Fukai and Huynh-Ngoc (1976a, b)
Alexandria Harbort (surface)	210.9	58-450			El-Sayed and El-Sayed (1980)
Aegean Sea		20-40			Aubert <i>et al.</i> (1980)
Aegean Sea	5.3	4.7-5.8			Fukai and Huynh-Ngoc (1976a, b)
Aegean Sea (Eastern)	5.6	4.8-8.9	1.0		Present work
Gulf of Elefsis	18.3	4.2-85	2.4	600	Present work

(all depths throughout the year), including high individual values.

cation in the Gulf reaches a maximum (Figure 3) and the bottom layer of the water column is practically anoxic. Therefore the drastic decrease of dissolved Zn and the concurrent increase of the Zn_{ss}/Zn_{tot} ratio (see Table I and Figure 3 for station 8 at

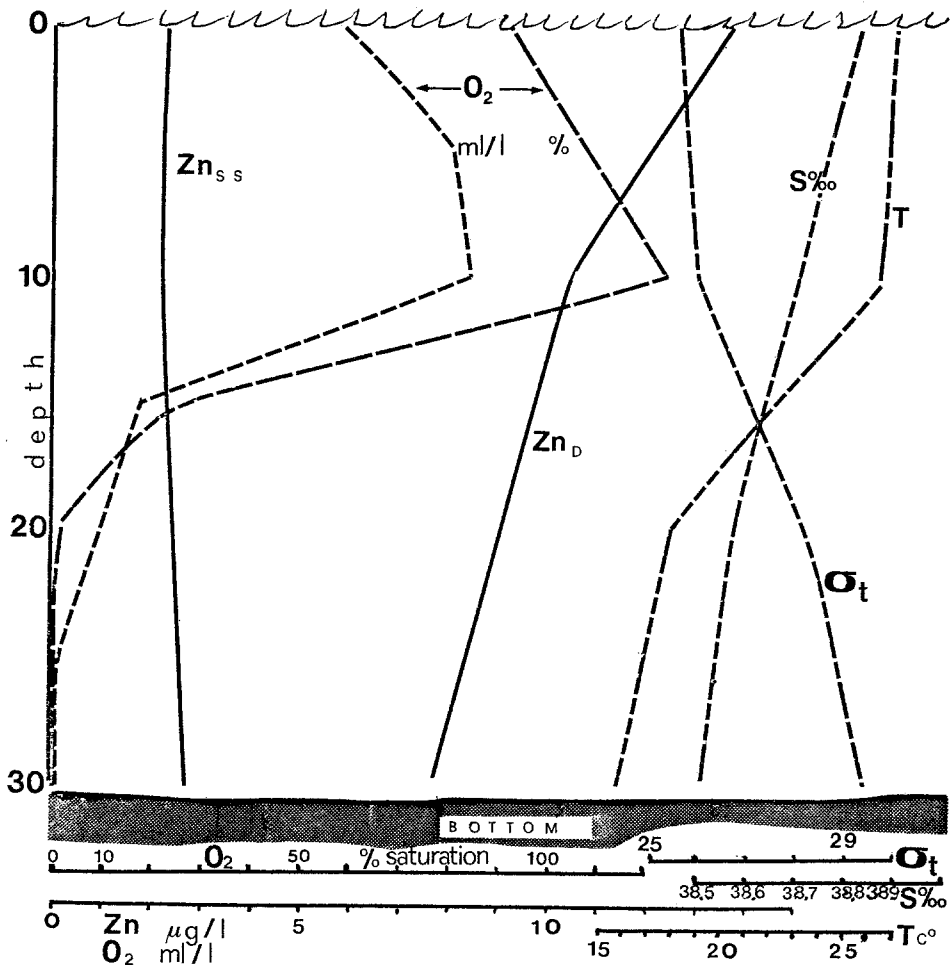


Fig. 3. Profile of zinc dissolved and particulate, dissolved oxygen, temperature, salinity and density (σ_t) at st. 8 (August 1977).

the deepest part of the Gulf) may be partly attributed to the minimum Zn inputs, the removal of Zn from the water column due to formation of sulphides and mainly to the ability of Zn to be readily adsorbed on newly formed particles (Davies and Leckie, 1978) sinking to the bottom. Uptake by marine organisms (such as zooplankton which had its seasonal maximum development in July) is another possible process by which the metal can be removed from the dissolved state (Krauskopf, 1956).

Resuspension of the uncompacted muds, formed under reductive conditions during summer, leads, later in the year when the water is again well mixed and aerated, to oxidation of the insoluble sulphides and moderate, slow liberation of Zn ions. This is

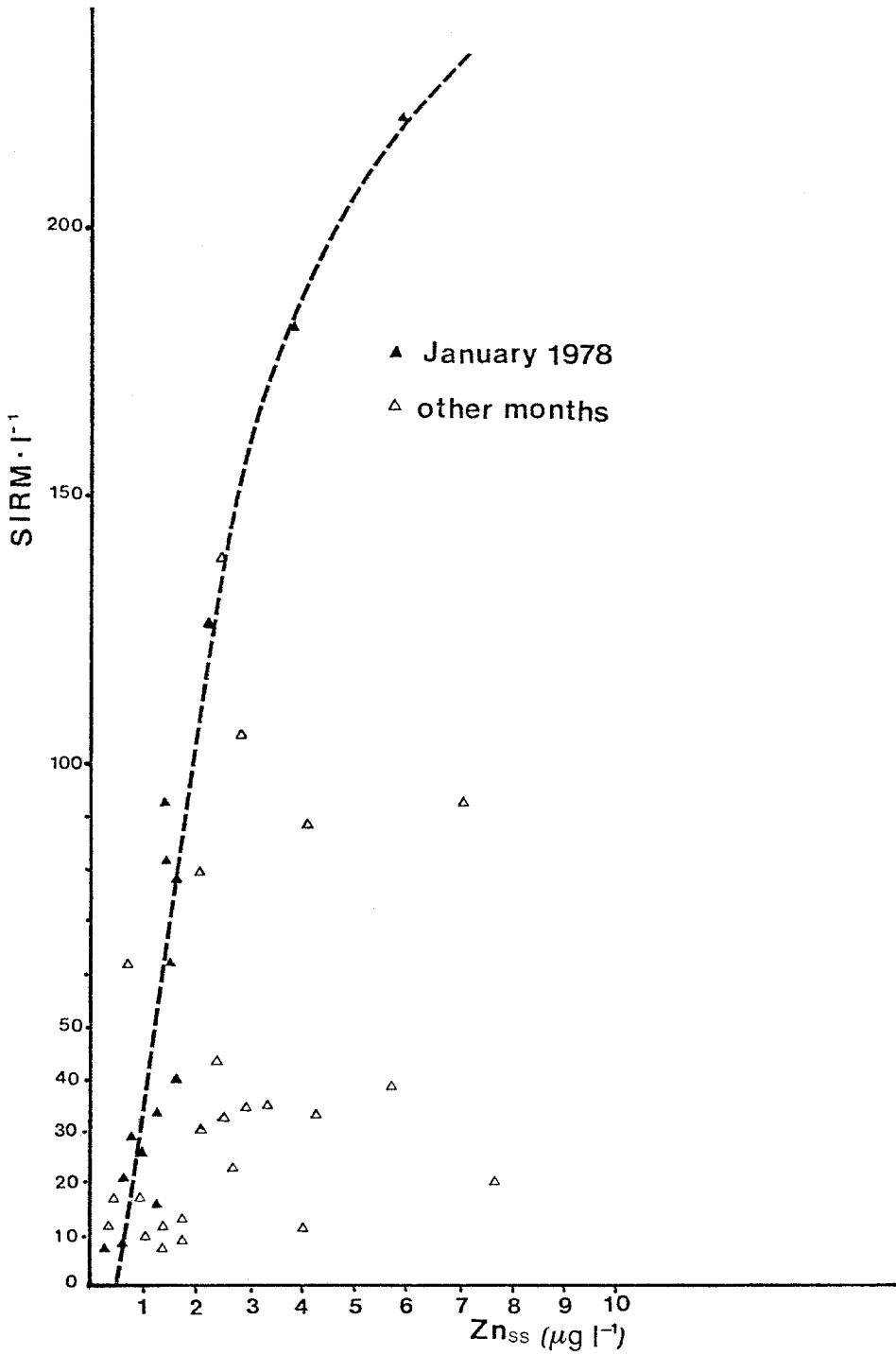


Fig. 4. The correlation between SIRM and total particulate zinc.

responsible for the almost constantly higher concentration of dissolved Zn at the bottom waters, even during periods of thorough mixing. The enrichment of the water in Zn from the sediments is normally augmented by the runoff during the rainy period. However when the rainfall is particularly heavy (like that of winter 1977–78) and because the water volume of the Gulf is small, dilution sometimes prevails, resulting in a minimum increase or even an occasional decrease of the Zn concentration.

It is noteworthy that a good correlation was found between the total particulate Zn and the saturation isothermal remnant magnetization (SIRM), particularly during January 1978 (Figure 4) when the Zn concentration was relatively high and the phytoplankton bloom minimal, as it is deduced from the chlorophyll *a* patterns. Apart from Fe (Scoullou *et al.*, 1979; Oldfield *et al.*, 1979), Zn is the only metal that shows such a good correlation, indicating a binding mechanism – probably adsorption – of Zn onto magnetically active particles that are rich in Fe.

A relatively high association between Fe and Zn and a tendency of Zn to be adsorbed onto solid Fe particles have been also observed by other investigators (Duursma *et al.*, 1975; El-Sayed and El-Sayed, 1980).

4.2. ZINC IN THE BOTTOM SEDIMENTS

The spatial distribution of total Zn in the surface sediments of the Gulf closely resembles those of the water, showing three very 'high' spots near the steel works, the

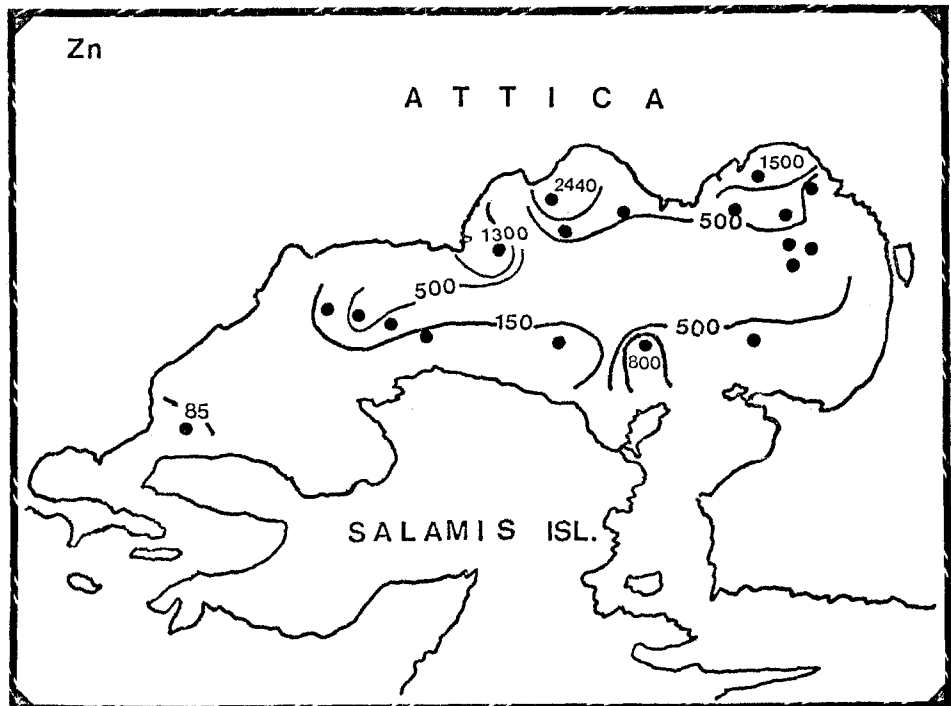


Fig. 5. Distribution of total zinc ($\mu\text{g g}^{-1}$) in the surface sediments of the Gulf of Elefsis.

shipyards, the cement and some other chemical factories (1500, 1300 and 2440 $\mu\text{g g}^{-1}$ respectively, see Figure 5). These point sources indicate the considerable contribution of the industrial wastes in the pollution of the area. Surface samples taken from the entrance of the eastern channel also had elevated concentrations, influenced probably by the Keratsini sewage outfall.

Relatively high concentrations were also found at the central deep part of the Gulf which becomes anoxic and very rich in organic C during summer. Enrichment of Zn in organic rich anoxic and oxic near-shore sediments has been reported by previous authors (Calvert, 1975) who have suggested that coprecipitation with sulphides and/or adsorption onto particulate organic material are the major removal mechanisms responsible for this enrichment (Krauskopf, 1956).

In the western and southern parts the concentration was considerably lower and in the western channel it was only 84 $\mu\text{g g}^{-1}$. In Table III, the Zn concentrations found in the Elefsis Gulf sediments are compared with those found in various other near-shore sediments. However the most valid comparisons are those made on the basis of the natural background levels of the same area. The upper 5 to 10 cm of all cores (Figure 6), except the one taken at the western channel, had considerably higher (up to ten times) total Zn concentrations, relative to those of the lower strata (60 to 80 $\mu\text{g g}^{-1}$), which are very similar to the surface Zn concentration of the 9–10 core (Figure 5). The reason for this differentiation is that the uppermost sediment layer (~ 1 m) at the locality from which the 9–10 core was taken, had been removed recently (1968) by dredging. A further support to this information was the non-detectable levels of Cs-137 in the same sediment. Therefore the Zn levels of the top centimeters of this core, resembling those of the lower layers of the other cores, can be considered as representing the natural background levels in the area.

The enrichment of the top layer in Zn indicates not only the recent character of the pollution but also the important role of both the redox reactions and the high content of organic matter in the surface sediments. The good correlation between Zn and organic C can be also partly attributed to the biological importance of Zn in the marine biosphere.

4.3. ZINC PARTITION AMONG VARIOUS SEDIMENT FRACTIONS

Table IV summarizes the results of duplicate Zn analyses in three typical samples which were subjected to the previously described physical separation procedures (A, B, C, AC). The Zn to Al ratios have been incorporated so that the Zn content can be broadly compared with that of the aluminosilicates in the final sample. The findings, although not very conclusive, showed that procedures A and B gave very similar, almost identical, sediment fractions and for this reason Zn concentrations and Zn/Al ratios were almost the same in both cases. Procedure C in samples I and II showed that smaller particles, rich in aluminosilicates are also richer in Zn, since the removal of the coarse carbonaceous components leads to an 'enrichment' of the sample in both Zn and Al. However sample III gave results distinctly different from that trend. Procedure AC, introduced in order to test the effect of grinding itself, gave higher Zn concentrations than either

TABLE III
Zn concentration in various near shore sediments in comparison with those of the Gulf of Elefsis

Location sampled	Zn concentration ($\mu\text{g g}^{-1}$ dry wt.)	Remarks	References
Unpolluted			
Soanich Inlet, Brit. Columbia			
a	88	oxic	Gross (1967)
b	80	anoxic	Gross (1967)
S.W. Africa	68		Calvert (1975)
Black Sea	147		Calvert (1975)
Baltic Sea	110		Manheim (1961)
<i>Mediterranean</i>			
Delta of Ebro, Spain	51.5-104	12 M HNO ₃	Obiols <i>et al.</i> (1980)
Côte d'Azur, continental shelf	55-110	<63 μm , HNO ₃ -HClO ₄	Cenciardini <i>et al.</i> (1980)
Tel-Aviv-Yaffa:			
a	22-85	Summer	Amiel and Navrot (1978)
b	20-47	Winter	Amiel and Navrot (1978)
Average near shore	95		Wedepohl (1960)
Polluted			
Swansea Bay	128		Bloxam <i>et al.</i> (1972)
Severn Estuary			
a	470		Butterworth <i>et al.</i> (1972)
b	280	<63 μm	Chester and Stoner (1974)
Firth of Clyde	165	<204 μm	Mackay <i>et al.</i> (1972)
Clyde Estuary	1680	silt	Perkins <i>et al.</i> (1973)
Sorford, W. Norway	20016		Skei <i>et al.</i> (1972)
Dutch Wadden Sea	350-490		Duinker <i>et al.</i> (1974)
Derwent Estuary Australia			
a	76	'low'	Bloom (1976)
b	5809	'medium'	Bloom (1976)
c	8907	'high'	Bloom (1976)
Mobile Bay, Alabama	250		Gambrell <i>et al.</i> (1980)

Table III (cont.)

Location sampled	Zn concentration ($\mu\text{g g}^{-1}$ dry wt.)	Remarks	References
<i>Mediterranean</i>			
Gulf of Fos	83-337	<63 μm , HCl-HNO ₃ , 3:1	Arnoux <i>et al.</i> ((1980a)
Cortiou (Marseille)	150-2000	<63 μm , HCl-HNO ₃ , 3:1	Arnoux <i>et al.</i> (1980b)
a	2550	max	Arnoux <i>et al.</i> (1980b)
b			
Gulf of Venice	60-870	min-max (8 N HNO ₃)	Angela <i>et al.</i> (1980)
a	90-200	average range	Angela <i>et al.</i> ((1980)
b			
Kastela Bay, Yugoslavia	1300	surface (max)	Stegnar <i>et al.</i> (1980)
a	33-85	subsurface	Stegnar <i>et al.</i> (1980)
b			
Lebanon coast	60.2	average	Shiber (1980)
a		(<1.75 mm, HNO ₃ :HClO ₄ , 3:1)	
b	12.8-154.6	range	Shiber (1980)
Nile, continental shelf	48.4	average	Toma <i>et al.</i> (1980)
a	20-100	range	Toma <i>et al.</i> (1980)
b			
Abu-Kir Bay, Egypt	102	average (2 N HNO ₃)	Saad <i>et al.</i> (1980)
a	9-758	range	Saad <i>et al.</i> (1980)
b			
Eastern Alexandria harbour, Egypt	52.6	average	El-Sayed <i>et al.</i> (1980)
a	12-174	range	El-Sayed <i>et al.</i> (1980)
b			
<i>Gulf of Elefsis</i>			
a	2440	(HF-HNO ₃) max	Present work
b	125-1500	range in surface	Present work
c	100	subsurface (max)	Present work
d	60-80	natural background level	Present work

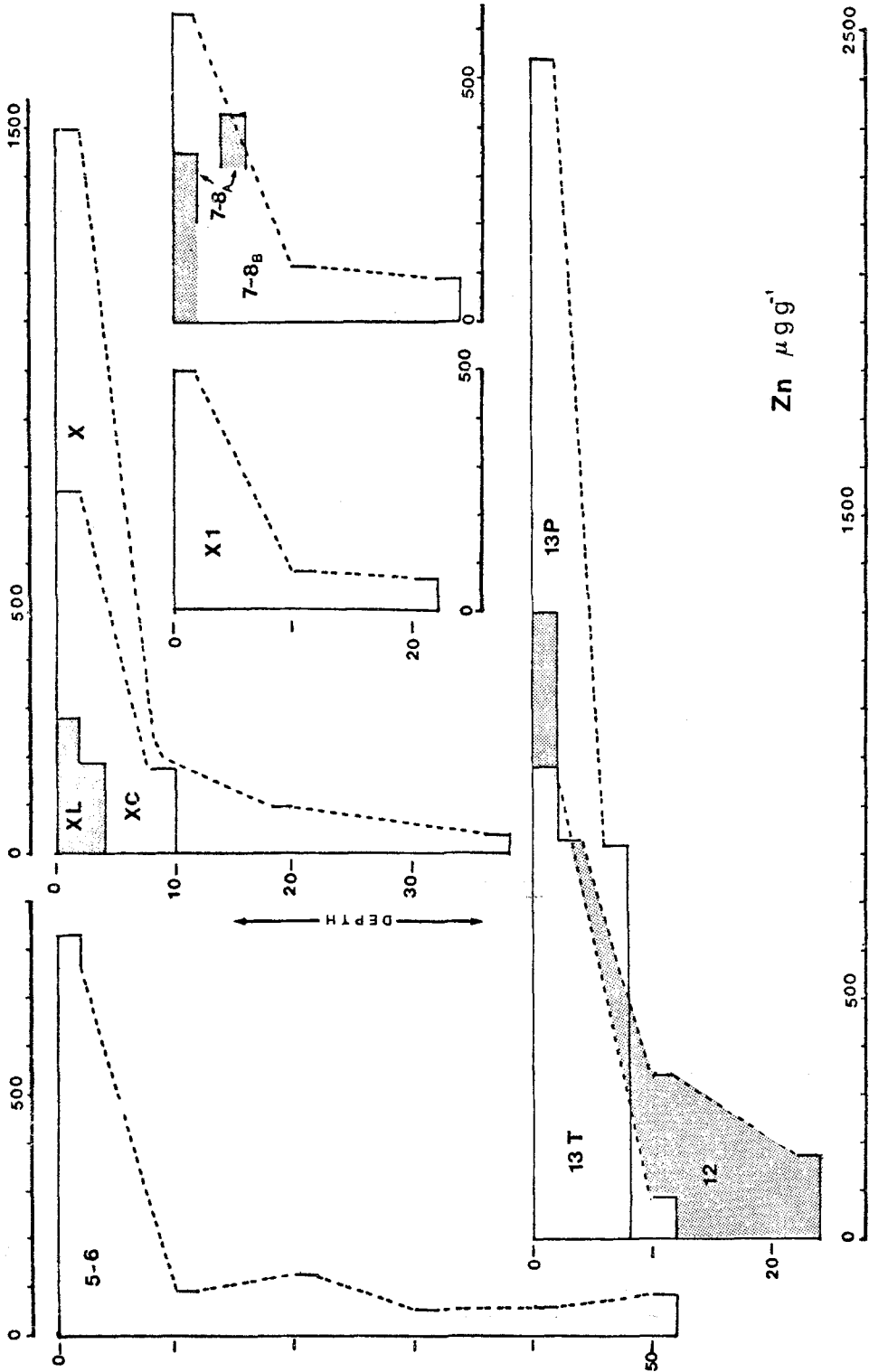


Fig. 6. Vertical distribution of total zinc in selected sediment cores (in $\mu\text{g g}^{-1}$).

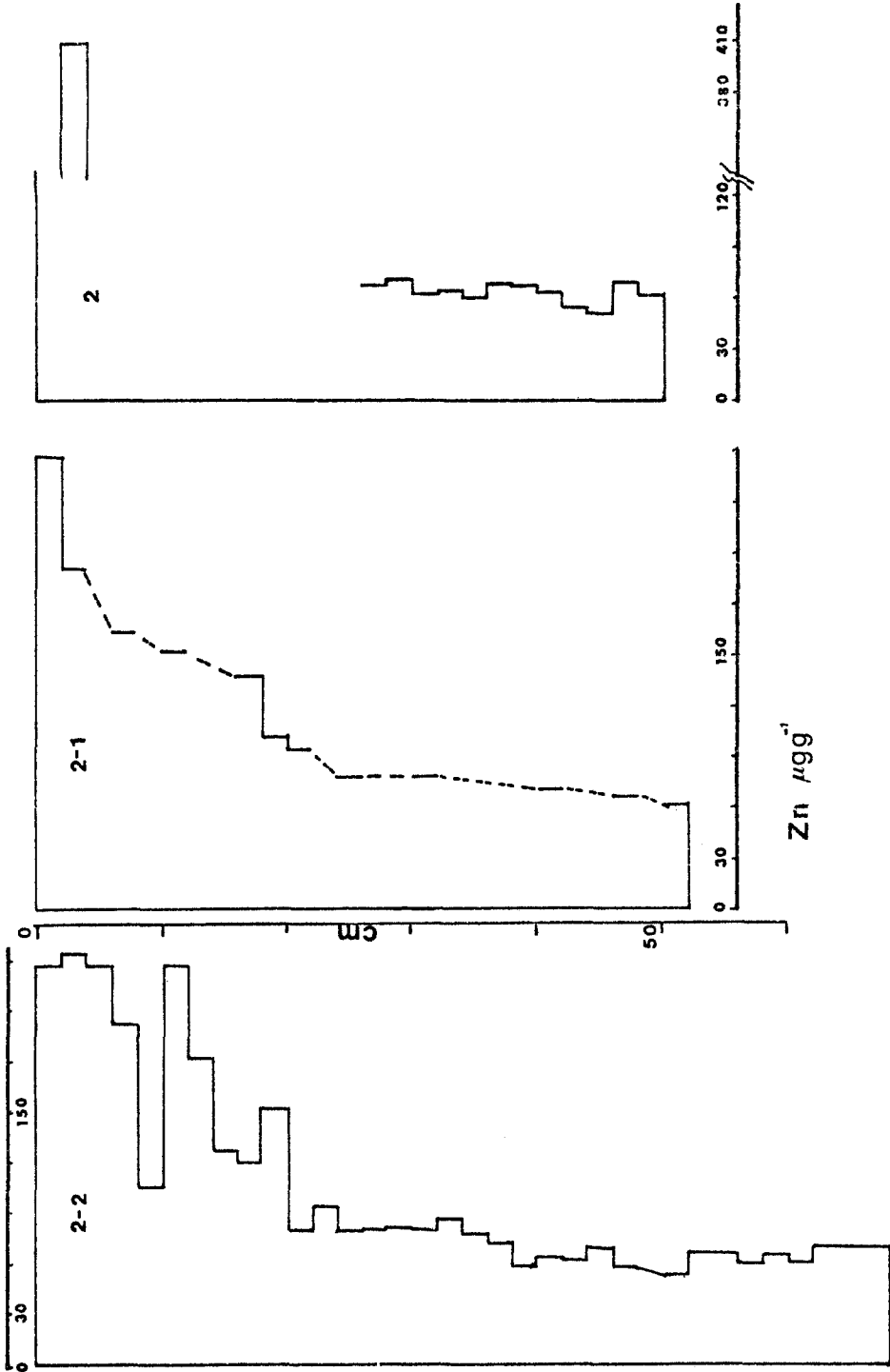


Fig. 6. Vertical distribution of total zinc in selected sediment cores (in $\mu g g^{-1}$).

procedures A or C, when these were used separately. Since the grinding will not cause a proportional decrease in the size of 'soft' and 'hard' sediment components, the results indicate that Zn, in some cases, can be present in higher concentrations in the $> 61 \mu\text{m}$ 'soft' particles.

TABLE IV
Measured concentrations of Zn in sediments as a function of physical separation procedure

Sample	Core	Depth (cm)	Process ^a	Zn ($\mu\text{g g}^{-1}$)	Zn : Al
I	3	20–22	A	96.0	0.20
			B	96.1	0.20
			C	96.9	0.15
II	8–11	60–62	A	71.0	0.20
			C	103.3	0.19
III	12	2–4	A	829.8	1.70
			C	711.6	1.35
			AC	959.1	1.85

^a See Section 3.2.

Table V gives the results of Zn partitioning among various leachable sediment fractions of samples taken in 10 cm intervals from a typical core (No. 2–2). The Al content, indicating the contribution of the lithogenous or land-derived component of the sediment, has been also incorporated in the Table. It is obvious that the 'easily extractable' fraction (leached with 1 M MgCl_2) represents only a very small portion of the total Zn incorporated onto the surfaces and inter-sheet positions of minerals from the overlying waters.

The acid reducing reagent – ARR (acetic-hydroxylamine hydrochloride) leaches the Zn defined as 'non-lattice held inorganic fraction' associated mainly with Fe and Mn oxides and carbonate minerals, together with that adsorbed onto all mineral surfaces. This fraction represents $\sim 36\%$ of the total Zn in the upper part of the core but considerably lower percentage at the bottom.

The EDTA leached Zn ($\sim 12\%$) is defined as the 'non-lattice held organically bound fraction' but is actually thought to comprise also a proportion of Zn leached from sulphides.

The highest percentage of the metal, particularly in the bottom of the cores, is associated with the non-leachable lithogenous fraction, which certainly is not attributed to the pollution.

These results indicate that the Zn pollution found in the upper layer of the sediment of the Gulf of Elefsis is largely due to reducible forms of Zn associated with inorganic and, to a lesser extent, organic particles either through complexation, coprecipitation and/or adsorption mechanisms.

TABLE V

Zinc concentration in several sediment fractions.

(1) Zn in $\mu\text{g g}^{-1}$, (2) as percentage contribution of each fraction, (3) Al in mg g^{-1}

Depth (cm)	Fraction	1 Zn	2 Zn	3 Al
0-2	T	236		48.5
	EE	2.4	1.0	0.005
	ARR	83.7	35.5	1.1
	EDTA	22.1	9.4	0.95
	NL		55.1	
10-12	T	239		38
	EE	2.6	1.1	0.005
	ARR	92.3	38.6	0.95
	EDTA	30.6	12.8	0.58
	NL		48.6	
20-22	T	81		27
	EE	2.0	2.5	0.006
	ARR	12.0	14.8	1.2
	EDTA	9.8	12.1	1.87
	NL		87.9	
30-32	T	82		43
	EE	2.1	2.6	0.01
	ARR	12.6	15.4	1.14
	EDTA	14.7	17.9	1.43
	NL		69.5	
40-42	T	65		43
	EE	0.4	0.6	0.01
	ARR	8.8	13.5	1.26
	EDTA	11.3	17.4	1.43
	NL		69.1	
50-52	T	53		32
	EE	2.3	4.3	0.01
	ARR	3.8	7.2	1.26
	EDTA	11.7	22.1	1.47
	NL		70.7	
60-62	T	60.5		44
	EE	0.6	1.0	0.006
	ARR	3.8	6.3	1.15
	EDTA	10.8	17.85	1.13
	NL		75.85	
68-70	T	91		45.5
	EE	2.2	2.4	0.006
	ARR	20.7	22.7	0.98
	EDTA	7.75	8.5	0.82
	NL		68.8	

T = total.

EE = easily extractable fraction.

ARR = acid reducing reagent (for the non-lattice held inorganic fraction).

EDTA = (for the non-lattice held organically bound fraction).

NL = non-leachable fraction.

5. Conclusions

The Gulf of Elefsis and particularly its eastern part, receiving high loads of dissolved and particulate Zn from industrial, trade and other anthropogenic activities and occasionally from the Athens sewage outfalls, is definitely polluted by Zn. Its levels are several times higher than those found in the 'open' Aegean Sea and the Mediterranean.

The dissolved species, either ionic or in weak complexes with organic ligands such as humic and fulvic substances (Schnitzer and Kahn, 1972; Millero, 1975; Scoullou, 1976) represent more than 80% of the total Zn content.

The distributions of Zn in sea water and sediments are regulated by direct input, planktonic activity, changes in the circulation pattern and redox reactions at the deepest part of the Gulf, which becomes anoxic during summer.

A linear correlation found between particulate Zn and magnetic properties supports the theory that adsorption, either on newly formed suspended solids, organic matter or magnetically active, rich in Fe particles, is one of the major removal mechanisms of Zn in the Gulf; precipitation with sulphides and coprecipitation-flucculation is another one.

The distribution of Zn in the bottom sediments provides a 'fingerprint' of the pollution and its history in the Gulf. Zinc concentrations in sediments are again comparable with those of known polluted areas in other parts of the world. Three point sources having extremely high Zn concentrations were found close to certain big industries. The deepest part of the Gulf which becomes seasonally anoxic and particularly rich in organic C has also elevated concentrations, although it is not directly affected by the industrial activities. This part can serve occasionally either as a 'trap' or a 'source' of Zn depending on the seasonal circulation and the development of redox reactions in the lower part of the water column.

The top layer (5 to 10 cm) of the sediment column is particularly enriched in Zn (in some cases 10 times above the natural background levels). This is mainly due to the contribution of the non-lattice held inorganic and, to a lesser extent, to organically bound Zn and indicates the recent character of the Zn pollution in the Gulf of Elefsis.

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