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Abstract

The present work examines the temporal evolution of industrial contamination in sediments caused by trace metals in the Elefsis Gulf, Greece. The current state of contamination as well as the related sources can be obtained from the study of the sediments. Trace metals, namely Ni, Cu, Fe, and Mn, were collected during 1984-2003 by the local monitoring network. The statistical analysis of the data and the contaminants isopleths patterns support the following conclusions: There is a strong correlation between the nearby coastal industrial activities and the distribution of the trace metals' concentration in sediments. There is no seasonal or annual variation of the distribution. The sediments' concentration of Mn in all sampling points and Cu in the center of the Gulf has decreased during the last years.

Keywords: Contamination; Trace metals; Sediments.

Introduction

The region of the Thriassion Plain area is well known for the concentration of industries and manufacturing activities. The legislated extent of industrial region that abuts with the sea is 25.000 acres. The coast's length is 15 km, out of which 12 km are occupied by the harbour activities of the industries located in the area. According to a study commissioned by the local Development Association (DATP, 2003), in 2001 the area of the Thriassion Plain hosted nearly 2200 establishments (including industries and manufacturing facilities). The region hosts some of the largest industrial compounds in Greece, including two oil refineries, two steel industries, two cement factories, and one industry of munitions. Large warehouses and oil distribution facilities, three units of used lubricant processing, one paper mill, a lot of chemical industries, industries and manufacturers of plastic products, quarries and a lot of smaller units also exist there.

Enormous damage was caused in the Elefsis Gulf during the period 1960-1980 by the steel industries disposing, directly into the sea, untreated toxic wastes such as (ammoniac liquid, phenols and cyanides), organic load from two spirit distilleries and oil residues from the two refineries (ABATZOGLOU 1988, ASIMAKOPOULOS & ABATZOGLOU 1989, DASSENAKIS, 2000). A major contribution was also made by the Central Sewage Pipe of Athens, it has been calculated that 20% of the sewage and outflow from this pipe reached the Elefsis Gulf. (MAKRA *et al.*, 2001, ALOUPI *et.al.*, 2000).

The oceanographic characteristics of the Gulf, are similar to those of a lake. Shallow (maximum depth 33m), no strong currents, anoxic conditions, water stratification, especially during the summer with a clearly defined thermocline, intensify the pollution problem, by favoring the accumulation of sediments and inhibiting the natural destruction/decomposition of pollutants (ABATZOGLOU 1988, ASIMAKOPOULOS & ABATZOGLOU 1989).

Metals are naturally present in the marine environment. Although concentration can be characterized as traces (μg/L) they may have toxic effects on marine biota.

Copper (Cu) in large concentrations inhibits the growth of sea-weed, is toxic for mussels and is bioaccumulated in marine organisms. Iron (Fe) is a common contaminant of the marine environment, mainly as $Fe(2+)$. This soon becomes $Fe(3+)$, through oxidation, forming thick hydroxides that coagulate and precipitate. Concentrations over 300μg/L can be harmful. Manganese (Mn) in the sea exists as $Mn(2+)$ and accumulates in the deepest parts by biochemical processes, with various effects on the lower members of the food chain. Concentrations higher than 100μg/L may have adverse effects. Nickel (Ni) over too in phyto- and zoo-plankton, can be harmful (ABATZOGLOU 1988, FYTIANOS 1996).

Several studies have addressed the problem of the Elefsis Gulf sediments' contamination by heavy metals (SCOULOS 1979, ABATZOGLOU 1988, KERSTEN *et al.*, 1997, MAVRAKIS *et al.*, 2000a), as well as the influence of pollution on marine life (MAKRA *et al.*, 2001). Furthermore, it has been made clear by other studies that trace metals' concentration in sediments offer a valuable record of accumulated pollution and can be used to identify, in a comprehensive way, 'hot spots' especially when the source is still in operation (DASSENAKIS *et al.*, 1996).

The main sources of contamination today are industrial wastes, the Ag. Georgios stream (tanneries, paper mill, used lubricant processing), ship yards, scrap metal yards, old ships waiting to become scrap metal, transient and docking ships – during the last years the traffic in the area of Elefsis harbor has increased rapidly – suspended atmospheric particles and drainage from a landfill located upstream in Ano Liossia.

The landfill at Ano Liossia is located about 6 km inland. This landfill receives more than 1 million tons of urban litter per year. It also receives 23.000 tons of solid industrial waste on an annual basis, 4.500 tons of which are toxic, 8.500 tons of petrochemical products and the remaining 10.000 tons is non toxic. As a consequence of the operation of the landfill the aquifer has been polluted by ammoniac and nitric ions, organic substances, calcium, magnesium, cadmium, chromium, lead, zinc, copper, and nickel at a distance of 1 km southwesterly from the landfill. A part of this drainage (presenting high concentrations BOD5, COD and trace metals) facilitated by rain water, end up in the seasonal river of Ag. Georgios and from there to the sea. This stream has been characterized as a receiver of industrial waste by an official act of the State with the pre-condition that they are completely treated to a level satisfying certain concentration limits. This treatment, however, is either non-existent or inadequate (DATP, 2003; MAVRAKIS *et al.*, 2000a; HELLENIC REPUBLIC, 1979; CHRISTIDES, 1995).

Table 1 presents the main trace metals emitted by the various industrial activities occurring in the Thriassion Plain area.

The aim of this study is the identification of those areas of the Elefsis Gulf, whose sediments are characterized by elevated trace metals' concentrations, utilizing the multi-year data obtained by of the Bureau of Pollution Control and Environmental Quality of the Development Association of Thriassion Plain (BPCEQ).

Materials and Methods

All the data used were obtained from the quarterly bulletins of BPCEQ for the years 1984-2003. The sampling for the control of marine pollution takes place at nine points, three in the center of the Gulf and six along the coastline. The coastal sampling points are located near important industrial activities. The locations of the sampling points are presented in Table 2 and Figure 1.

All sampling and analysis were performed by BPCEQ according to APHA-AWWA-WPCF directives (APHA-AWWA-WPCF, 1975). Samples were collected with a 1L grab and the initial treatment consists of simple wet-sieving, and drying at 40-50°C for one day. The sieve used has a mesh finer than 2mm. The samples are consequently subjected to Microkjeldahl digestion, using a mixture of concentrated HNO_3 and H_2SO_4. The non-soluble residue, mostly silicates, are removed by filtering the solution through a 0.45 μm or glass-fibre filter. Trace metals' concentrations in the final solution were measured using a Perkin Elmer 2380 Atomic Absorption Spectrophotometer. The reproducibility of the method is assessed, through repetitive analyses of the samples, to be in the order of 2% for the final measurement reported.

Nickel (Ni), Copper (Cu), Iron (Fe) and Manganese (Mn) were selected since their presence in the sediments forms a stable criterion for the assessment of the pollution of marine environment over time (ABATZOGLOU 1988, VOUGAS *et al.*, 1989; MAVRAKIS *et al.*, 2000a; MAVRAKIS *et al.*, 2000b).

The data available were aggregated on a five-year basis in order to obtain a more clear view of the temporal evolution of trace metals' concentrations in the sediments of the Elefsis Gulf. Table 3 presents the basic statistics, for each 5-year period, for the above mentioned

Table 1
Heavy metals' emissions per industrial activity.

Activity	Pollutant	Activity	Pollutant
Pharmaceutical industry	Pb, Zn	Cement industry	Cr, Pb
Iron and Steel industry	Cr, Pb, Zn, Mn, Fe	Glass industry	Pb
Petrochemical industry	Cr, Pb, Zn	Textile industry	Cr
Tanneries	Cr	Paper industry	Cr, Pb, Zn
Oil Refineries	Cr, Pb, Zn, Ni, Cu	Ship yards, scrap metal yards etc.	Cr, Pb, Zn, Mn, Fe

Table 2
Locations of BPCEQ marine pollution sampling points.

COASTAL	Depth (m)	CENTRE	Depth (m)
A1 - Skaramaga ship yards	17	K1 - 800m off Skaramaga ship yards	23
A2 - ELDA refinery	2	K3 - 1500 m off Steel and iron	16
A4 - PETROLA refinery	13	K5 - 1500 m off "Eftaxia"	33
A5 - Stream of Saint George	2		
A8 - Bakopoulos ship breaking	7		
A11 - Elefsis ship yards	18		

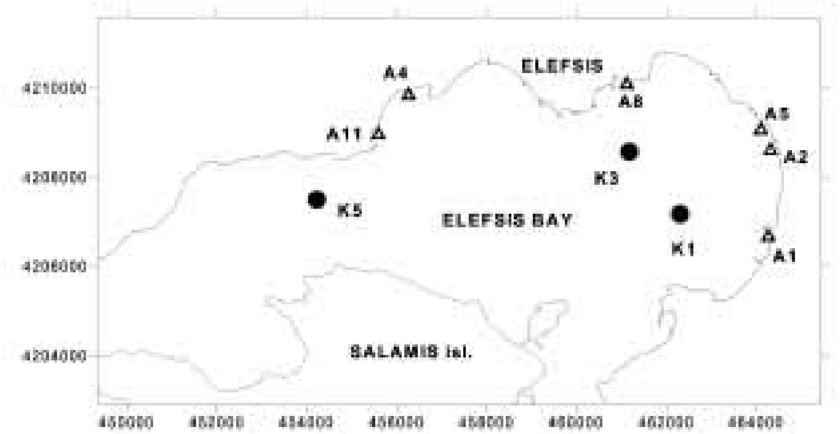

Fig. 1: Map of Elefsis Gulf and locations of BPCEQ marine pollution sampling points. (Map scale: 1:150000, Greek Coordinate system EGSA 87).

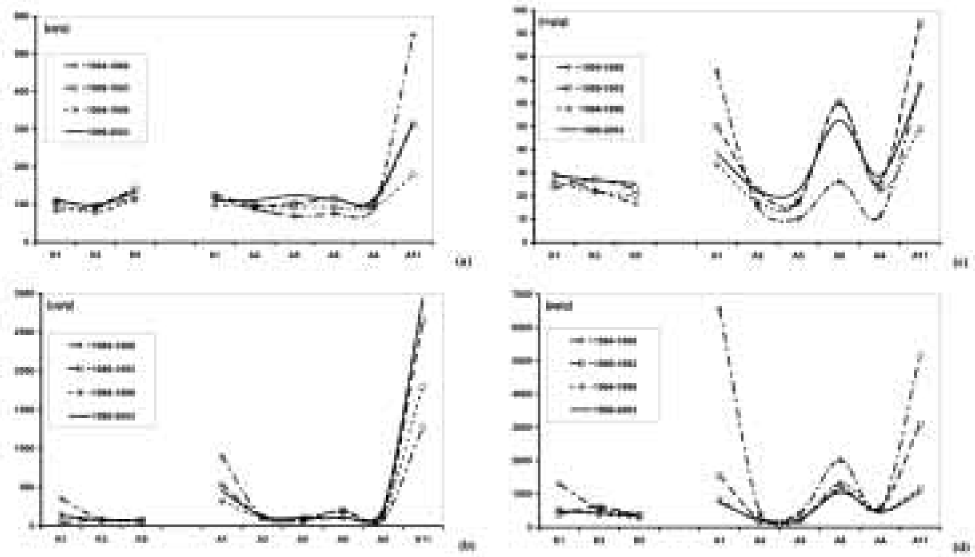

Fig. 2: Temporal variation of trace metals' concentration in the sediments of Elefsis Gulf: a) Nickel ($\mu g.g^{-1}$), b) Copper ($\mu g.g^{-1}$), c) Iron ($mg.g^{-1}$) and d) Manganese ($\mu g.g^{-1}$).

contaminants, and Figure 2 illustrates their temporal variation.

For the better comprehension of the environmental problem caused by the accumulation of industrial activities, we have generated maps illustrating the distribution of trace metals' content of the sediments (Figure 3). The necessary interpolation for the creation of the maps was done using Radial Basis Functions (YU, 2001, SIFAKIS *et al.*, 1998), using all the data available from each sampling point. The distributions produced this way are free from spurious extreme values that might be present for a single event.

Table 3
Average, standard deviation and range for Ni, Cu, Fe, and Mn concentration measurements in the sediments of Elefsis Gulf, on a 5-year basis, from 1984 to 2003.

	K1		K3		K5		A1		A2		A5		A8		A4		A11	
	Avg	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**	**Avg**	**Stdv**
Cu ($\mu g.g^{-1}$)																		
1984-1988	351.3	278.9	87.7	17.4	80.2	16.5	898.3	112.7	115.1	24.4	111.2	40.7	185.7	28.9	84.6	84.6	1273.7	858.1
1989-1993	44.4	19.8	79.5	38.5	72.0	22.2	532.8	202.4	110.9	28.7	69.2	52.1	206.3	18.7	144.4	85.8	2649.2	376.1
1994-1998	143.8	76.7	72.4	36.1	54.2	45.8	319.5	182.5	106.2	45.7	81.1	60.3	106.7	25.1	155.2	47.0	1793.2	1219.0
1999-2003	130.3	109.1	74.1	31.3	82.3	29.5	449.5	98.9	127.4	25.8	104.4	49.4	114.2	58.8	201.1	36.9	2924.7	1270.1
Range	(12.9-720.0)		**N**	29				**Range**	(26.8-4516.0)			**N**	28					
Fe ($mg.g^{-1}$)																		
1984-1988	29.5	15.7	22.5	9.6	16.7	5.6	73.7	44.8	15.6	8.9	10.2	10.2	26.1	8.4	11.1	23.6	68.0	59.4
1989-1993	23.7	2.6	26.9	9.0	23.2	2.1	50.1	20.2	22.5	3.9	17.6	4.4	60.1	1.8	25.4	6.3	94.3	42.6
1994-1998	26.1	12.1	21.8	7.8	20.3	6.2	33.7	12.1	17.2	5.4	16.9	6.4	60.2	3.8	22.7	20.9	48.8	19.9
1999-2003	28.7	7.6	26.9	4.9	25.3	3.2	38.6	7.9	22.3	4.7	22.4	3.6	52.6	4.0	28.6	9.4	66.1	18.6
Range	(8.3-52.0)		**N**	28				**Range**	(2-163.0)			**N**	28					
Mn ($\mu g.g^{-1}$)																		
1984-1988	1307.8	1242.2	558.8	265.6	391.4	76.9	6560.0	1895.9	444.2	233.1	429.4	264.6	2016.5	197.3	543.4	1686.7	5160.5	4334.4
1989-1993	399.1	33.0	608.0	172.8	353.3	28.0	1545.6	1012.6	249.7	27.4	250.1	66.6	1147.2	76.3	562.8	143.3	3119.6	866.9
1994-1998	527.9	315.1	387.7	137.3	272.6	85.2	821.8	489.0	175.2	59.0	190.4	192.0	1311.9	64.4	497.3	639.0	1170.8	519.5
1999-2003	482.0	259.6	426.0	60.9	340.7	49.9	733.5	276.4	238.9	73.7	246.8	58.0	1047.6	60.7	474.3	289.0	1054.7	242.8
Range	(158.5-2720.0)		**N**	29				**Range**	(63.3-10920.0)			**N**	28					
Ni ($\mu g.g^{-1}$)																		
1984-1988	84.2	84.2	91.4	91.4	117.8	117.8	116.5	9.2	88.3	3.9	69.6	11.3	75.5		90.0		550.0	
1989-1993	109.8	26.4	97.9	19.2	141.2	29.5	126.2	33.2	97.7	36.1	102.1	44.0	115.8	33.8	105.8	51.6	313.2	205.5
1994-1998	99.2	33.5	79.6	27.7	112.6	35.4	97.7	33.7	93.3	36.1	93.3	31.6	92.7	25.3	92.7	28.4	179.4	63.8
1999-2003	111.9	15.0	98.2	10.6	132.4	20.9	110.8	14.4	111.3	21.4	123.8	14.4	114.7	21.8	113.3	13.5	315.9	206.1
Range	(39.8-184.4)		**N**	25				**Range**	(28.4-734.0)			**N**	26					

Results and Discussion

The spatial distribution of the measured trace metals' concentrations strongly suggest that the main sources of the contamination of Elefsis Gulf are land based.

From Figure 3 we can see that Nickel (Ni) presents almost uniform distribution with the exception of point A11 (Elefsis ship yard), where its concentration presents a peak being almost double that at the rest of the sampling points. Copper (Cu) presents the larger concentrations in sampling points A01 and A11 (Skaramaga and Elefsis Ship yards), while iron (Fe) and manganese (Mn) concentrations are elevated in sampling points A01, A08 and A11 (Skaramaga ship yard, Bakopoulos ship breaking, and Elefsis ship yard).

Figure 2, presenting the temporal evolution of the examined contaminants, indicates that there is a marked reduction in Mn concentration while Cu is also reduced but to a lesser extent. For all sampling points the 5-year period 1994-1998 corresponds to the lowest concentrations of all four contaminants.

Even though the trace metals examined are produced by all industrial activities, the conclusion drawn from the distributions in Figure 3, is that the main sources are the two large shipyards, Skaramaga and Elefsis (places A01 and A11 respectively). The concentrations of the contaminants at these points are roughly double the concentrations measured in the bottom of the center of the Gulf, in points K1, K3, and K5. It must be noted that the concentrations measured in Elefsis Gulf sediments are larger than those measured by other researchers at Aegean ports (ANGELIDIS & ALOUPI, 1995, 2001), but also at coastal industrial areas with varying characteristics (DASSENAKIS *et al.*, 1996), Also the range of concentration values found by BPCEQ is similar or a little higher compared to other heavily industrialized coastal areas such as the Thermaikos Gulf (KARAGEORGIS *et al.*, 2003). Indicative concentrations obtained by other researchers are presented in Table 4.

Finally, according to KARAVOLTSOS *et al.,* 1999, the geomorphology of the Thriassion Plain - Elefsis Gulf basin seems to be playing a decisive role in the trace metal content of the sediments in the Elefsis Gulf, since they favor the continuous accumulation of the pollutants considered herein, hindering, at the same time, their natural destruction. Typical examples are sampling points A11, A08 and A01. The concentration distributions presented in Figure

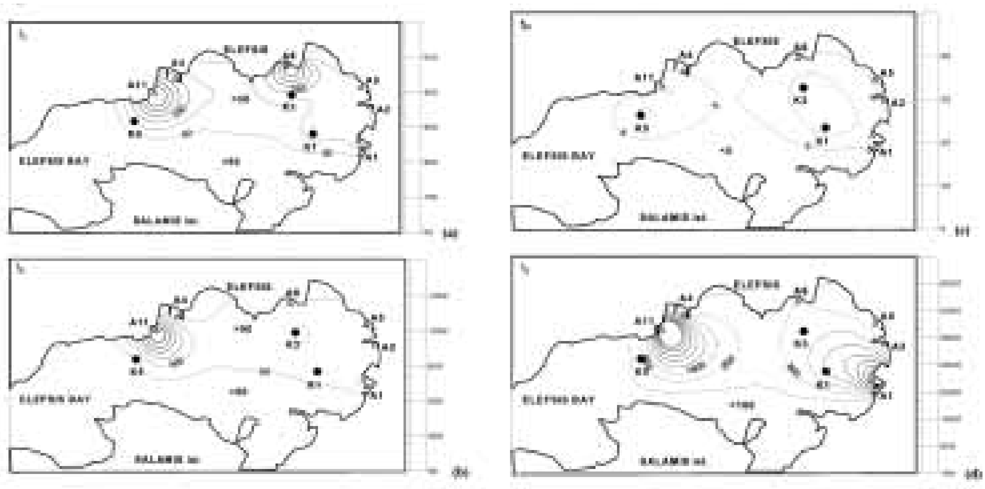

Fig. 3: Spatial distribution of trace metals' average concentration in the sediments of Elefsis Gulf, for the period 1984-2003: a) Nickel ($\mu g.g^{-1}$), b) Copper ($\mu g.g^{-1}$), c) Iron ($mg.g^{-1}$) and d) Manganese ($\mu g.g^{-1}$).

Table 4
Trace metals' concentrations measured in the sediments of marine sites in the Aegean and the Mediterranean.

Area	Cu (μg.g-1)	Fe (mg.g-1)	Mn (μg.g-1)	Ni (μg.g-1)
*Gulf of Elefsis (Scoulos, 1979)	25-150		350-1000	40-80
*Thermaikos Gulf (Chester & Voutsinou, 1981)	5-70		340-2600	75-440
Thermaikos Gulf (Karageorgis et al., 2003)	42-264			57-407
Rhodes Harbour (Angelidis & Aloupi, 1995)	9-101	0.6 –24.3	4-920	
Lesvos island (Angelidis & Aloupi, 2001)	11-41		331-552	246-698
*Mediterranean offshore, (Jeftic, 1990; UNEP, 1993)	10-49		9-46	52-2560
*Mediterranean background, (Jeftic, 1990; UNEP, 1993)	15			

*Adopted from Dasenakis *et al.*, 1996

2, are closely related, in terms of both pollutant kind and quantity, to the coastal morphology as well as the activities/sources located along the coast, that have remained unchanged throughout the examined period.

Furthermore, the lowest part of the Ag. Georgios stream is adjacent to the site where a nearby steel industry deposits metallurgic residues in the form of dust that can either be easily washed down by the rain or carried by the wind directly into the stream or the nearby coast. This dust obviously is another significant contributor to the trace metal content in the sediment of the nearby sampling point A5.

Conclusions

The results of the analysis presented above can be summarized as follows:

1. Both the temporal evolution of the pollutants' concentration and the related distributions presented in Figure 3 indicate that there is a close correspondence between elevated pollutant concentrations and the related sources located along the coast, either industrial activities or sediment sources.

2. Indeed sediments offer a valuable record of accumulated contaminants and can be used both to identify significant sources and monitor the temporal evolution of their activity and the related impacts.

3. Trace metals' (Ni, Cu, Fe, and Mn) distributions as observed in the sediments of the coasts and center of the Elefsis Gulf are directly linked to the industrial activity, having as main sources the shipyards of Skaramaga and Elefsis with the coastal sampling points having the higher concentrations.

4. Trace metals' concentration in the center of the Elefsis Gulf (sampling points K1, K3 and K5) are uniform for all metals except copper that seems to be higher in the eastern part of the Gulf.

5. During the last few years there is a slow yet perceptible improvement of the contamination situation in the Elefsis Gulf. The improvement is clear regarding Manganese, in all sampling points. Copper concentration is also reducing except for the two refineries and the Elefsis shipyard (points A2, A4 and A11) where the concentration is growing. Iron is generally rising while Nickel seems to be stabilized in all positions.

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