

LEVELS OF SEVEN PCB CONGENERS IN THE GULF OF ELEFSIS

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Despite the fact that PCB's have been identified since the sixties as some of the most acute pollutants of the Mediterranean Environment, it is surprising how little concrete information is available, even today, about their actual levels in some parts of the Mediterranean Sea. Information about their speciation between dissolved and particulate phases and at various depths of the water column, as well as between the water and sediments of the site, are also rare. In the present work we present the results of a survey carried out in the Gulf of Elefsis, a semi-enclosed embayment near Athens which receives the effluents of a number of industries and is affected also by the Athens sewage outfalls which are located near its eastern entrance (Fig. 1.) The substances studied were the following PCB congeners: PCB-18, -28, -52, -101, -153, -138, and -180. The focus of the present paper is the discussion of the levels of their concentrations in water, suspended solids and sediments taken from five sites shown in the map. Solid-phase extraction (C₁₈) procedure applied prior to the separation. Single PCBs were determined by HRGC-ECD on two capillary columns of different polarity, with internal standard. In the Tables 1 and 2, the mean - minimum - maximum concentrations of the PCB congeners are given from the water samples (suspended solids and dissolved water phase) during the winter and summer of 1992. The mean concentrations of the PCB congeners in sediments and their minimum - maximum values are presented in Table 3. The sediment samples have a total organic carbon content from 4.65 to 1.36 % (dry weight). The concentrations show the real tendency of the PCBs and to a lesser extent of other organochlorine compounds to accumulate more in suspended solids and sediments than in the dissolved water phase following their hydrophobic nature. Some discrepancies from the general rule could account on the existence of colloidal determined with the dissolved phase of the water samples (BAKER *et al.*, 1986; ALBAIGES *et al.*, 1991; KAMLET *et al.*, 1998).

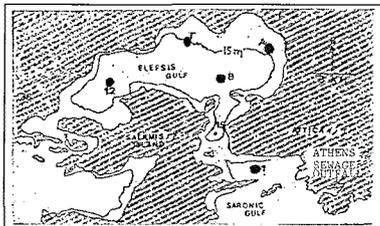


Fig. 1. Map of the Elefsis Gulf and the sampling grid

	Concentrations - Winter			Concentrations - Summer		
	Mean	Mini.	Maximum	Mean	Mini.	Maximum
1. PCB-18	0.644	M.A	0.92	0.546	0.28	0.86
2. PCB-28	1.394	0.93	2.56	2.016	0.92	2.8
3. PCB-52	M.A			M.A		
4. PCB-101	1.372	0.95	2.91	1.68	0.96	2.65
5. PCB-153	0.518	0.211	1.00	0.582	0.23	1.26
6. PCB-138	0.155	M.A	0.39	0.045	M.A	0.15
7. PCB-180	M.A			0.035	M.A	0.12
SUM PCBs	4.083			4.904		

Table 1. Mean - Minimum - Maximum Concentrations (ng/lit) of the PCBs congeners in Suspended Solids during the winter and summer of 1992 in the Gulf of Elefsis

	Concentrations - Winter			Concentrations - Summer		
	Mean	Mini.	Maximum	Mean	Mini.	Maximum
1. PCB-18	0.052	0.02	0.1	0.030	M.A	0.08
2. PCB-28	0.57	0.1	0.88	0.263	0.11	0.43
3. PCB-52	M.A			M.A		
4. PCB-101	0.173	0.06	0.5	0.166	0.05	0.5
5. PCB-153	0.687	0.078	1.23	0.585	0.053	1.65
6. PCB-138	0.031	M.A	0.115	0.02	M.A	0.028
7. PCB-180	M.A			M.A		
SUM PCBs	1.513			1.064		

Table 2. Mean - Minimum - Maximum Concentrations (ng/lit) of the PCBs congeners in the Dissolved Water phase during the winter and summer of 1992 in the Gulf of Elefsis

In an attempt to assess the total concentrations of PCBs from Table 3, we have included in Table 4 mean concentrations of PCBs in sediments, with their minimum - maximum values, from different regions of the Mediterranean Sea, quoted directly from UNEP's MAP Technical Reports Series n°39 (1990) keeping in mind the different methodologies used.

Area	Concentrations - Sediments		
	Average	Minimum	Maximum
Aegean Sea *	155	0.6	775
Coastal France & Spain*	85.5	0.2	15850
Northern Adriatic Sea*	24.1	N.D	332
Southeastern Med. Sea*	2.2	0.6	51.1
Gulf of Elefsis ** (present work)	48.05	7.68	119.5

* In most cases the concentrations have been expressed in comparison to Aroclor reference standards or as a concentration of dechlorobiphenyl (product of the perchlorination method)

** The total of PCBs has been expressed as a summation of all PCB congeners

Table 4. Average - Minimum - Maximum Concentrations of PCBs in sediments from different regions of the Mediterranean Sea (µg/Kg, dry weight)

Despite the fact that the maximum values determined in the Gulf of Elefsis are among the lowest included in the Table, the mean and especially the minimum values are particularly high. This reflects a generalised pollution due to the fact that the Gulf plays effectively the role of a trap of the pollution generated by the neighbouring industries and the sewage outfalls as a result of the geomorphology of the area.

REFERENCES

- BAKER J.E., CAPEL P.D. & EISENREICH S.J., 1986, *Environ. Sci. Technol.*, 20, 11: 1136-1143
 ALBAIGES, J., BAYONA, J.M., VALLS, M., FERNANDEZ, P., PORTE, C., TOLOSA, I., 1991, *In* MAP Technical Report Series n° 39
 KAMLET M.J., DOHERT, R.M., CARR P.W., MACKAY D., ABRAHAM M.H. & TAFT, R.W., 1988, *Environ. Sci. Technol.*, 22: 5

TRACE METALS DISTRIBUTION IN A DREDGE MATERIAL DISPOSAL SITE OF THE NORTHERN TYRRHENIAN SEA

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About 100.000 m³ of sediments dredged in the harbour of Livorno (of the 507.000 m³ authorized) had been dumped in a circular area of about 0.2 km² at a depth of 40 m, when the present study was carried out. Sediments were collected by a gravity core or by box corer in 19 stations (Fig. 1) during March 1992.

Subsamples for chemical and grain size analysis were obtained from 3 cm sections of the cores. Harbour dredged sediments were characterized by elevated sand content whereas the natural sediment texture in the disposal area is silty clay (IMMORDINO *et al.*, 1993). Surficial grain size composition shows an increase of the sand percentage in the dumping site and westwards (Fig. 2); a sand increase was also evident in the deeper sections of O5 core (8-11 cm: 33.1%; 16-19 cm: 32.0 %), inside the disposal site. The more elevated sand content in the south-east stations may be due to a northwest transport of biodepositional sediments from Meloria Shoals (GABELLINI *et al.*, 1994). Lead, cadmium and chromium concentrations were determined by GFAAS and mercury by CVAAS, after total digestion with HF/HClO₄/HNO₃/HCl mixture in a microwave system under pressure (GIANI *et al.*, 1994). On the basis of previous studies (ENEA, 1992) lead and cadmium concentrations resulted more elevated in harbour sediments (Pb: 26 - 213 mg/kg d.w.t., Cd: < 5.3 mg/kg d.w.t.) than in the disposal site before dumping (Pb: 29 mg/kg d.w.t., Cd: 0.11 mg/kg d.w.t.). Mercury concentration in harbour sediments were highly variable, chromium on the contrary was less concentrated in harbour sediments. Comparisons with our data are complicated by the use of different acid digestion (hot HNO₃/HCl mixture) which not always allow the total dissolution of the matrix. The Cd and Pb surficial distributions show similar patterns (Fig. 2). Lead and cadmium, as well sand, seem to be useful tracers of the bulk of the dredge material. Lead concentrations found in surficial sediments range from 27 to 54 mg/kg with an average content similar to that found by LEONI *et al.* (1991) in silty clay and clayey silt of the Northern Tyrrhenian Sea, considered polluted by a diffuse anthropogenic input. Pb concentrations decrease from the top downwards in the cores, reaching 16-29 mg/kg in the 16-19 cm sections. The profiles are similar to the ones found in other short cores of the Northern Tyrrhenian Sea (LEONI *et al.*, 1991). Cadmium reaches the maximum concentrations in the O5 and P5 (up to 1.13 mg/kg) stations, these values are up to 10 times more elevated than in stations less influenced by the dumping. Cadmium distribution along the cores shows an increase at the top layer at the disposal site and in the stations S5 and R2, probably due to the Arno river sedimentation. The more elevated mercury concentrations correspond to the core collected inside the disposal site and are about three times more elevated than the average surficial concentration of all the other stations (0.11±0.02 mg/kg d.w.t.). Average chromium concentration in the stations less influenced by the dumping is 265±98 mg/kg d.w.t. with a decrease in the stations inside and around the dumping site (176±59 mg/kg d.w.t.), probably due to a lower chromium content in the dumped harbour sediments. Other elevated concentrations have been reported by LEONI *et al.* (1991) south of the study area (127-176 mg/kg d.w.t.), and by COSMA *et al.* (1980) in the zone just north of the study area (300 mg/kg as average value). Further determinations on the samples collected over a wider area in a survey carried out in 1994, will allow a better evaluation of the Arno river influence in the study area.

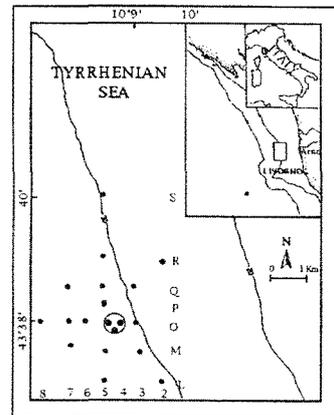


Fig. 1. Sampling stations (●) in the dumping site (○) and in the surrounding area.

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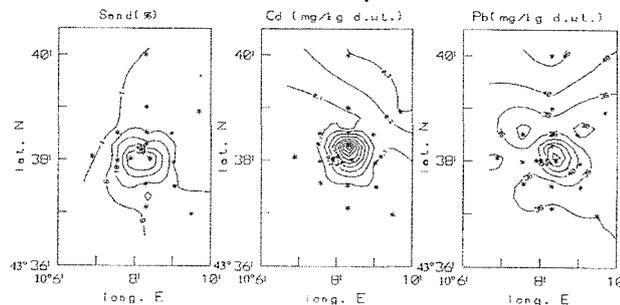


Fig. 2. Surficial distribution of sand, cadmium and lead.

REFERENCES

- COSMA B., DRAGO M., PICCAZZO M. and TUCCI S., 1980. Heavy metals in high Tyrrhenian sea sediments (...). *Atti Soc. Tosc. Sci. Nat., Memorie, Serie A*, 87: 145-161.
 ENEA, 1992. Rapporto finale per la caratterizzazione del sito di discarica dei fanghi di escavo del porto di Livorno in relazione allo sversamento dei primi 100.000 mc di materiale. ENEA, vol. 1-3.
 GABELLINI M., PELLEGRINI D., GIANI M., SPAGNOLI F. and ZANOLI S., 1994. Dati preliminari sulle variazioni dei caratteri granulometrici dell'area di scarico dei materiali dragati dal porto di Livorno. *In* Atti del X congresso A.I.O.L., 367-374.
 GIANI M., GABELLINI M., PELLEGRINI D., COSTANTINI S., BECCALONI E. and GIORDANO R., 1994. Concentration and partitioning of Hg, Cr and Pb in sediments of dredge and Disposal Sites of the Northern Adriatic Sea. *Sci. Total. Environ.*, in press.
 IMMORDINO F. and SETTI M., 1993. Caratterizzazione granulometrica e mineralogica dei sedimenti superficiali dell'alto Tirreno tra La Spezia e Livorno. *Serie Studi Ambientali "Arcipelago Toscano"*, ENEA, 51-64.
 LEONI L., SARTORI F., DAMIANI V., FERRETTI O. and VIEL M., 1991. Trace element distributions in surficial sediments of the Northern Tyrrhenian Sea: contribution to heavy metal pollution assessment. *Environ. Geol. Water Sci.*, 17: 103-116.