

Speciation Studies of Trace Metals in the Gulf of Elefsis, Greece*

Michael J. Scoullou and Alexandra S. Pavlidou

*University of Athens, Department of Chemistry, Division III, Environmental and
Marine Chemistry, Panepistimiopolis 15771 Athens, Greece*

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A method for differentiating trace metal species on the basis of relative lability has been applied for Pb, Cd, Zn, in microenvironments of the Gulf of Elefsis. Species are classified as »very labile«, »moderately labile«, »slowly labile« and »inert« depending on the characteristic time scale of the measuring technique using differential pulse anodic stripping voltammetry (DPASV) and the retention on Chelex-100 resin in successive column and batch procedures. The results show that in two extremely different microenvironments (with S of about 17‰ and ~45‰) the slowly labile and inert fractions prevail particularly at the surface layer, whereas in the main water body of the gulf the very labile fraction is the predominant one. However at the thermocline and below it the »inert« fraction increases considerably paralleling, broadly, the particulate metal distributions.

INTRODUCTION

It is well known that the total concentration of a metal may not correlate well with its impact on the aquatic environment. The speciation of the trace metals dictate their ecological and geochemical significance and cycling. In particular the study of speciation of metals in natural, polluted and unpolluted water is necessary for the meaningful interpretation of their ability to remain dissolved in ionic or ionic pair forms, their tendency to form complexes, colloids and particles and consequently of their availability, bioconcentration and toxicity to organisms.¹⁻⁶

* Dedicated to Marko Branica on the occasion of his 65th birthday.

Despite of the global recognition of the need for speciation studies relatively little has been done until now in this topic, particularly in Mediterranean nearshore marine systems.

In the present work an electrochemical method among the ones used with great success by Branica and his coworkers,⁷⁻¹⁴ for the study of speciation in aquatic systems, namely, the differential pulse anodic stripping voltametry (DPASV), is used. More specifically, an adaptation of the method of P. Figura and B. McDuffie^{15,16} was used. The time scale of measurement was the one suggested by the aforementioned workers, for the study of chemical speciation of three of the most toxic trace metals, (namely Pb, Cd and Zn) in selected sites of particular interest of the gulf of Elefsis, an important area on which our laboratory works for more than twenty years.¹⁷⁻²⁵

Among the important features of the area two are the most relevant for the present study: (I) the fact that it receives significant loads of industrial pollution and therefore has relatively high metal concentrations allowing safer determination of minor chemical species and better understanding of various biogeochemical mechanisms; (II) the large variety of »microenvironments« it contains. The conditions prevailing in these sites cover a wide range of typical and more »exotic« cases and are relatively stable, allowing repeatable measurements and verifications. These subsystems could be considered as representative of similar microenvironments found in other parts of the Mediterranean coastal waters.

The sites selected include a brackish lagoon (the Koumoundouros lake), a very saline shallow lagoon (Vourkari), a marine area receiving waters from small underwater springs (Loutropyrgos, Megalo Pefko) and the deepest part of the gulf which has intermittently anoxic conditions with quite stable summer thermocline.^{18,19,23}

In our previous works for zinc and lead we have studied the speciation between the total dissolved and particulate metal forms as well as the different leachable fractions of the various metals in seabottom sediments but we did not consider dissolved species of different lability.^{19,21-26} This is, to the best of our knowledge, the first attempt to study metal speciation in the gulf of Elefsis or in any other similar greek system and the first in which DPASV in combination with the use of Chelex-100 is employed.

EXPERIMENTAL

Sampling: The samples were collected in August 1994 in acid cleaned polyethylene bottles. Samples from the various microenvironments (Figure 1) were taken 15-20 cm below the surface and from depths discussed in other parts of the present work.

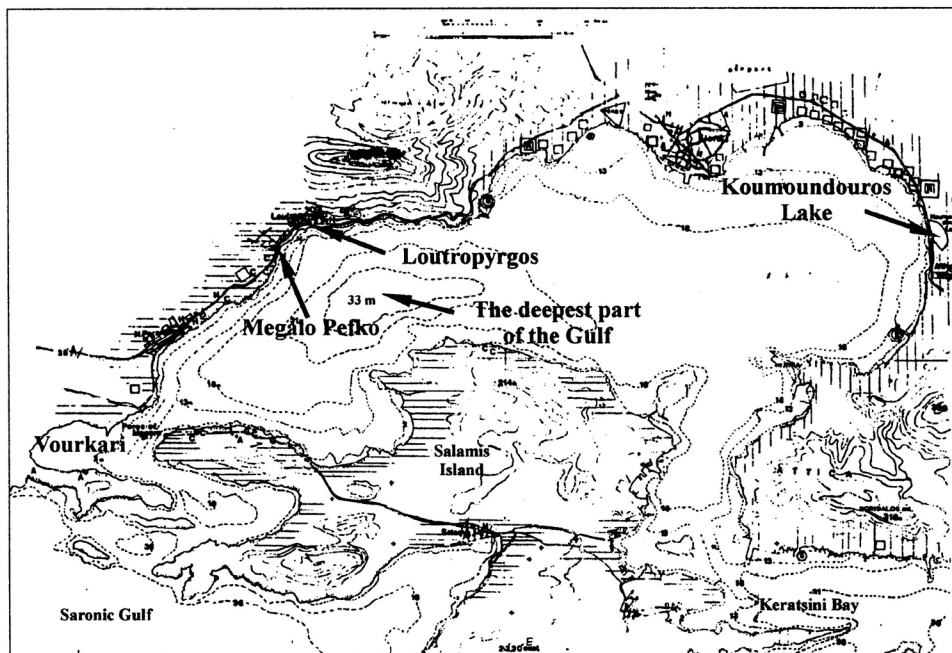


Figure 1. Map of the microenvironments of the Gulf of Elefsis.

Samples of the »surface microlayer« were collected by applying carefully a wide perspex plate on the surface of the sea and by collecting the water attached on the surface of the plate in polyethylene bottles.²⁷

All samples were filtered through 0.45 μm Nuclepore filters. The filtered samples were stored at +4 °C until analysis.²⁸

Analysis: Analytical grade Chelex-100 of 200–400 mesh and concentrated HNO_3 and HClO_4 70% were used.

To ensure low trace metal blanks, a Milli-Q water purification system was used. A buffer of 2.5 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}/\text{pH}$ 6.3 which has been pretreated with Chelex-100, was used for the determination with differential pulse anodic stripping voltametry (DPASV).

Na-Chelex-100 was slurried into 0.8 cm i.d. metal free glass columns containing styrofoam frits and converted to the Ca form with CaCl_2

1 M. The CaCl_2 solution has been pretreated with Chelex-100 to low trace metal blanks.

A flow rate of 3.5–4.0 mL/min was used throughout, giving a contact time of 9–10 sec.¹⁵

For the DPASV an AMEL model 433 Polarographic Analyser was employed, using hanging mercury drop electrode (HMDE).

Each metal was determined separately using deposition potential of: -600 mV for Pb, -800 mV for Cd and -1200 mV for Zn.¹⁵ The deposition time was 300 seconds for Pb and Cd and 60 sec for Zn.

All glassware and polyethylene bottles were pretreated with 10% solution of HNO_3 for two days.

To minimize adsorptive losses of trace metals from water samples, all the glassware were equilibrated with purified 2 mM CaCl_2 in 2 mM tris(hydroxymethyl)amino methane/HCl overnight before use.¹⁸

Particulate matter was determined after the filtration of known volume of the sample through preweighed $0.45 \mu\text{M}$ Nucleopore membrane filters. The filters holding the known weight of particulate matter were digested in specially designed PTFE containers placed on a hot plate by using con. HNO_3 .

Speciation Procedure: The applied speciation scheme (Figure 2) determined by the chosen time scale of measurements, the different contact times with Chelex-100 (in column or batch experiments), the manner of sample stirring and the thickness of diffusion layer in DPASV measurement, allows according to Figura and McDuffie^{15,16} to classify the soluble metal species, into four »general« fractions:

- a) *Very Labile fraction* which is determined with direct ASV analysis of the sample.
- b) *Moderately Labile fraction:* The sample was passed with a contact time of 9–10 sec through Ca-Chelex column to collect the moderately labile fraction together

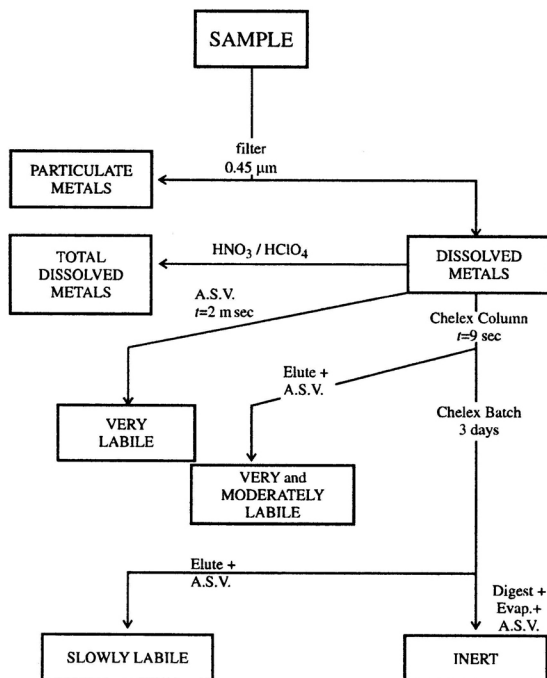


Figure 2. Flow chart of trace metal speciation scheme.

with the very labile one. The difference between retained and very labile fraction gives the moderately labile fraction.

c) *Slowly Labile fraction*: The effluent from treatment (b) was stirred for three days with Ca-Chelex resin. The resin retains the slowly labile fraction.

d) *Inert fraction*: The effluent from (c) contained the inert fraction which was treated with con. HNO_3 and HClO_4 70%.

The *total dissolved metal* is determined after treatment of the sample with con. HNO_3 and HClO_4 70%.

RESULTS AND DISCUSSION

Table I gives the physicochemical parameters characterizing each sample.

The total concentrations of each metal together with those of the four fractions are given in Table II.

TABLE I
Physicochemical conditions in the stations studied

a/a	Area	Depth (m)	T (°C)	pH	D.O. (p.p.m)	S ‰
1	Koumoundouros lake	0.25	16.3	8.07	11.0	17.24
2	Koumoundouros lake (surface film)	surface film	16.3	8.07	11.0	18.10
3	Outlet of Koumoundouros lake (marine site)	0.25	16.0	8.00	13.0	39.87
4	Gulf of Elefsis (surface)	0.25	16.9	7.61	7.9	39.94
5	Gulf of Elefsis (above thermocline)	20	14	-	7.9	39.94
6	Gulf of Elefsis (below thermocline)	25	7.0	6.66	0.2	40.81
7	Gulf of Elefsis (bottom)	33	7.0	6.60	0.2	-
8	Vourkari	0.25	22.5	8.32	10.5	45.71
9	Vourkari (surface film)	surface film	22.5	8.32	10.5	>45.7
10	Loutropyrgos (surface)	0.25	16.5	8.32	10.7	39.4
11	Loutropyrgos (bottom)	3	16.5	8.32	9.0	38.9
12	Megalo Pefko	0.25	18.2	8.30	15.2	40.7

D.O = Dissolved Oxygen

The Koumoundouros Lake.

This coastal lake is in fact a brackish lagoon known from the antiquity but it has suffered during the second part of the present century from many human interventions and heavy pollution. Its size and depth have been

TABLE II
Metal speciation results

Pb					
AREA	Very Labile	Moderately Labile	Slowly Labile	Inert	Total
Koumoundouros lake	0.73	0.63	0.75	1.81	3.92
Koumoundouros lake (surface film)	0.20	0.28	0.55	2.80	3.83
Outlet of Koumoundouros lake	1.59	0.05	0.27	0.79	2.71
Vourkari	0.98	0.58	0.33	1.14	3.03
Vourkari (surface film)	2.45	1.36	2.53	2.53	8.87
Elefsis surface	0.73	0.26	0.48	0.59	2.05
Elefsis above thermocline	0.68	0.50	0.38	1.00	3.05
Elefsis below thermocline	0.30	0.37	0.54	2.26	3.46
Elefsis bottom	0.45	0.73	0.95	1.40	3.53
Loutropyrgos surface	0.29	0.69	0.37	0.99	2.33
Loutropyrgos bottom	0.64	0.42	0.45	1.32	2.83
Megalo Pefko	0.59	0.64	0.74	0.80	2.78
Cd					
AREA	Very Labile	Moderately Labile	Slowly Labile	Inert	Total
Koumoundouros lake	0.41	6.55	0.58	1.10	8.64
Koumoundouros lake (surface film)	1.90	5.06	1.24	2.13	10.34
Outlet of Koumoundouros lake	1.01	0.45	0.38	0.98	2.81
Vourkari	1.54	0.87	0.75	1.14	4.30
Vourkari (surface film)	0.39	0.33	2.95	1.57	5.24
Elefsis surface	0.44	0.88	0.42	0.92	2.63
Elefsis above thermocline	2.07	1.33	0.28	0.56	4.24
Elefsis below thermocline	2.41	1.35	0.28	0.65	4.69
Elefsis bottom	2.43	0.92	0.54	0.38	4.26
Loutropyrgos surface	0.44	0.19	0.12	0.06	0.81
Loutropyrgos bottom	0.49	0.22	0.15	4.98	5.83
Megalo Pefko	0.08	0.31	0.19	0.26	0.83
Zn					
AREA	Very Labile	Moderately Labile	Slowly Labile	Inert	Total
Koumoundouros lake	1.82	5.63	7.23	3.89	18.57
Koumoundouros lake (surface film)	4.33	3.41	7.51	3.19	18.43
Outlet of Koumoundouros lake	0.92	3.72	3.74	2.85	11.22
Vourkari	10.09	4.52	3.88	4.30	22.79
Vourkari (surface film)	0.88	0.73	13.83	8.19	23.63
Elefsis surface	4.63	2.91	6.54	3.75	17.83
Elefsis above thermocline	4.01	4.10	6.00	8.65	3.00
Elefsis below thermocline	4.79	3.59	3.72	9.37	21.47
Elefsis bottom	2.05	4.63	2.51	2.53	2.00
Loutropyrgos surface	4.85	1.62	3.38	3.00	12.85
Loutropyrgos bottom	4.26	1.42	2.70	11.64	20.02
Megalo Pefko	0.66	6.40	6.05	4.87	17.97

drastically reduced and its salinity increased because the natural freshwater inputs (mainly underwater springs) it receives have been minimized.

The overflowing water leaves the lagoon through a narrow and very shallow channel in which surface and subsurface waters of the lagoon are mixed thoroughly and then discharge into the gulf of Elefsis, creating in the vicinity of the outlet significant salinity gradients.

All metals show similar distributions in the area of discharge. Their total dissolved metal concentration is higher in the lagoon and decreases gradually towards the sea, due mainly to the dilution of the heavily laden with metals brackish lake water by the marine one, though the latter is also quite polluted. The dilution effect is more obvious for Cd and Zn when comparing the concentrations in the lake to those of Elefsis, above the thermocline. This is not the case for Pb which has at the outlet a particularly high labile fraction contribution also to a high total Pb concentration.

The speciation of all three metals changes dramatically at the discharge site. In all cases the percentage of the »very labile« fraction increases significantly in the area of the discharge at the expense of the less labile species present in the lagoon. This might be attributed to the fact that in the marine environment the metals studied are present mainly as »very labile« ions and chloro-complexes.

The distribution of the metals in the lagoon is interesting and differs from metal to metal. The total metal concentrations are very high (Table II) due to local industrial and heavy traffic pollution entering the lagoon partly *via* the atmospheric fallout and runoff, partly through direct discharges and partly from leakage from the polluted underground water horizon. It is noteworthy that crude oil refineries, ironworks and military installations operate in the vicinity of this site.

The total concentrations of Pb and Zn in the bulk of the lake water is similar to that found at the surface layer (Table II), though the latter was enriched in Cd. However, the partitioning of the metals in the various fractions is quite different in the two compartments.

For Pb the »inert« fraction prevails and its contribution at the surface layer exceeds the 73% whereas in the water column is around 46%.

Concomitantly the »very« labile and »moderately« labile fractions together represent 12.5% (surface layer) and 34.5% (subsurface), respectively. In »slowly« labile fraction the difference is less impressive. Batley and Gardner²⁹ have reported 40–80% of dissolved Pb in the form of inorganic colloidal fraction in sea water. It is noteworthy that in fresh waters even at low pH most of the Pb appears as an »inert« inorganic species, possibly $\text{Pb}_2(\text{OH})_2\text{CO}_3$.²⁸ This species as well as $\text{PbCO}_3 \cdot 2\text{PbO}$ are also among the ones found in automobile exhaust gases and in airborne particles generated

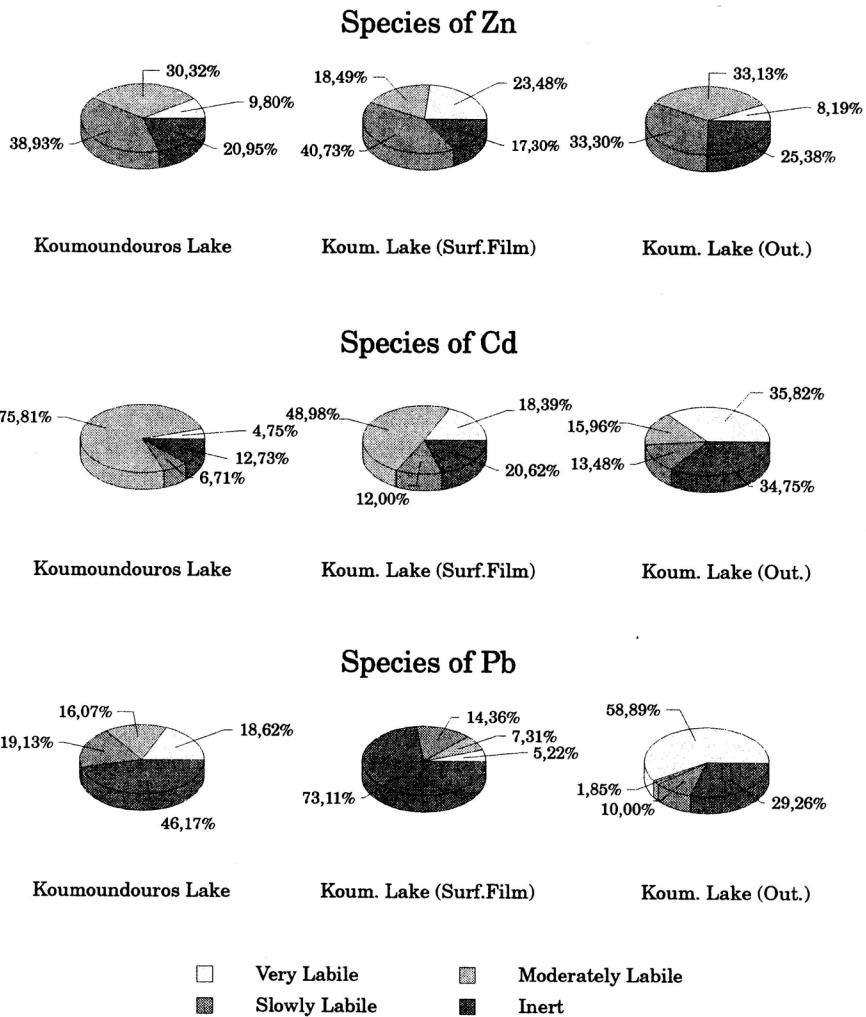


Figure 3. Percentage distributions of dissolved fractions of Zn, Cd and Pb in Koumoundouros Lake.

by the very heavy traffic of the national road which is located on the narrow strip of land which separates the sea from the lagoon (see Figure 1).

For Cd the prevailing fraction is the »moderately labile« one which represents more than 75% of the total in the subsurface and almost 49% at the surface layer. The considerably higher percentage contributions of »moderately« and »slowly« labile fractions in the case of Cd compared to Pb, could be attributed to their tendency to form mainly ionic (Cd^{2+}) species and car-

bonato complexes (CdCO_3) in fresh and brackish water at high pH and to be adsorbed less on colloidal particles, thus not forming »inert« pseudo-colloids.^{30,31}

Zinc shows almost the same pattern as Cd. The prevailing forms are the »slowly« and »moderately« labile fractions. Because the three main Zn species computed to be present in marine waters are Zn^{2+} (27%); chloro complexes (47%) and ZnCO_3 (17%), whereas in fresh waters the dominant inorganic forms are Zn^{2+} (50%) and ZnCO_3 (38%),^{30,31} in the brackish lagoon the percentages are expected to be intermediate with high presence of ZnCO_3 . The latter and particularly the basic carbonato complexes of Zn as well as any of its organic complexes have relatively low lability.²⁸

Despite any differences, the very important common feature is that the »inert« and »slowly labile« fractions for all three metals represent at the surface film a considerably higher percentage than in the under-surface statum which, in turn, is enriched in the »very« and »moderately« labile species.

This conclusion may lead to two hypotheses:

a) That a considerable proportion of the metals studied, enters the system in the form of very fine dry particles, dust or aerosols rich in carbonates, resulting to an enrichment of the surface with less labile species which dissolve to a certain extent rather easily to produce in the under-surface water more labile forms.

b) That there is an *in situ* formation of relatively stable organic complexes with ligands of high molecular weight such as humic and fulvic acids *etc.*, which either dissolved or dispersed and adsorbed on fine inorganic absorbents, such as hydrated iron oxides, form non-labile colloids and pseudo-colloids. These metal species could be accumulated in foams and the rich in hydrocarbons and surfactants surface films which cover frequently polluted water bodies with high productivity, such as the Koumoundouros lake.

It is most probable that both the aforementioned mechanisms could co-exist and contribute to a certain degree in a combined way.

Vourkari

This is a very shallow lagoon with depths not exceeding 1 m. The most prominent characteristic of this site is the very high salinity prevailing during the summer months (higher than 45), with even higher values at the surface microlayer.

As expected, after a heavy rainfall, the runoff from the surrounding rural land (which is neither industrial nor touristic but partly agricultural, partly forested and partly inhabited with relatively few houses without direct discharge to the lagoon) results to an abrupt decrease of the salinity and to rapid flashing out of the otherwise rather stagnant water.

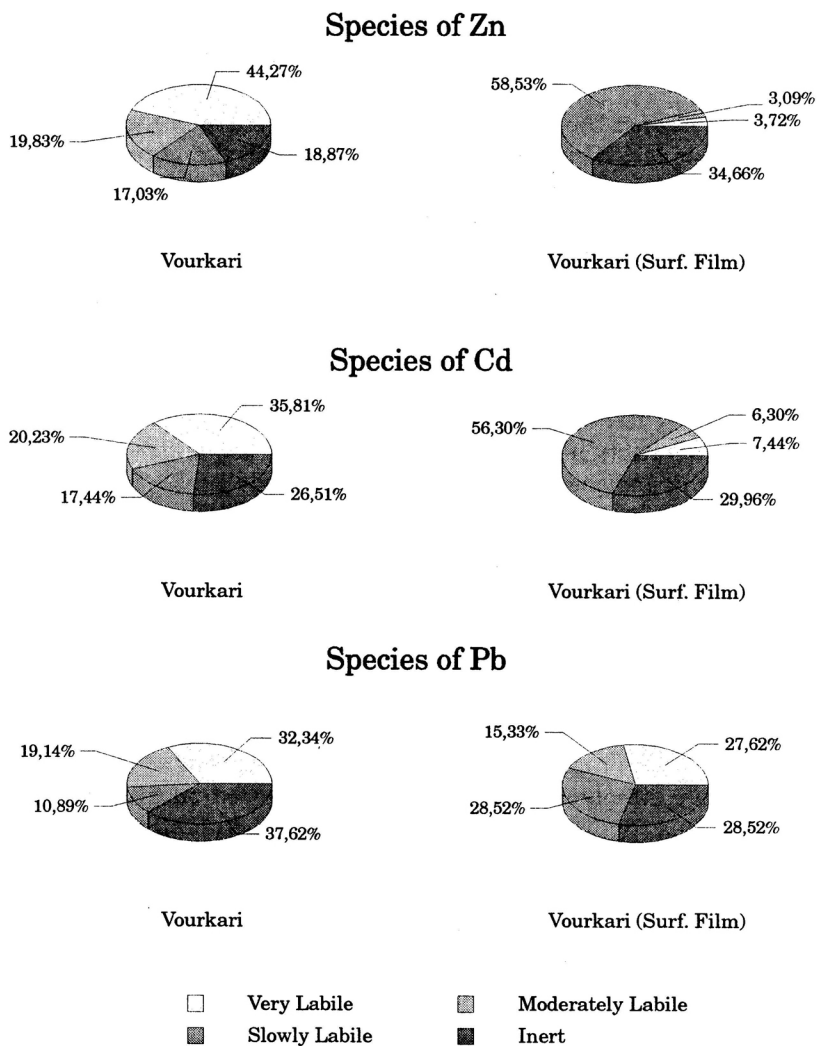


Figure 4. Percentage distributions of dissolved fractions of Zn, Cd and Pb in Vourkari.

The sampled site was at the northern part of the lagoon and had a depth of 40 cm.

It is noteworthy that although the area does not receive direct industrial discharges and is located at some distance from traffic routes the trace metal concentrations determined there are relatively high, most probably due to important (non-point) pollution distributed *via* the atmosphere, combined

with the very restricted water circulation and the relatively long residence time during the summer period.

For all three metals, the non-labile fraction (»slowly« labile and »inert«) is much higher at the surface layer than in the underlying water column.

Especially for Cd and Zn, the contribution of the »very labile« and the »moderately labile« fractions at the surface film are particularly small, paralleled by an impressively high percentage (more than 86%) of the non-labile (especially »slowly« labile) fraction.

The important common feature for all three metals is the presence of a higher concentration of non-labile fraction at the surface layer compared to the subsurface water, a feature which appears to be similar to that observed at the Koumoundouros lake, despite the great difference between the two lagoons, particularly in the salinity of their waters. These results show that the given conditions, despite the very high Cl^- concentrations, do not seem to favour the formation of high concentrations of »very« or »moderately« labile ions and chloro complexes such as CdCl^+ and CdCl_2 or ZnCl^+ and ZnCl_2 , or more »exotic« species such as CdCl_4^{2-} . Although carbonato and carbonato-hydroxy complexes of Pb, Zn and eventually Cd and even pseudo-colloids and complexes with organic ligands, could be probably forms prevailing at the surface layer of the Vourkari lagoon, one should not overlook the strong influence exerted on Cd-chloro complexes by the presence of »inert« cations, such as Li^+ , Na^+ , Mg^{2+} and Al^{3+} .³² Similarly, Pb complexation with chloride ions is strongly influenced by the presence of »inert« cations.³³

Loutropyrgos – Megalo Pefko

These sites along the northern coast of the gulf of Elefsis are characterized by very limited industrial or touristic activities and no hotels, campings or direct discharges of sewage or waste waters by houses or municipal installations. Interesting features on which our sampling was focused were the small underwater springs, the massive growth of seaweeds and the presence of many benthic species, such as mussels and clams which are frequently collected by divers. Few mussel-growing farms also operate there. These activities together with the springs contribute to resuspension of fine seabottom sediments and enrichment of the water column with nutrients emanating from the sediments.

The samples examined were taken from surface and near bottom water (3 m depth).

The major features observed in these stations are: (a) the higher total metal concentrations determined in the near bottom samples of Loutropyrgos for the three metals studied, compared to those of the upper part of the water column and those found in the Megalo Pefko station; (b) the significant increase of the »inert« fraction of all metals at the near bottom samples

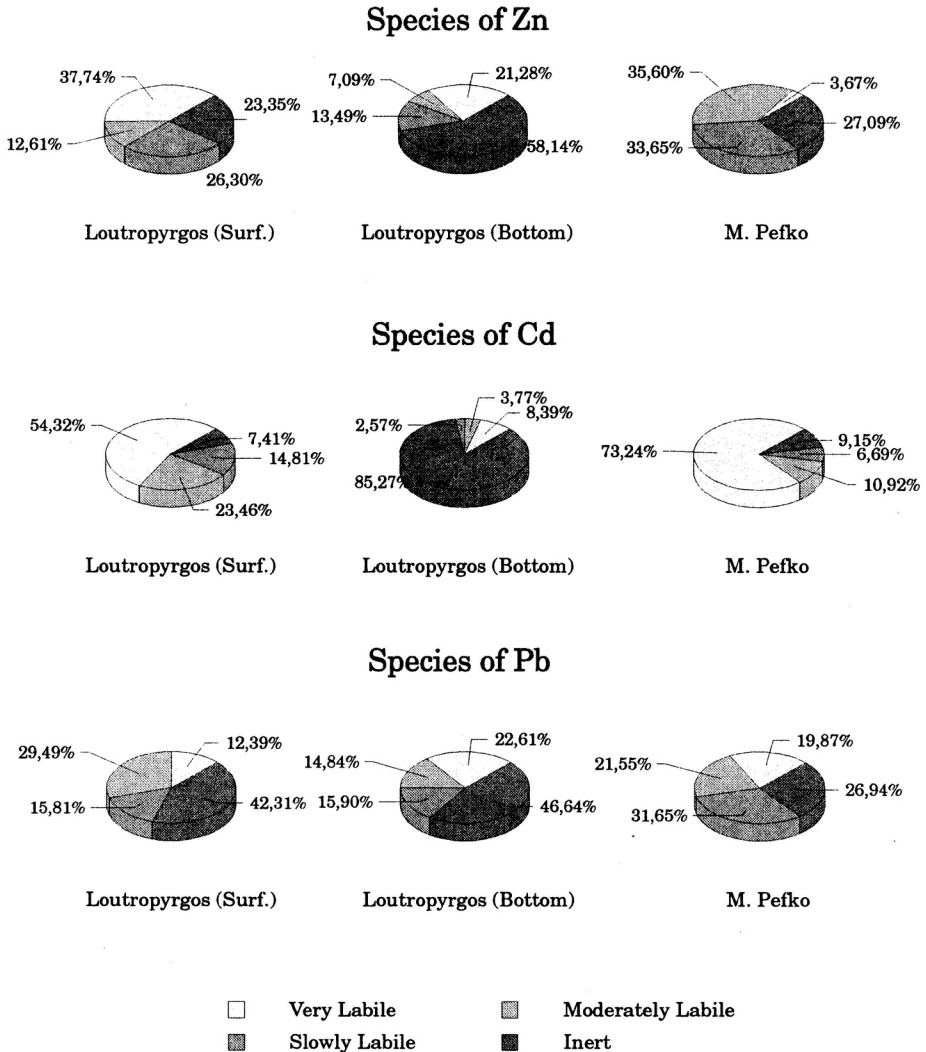


Figure 5. Percentage distributions of dissolved fractions of Zn, Cd and Pb in Loutropyrgos – M. Pefko.

compared to the surface ones. This feature may be attributed to the mechanical resuspension of colloids combined with the fact that the area is particularly rich in biogenic organic matter deriving from the degradation of the abundant biota present. The vertical distribution of dissolved oxygen concentration and its consumption noted in the near-bottom waters (despite the fact that they are shallow) indicate the presence of rapid biodegradation

and some redox reactions producing, in the sediment – water interface and the underlying waters, organic ligands able to form non-labile metal complexes.

Gulf of Elefsis (The Deepest Part)

The hydrology and topography of the area favour the creation of intermittently anoxic conditions prevailing during August at the deepest part of

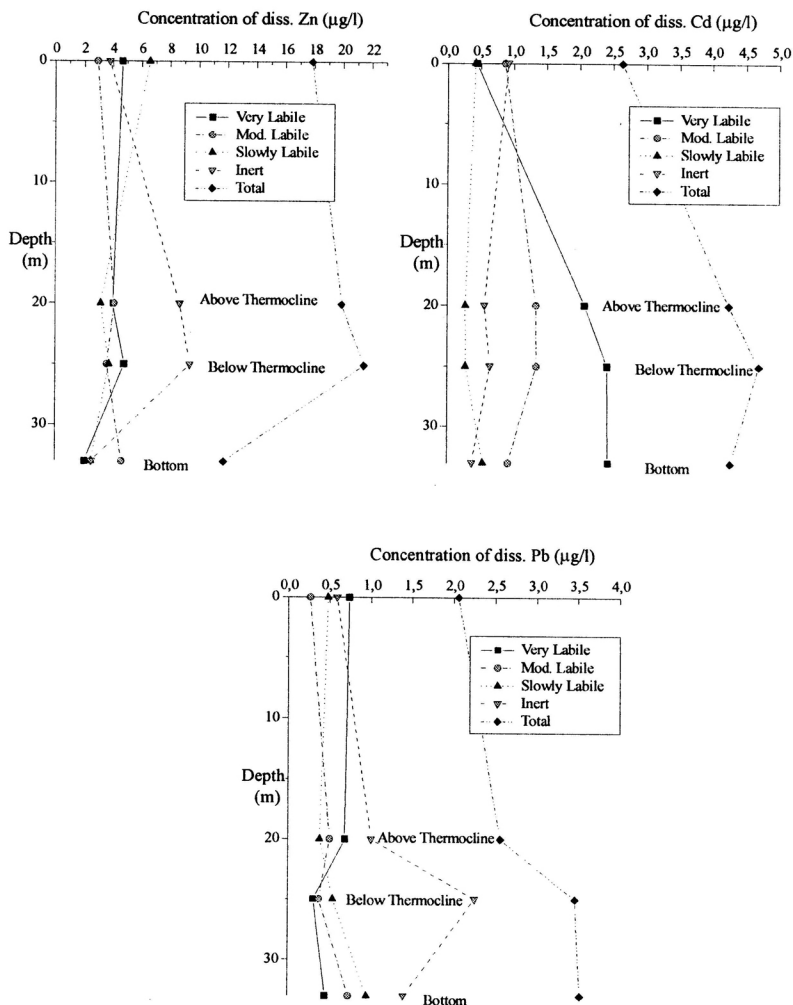


Figure 6. Vertical distributions of the concentrations of the various dissolved fractions of Zn, Cd and Pb.

the gulf of Elefsis. These conditions which have been described in previous works,¹⁸⁻²³ make this station very important for the study of the speciation of metals.

Four samples were collected from the surface (below the surface film); just above the thermocline (20 m depth); just below the thermocline (25 m depth) and near the sea bottom (33 m depth), avoiding as much as possible any disturbance of the sediments.

The meteorological conditions in the area have prevented the collection of a surface layer sample at this station, despite our repeated attempts.

Figure 6 presents the concentration profiles for total dissolved Pb, Cd and Zn and for each labile fraction of every one of the metals studied. Figure 7a shows the profile of the concentrations of the particulate forms of the metals in $\mu\text{g/l}$ whereas Figure 7b shows the metal content of the particulate matter in each depth (in $\mu\text{g/g}$).

Figure 8 presents the percentage contributions of the various labile fractions in each sample.

The main pattern of Pb shows a decrease with depth of the »very labile« fraction followed by an increase of all other forms, especially the »inert« one and of course of the total dissolved Pb concentration. The increase of the »inert« fraction is very impressive at the lowest part of the thermocline.

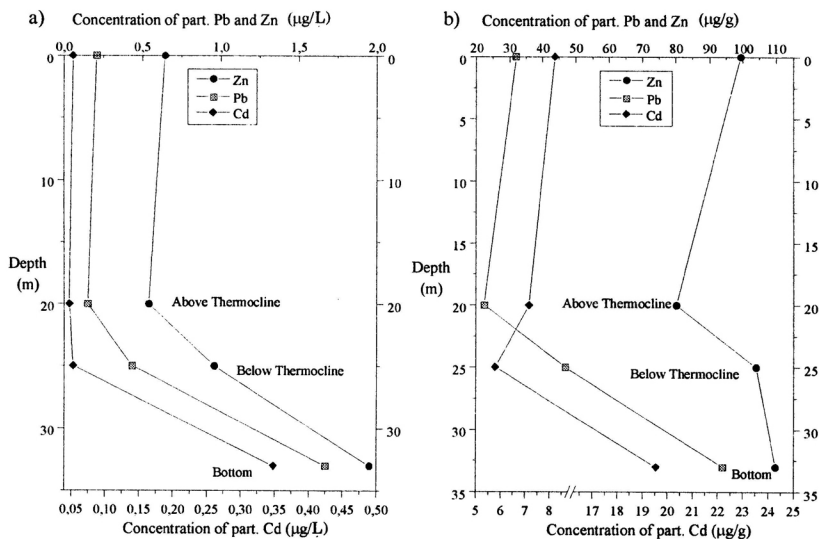


Figure 7. a) Vertical distribution of the concentrations in $\mu\text{g/L}$ of the particulate species of Zn, Cd and Pb. b) Vertical distribution of the concentrations in $\mu\text{g/g}$ of the particulate species of Zn, Cd and Pb.

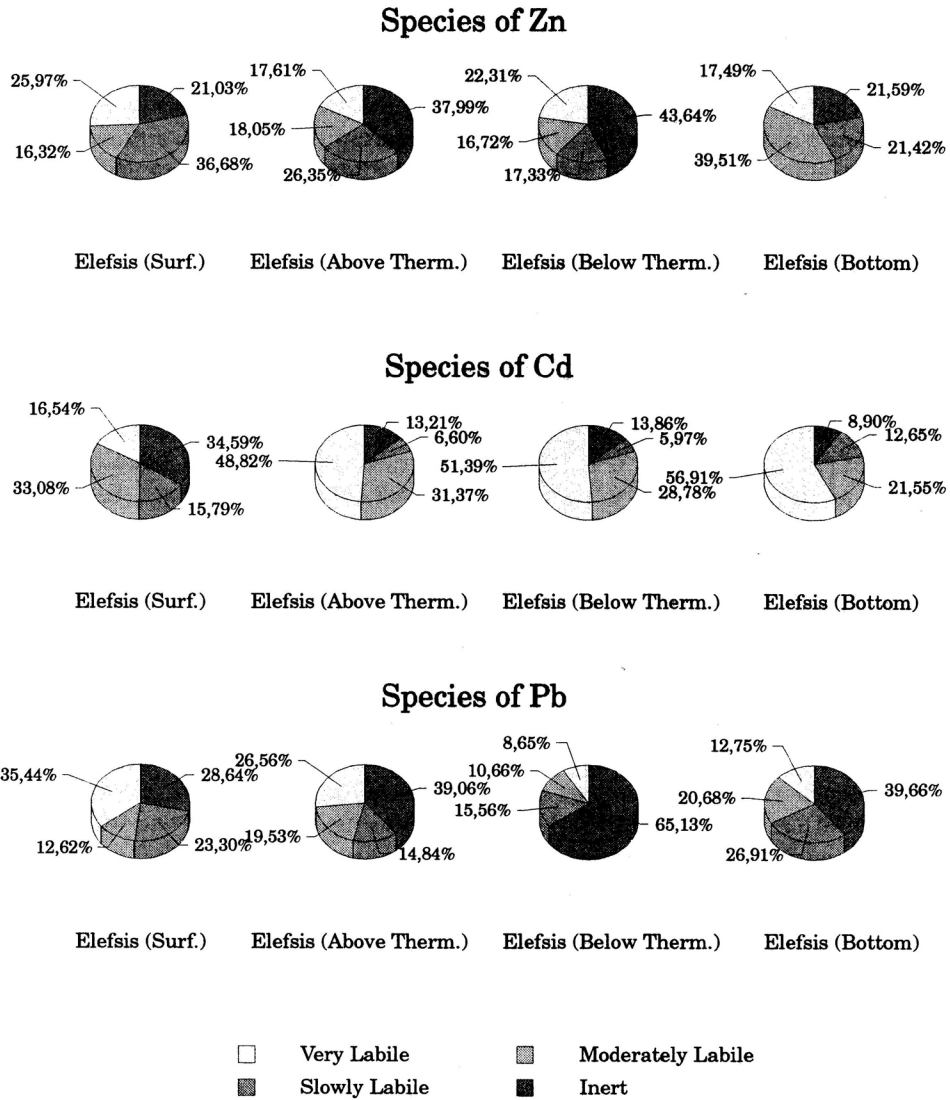


Figure 8. Percentage distributions of dissolved fractions of Zn, Cd and Pb in Elefsis (Deepest part).

It is most probable that the peak of the »inert« fraction is due to accumulation of electrochemically inactive Pb species and rich in Pb colloids on the strong density gradients present. It is also noteworthy that in the highly stratified waters below the thermocline there is a very impressive decrease of the »inert« fraction followed by a rapid increase of the concentra-

tion of particulate Pb, which reaches its maximum near the seabottom, paralleled by an impressive increase of the content of the particulate matter in Pb. The odour of the water samples below the thermocline indicates the presence of hydrosulfide, which could be present even in the oxic layer of stratified waters.³⁴ When hydrogen sulfide anions, HS^- and metal ions co-exist in solution electrochemically »inert« complexes such as PbHS^+ and $\text{Pb}(\text{HS})_2$ and mainly $\text{PbS}(\text{HS})^-$ are formed.³⁵ These species together with other metal sulfides are transformed into particles enriched in metal where PbS prevails. This explains the rapid decrease of »inert« species with simultaneous increase of particulate Pb. These results are also in agreement with previous findings and the distribution on Pb in the sediments of the area.²⁵

A similar to the aforementioned feature concerning a peak in the concentration of the Zn species is observed in the entire zone above and below the thermocline. However, the final dissolved Zn concentration at the bottom is lower than that at the surface. The »moderately« labile fraction of Zn shows an increase with depth, but the concentrations of both the »very« labile and »slowly« labile fractions decrease towards the bottom. The concentration of »inert« Zn also shows a peak in the thermocline followed by a rapid decrease, paralleled by a significant increase of particulate Zn below the thermocline with a maximum around 2,0 $\mu\text{g/l}$ near the sea bottom.

The interpretation of this profile is analogous to that of Pb. »Inert« dissolved species (*e.g.* $\text{Zn}(\text{HS})_3^-$) accumulated at the thermocline are transformed into insoluble species in the near sea bottom waters.

Similar downward distributions of dissolved and particulate Zn have been recorded also in the past in the same station and were attributed to the formation of particulate Zn species (including ZnS) at the expense of dissolved ones.²²

Cadmium, even in the upper part of the water column shows a small downward decrease of its »inert« fraction concentration paralleled by an impressive increase of the »very« labile form which has its maximum just below the thermocline. The other two fractions show less important fluctuations. The total dissolved Cd concentration near the bottom is slightly lower than that at the thermocline.

Perhaps Cd which has been taken up during primary production at the surface waters is released combined with organic matter (thus as »inert« fraction) at the upper part of the water column and decomposes gradually in deeper waters. The tendency of Cd to form, in general, labile species mainly Cd^{2+} and CdCl^+ in well oxygenated waters is well known;^{7,8} the formation of Cd sulfides at the oxygen poor waters and the anoxic water-sediment interface seems to have produced the particulate species CdS than the non-labile dissolved CdSH^+ , $\text{Cd}(\text{HS})_2$ or $\text{Cd}(\text{HS})_3^-$ species.^{35,36}

CONCLUSIONS

Metal speciation studies in sea waters under suitable experimental conditions are important for the in depth understanding of biogeochemical phenomena.

In the present work an attempt is made to expand the spectrum of their application by introducing them in the study of »extreme«, but real natural microenvironments which are part of a larger, important system.

Through this approach the understanding of the mechanisms of generation, transformation, transport and distribution of different labile and particulate metal species in the marine environment is enhanced.

The Gulf of Elefsis has provided an ideal natural laboratory for speciation studies but it is expected that analogous conditions could be identified in many other parts of the Mediterranean and other seas for the application of similar approaches.

The study of the distribution of species of different lability of Pb, Zn and Cd in two extremely different in nature lagoons, namely the Koumoundouros lake, (which is a brackish, heavily polluted by industry water body) and Vourkari, (which is a rather »remote« and rural, very saline shallow lagoon) gave some impressively comparable results. Despite the specific difference in levels and percentage contributions of various labile fractions present, the »inert« forms of all the metals studied, attributed mainly to inorganic pseudo-colloids and carbonates, were significantly enriched at the surface layer of both lagoons.

Exactly the opposite is the case in the coastal marine areas (Loutropyrgos, Megalo Pefko) which have high benthic biota productivity and high bottom water turbulence due to underwater springs and anthropogenic activities at the sea bottom. In this case the »inert« and less labile species are found in the bottom waters and are attributed, mainly, to metal complexes with organic ligands.

The concentration peaks of the »inert« Pb and Zn species determined in the deepest, highly stratified part of the Gulf of Elefsis was found around the stable thermocline. Near the sediment-water interface where redox reactions seem to play an important role the particulate species predominate at the expense of the »inert« dissolved ones.

The bulk of the results from the entire region indicate that the »inert« dissolved metal fraction behaves, to a large extent in a way similar to very small, light particulates and it is accumulated easily either on water surfaces and along density gradients or in areas of high turbidity.

This is consistent with the fact that the »inert« fraction includes trace metal complexes with organic ligands deriving, to a large extent, from biodegradation and metabolism.

In general this fraction could be formed authigenically but it is possible to enter the system also *via* the atmosphere and runoff from industrial and natural sources.

Although the predominance of the »inert« and »slowly« labile fraction in interfaces is clear, the labile forms (»very« and »moderately« labile species), corresponding to ions and ion pairs, predominate in the bulk of the water column, even in this heavily polluted and enclosed water body, with restricted circulation and high loads of particulate matter.

These findings come from our first attempt to study the speciation of Pb, Zn and Cd in the gulf of Elefsis by employing a method very well developed and used by Prof. Branica and his laboratory, namely DPASV, in combination with Chelex-100, in microenvironments of an extremely complex natural system and in this respect they should be considered as preliminary.

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SAŽETAK

Ispitivanje kemijskih oblika tragova metala u zaljevu Elefsis, Grčka

Michael J. Scoullou i Alexandra S. Pavlidou

U ispitivanjima Pb, Cd i Zn u zaljevu Elefsis primijenjena je metoda koja razlikuje ionske vrste tragova metala prema njihovoj relativnoj labilnosti. Korištena je diferencijalna pulsna voltometrija anodnog otapanja (DPASV) uz različita vremena zadržavanja na smoli Chelex-100 primijenjenoj na koloni ili dodanoj u masu otopine. Rezultati pokazuju da u dva različita mikrokoliša zaljeva (sa salinitetom 17 i 45‰) u površinskim slojevima prevladavaju manje labilne i inertne vrste, a u glavnini vodene mase prevladava labilna vrsta metalnih iona. Međutim, na termoklimi i ispod nje povećava se količina inertne vrste prateći paralelno raspodjelu metala u partikularnoj tvari.