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Application of ecological risk indicators for the assessment of Greek surficial sediments contaminated by toxic metals.

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Abstract

The present research investigates the partitioning of six selected toxic metals (Ni, Cr, Pb, Zn, Cu, As) in eight sediment samples; half of them were collected from Elefsis gulf and the other half were taken from Koumoundourou lake, Athens, Greece. Each one of them was treated by applying Tessier's five step sequential extraction procedure. Regarding gulf sediments, the results indicated that Cu exhibits a strong affinity to the organic matter with percentages ranging from 65% - 78%. Considerable amount of Zn (32%-40%) is bound to the Fe-Mn fraction and the non-residual fraction, while Cr and Ni are bound to the organic fraction, an observation that suits all toxic metals examined. Regarding lake sediments, Pb is the predominant metal bound to Fe-Mn (48% - 51%). It is also noteworthy the percentage of Zn bound to carbonated fraction (5% - 15%) indicating biological availability. Concluding, the application of several ecological risk indicators demonstrated that Elefsis gulf sediments correspond to a moderate pollution level, with Pb and Ni being less bioavaliable than in the lake's samples, in contrast to Zn which is more bioavaliable. Finally, Koumoundourou lakes' basin is characterized of "low risk".

Keywords: toxic metals; partitioning; sequential extraction; sediments; risk assessment

1. Introduction

Toxic metals are considered to be pollutants of great significance mainly due to their toxicity, high persistence, and non-degradability. (Lim et al., 2008; Weng et al., 2008; Kumar et al., 2008; Wang et al., 2011)**.** Toxic metals present in sea or lake sediments may potentially be released into the water, thus severely affecting its quality and consequently contaminating the entire aquatic environment (Laing et al., 2007; Zhong et al., 2006; Yang et al., 2009)**.**

Metals are ubiquitous in the environment, in various forms, and their presence has been increasing throughout the years, mainly due to anthropogenic derived inputs. The total concentration of a metal in a soil or sediment sample can be of great importance and assistance for many geochemical applications, but it is considered a rather inadequate indicator of its bioavailability and toxicity (Meyer, 2002; Hahladakis et al., 2013). Consequently, total concentrations of metals should not be used for the assessment of their environmental impact, without taking into account the available fraction of the examined metal in the sediment/soil sample (Smith, 2011; Giacalone et al., 2005)**.** Consequently, the metal properties are in direct dependence on the physicochemical form in which they appear (Davidson et al., 1994), a phenomenon characterized by the term ‘‘partitioning’’ or “speciation” (Ure et al., 1993; Giacalone et al., 2005).

Partitioning, according to Tack and Verloo (1995), is “the identification and quantification of the different, defined species, forms or phases in which an element occurs” and it is basically a function of the mineralogy and chemistry of the soil/sediment sample (Tessier et al., 1979). The partitioning of each metal is then determined by the use of sequential extraction procedures (SEPs), followed by subsequent analysis of the soluble metals using, most of the time, analytical techniques such as atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP). There are various leaching tests and SEPs that have been designed and implemented with the aim of deducing information regarding the mobility and/or bioavailability of metals/metalloids in soils/sediments. SEPs employ different extraction steps with the aim of providing information on the origin, bioavailability and transport of multiple elements in the examined soils/sediments. All the aforementioned reasons make these procedures valuable tools both in contaminant analysis as well as for the evaluation of potential disposal options and the reuse of dredged sediments (* Petrucci et al., 2011).

There are a number of SEPs applied, under a variety of reagents and conditions, to achieve successful extraction of metals (Bacon and Davidson, 2008). Most of these consist of a number of steps which are within the range of 3 and 8 (Oyeyiola et al., 2011). A precise quantification of the examined elements is usually determined by the use of various chemical solutions, of different strengths and/or reactivities, so as to obtain the desirable release of the contaminants from the different soil/sediment fractions (Ryan et al., 2008). The theory behind all SEPs is that the most mobile metals/metalloids are released in the first fraction and continue to be released in order of decreasing mobility. Tessier et al. (1979) determined that there are five fractions in which the mobility of contaminants could be affected by the different environmental conditions; these fractions are the 1) exchangeable, 2) the carbonate, 3) the Fe and Mn oxide, 4) the organic, and finally 5) the residual. Metals, mainly of anthropogenic derived sources, are expected to be affiliated with the first four fractions, while metals that will be found in the residual fraction are, most of the time, considered to be natural entities originated from the parent rock (Ratuzny et al., 2009).

The main objective of this research is the use of Tessier's protocol for a sequential extraction analysis in sediments collected from lake Koumoundourou and Elefsis gulf, Athens, so as to determine the partitioning of six selected toxic elements (Ni, Cr, Pb, Zn, Cu, As), their mobility order and their bioavailability. The selection of the aforementioned elements was mainly done according to their initial concentrations in the samples and their environmental significance. An ecological risk assessment along with a comparison regarding the contamination level of these two adjacent areas is also attempted.

2. Materials and methods

2.1. Study area and sample collection

Koumoundourou lake (Fig. 1a) is surrounded by many industrial sources. The Athens-Corinth national road separates the lake from the adjacent Elefsis gulf, though both aquatic systems are linked together via a narrow weir and a pipeline. Koumoundourou lake covers an area of approximately 147,000 m^2, while it is about 600 m long and 400 m wide. Its shoreline perimeter is nearly 1,700 m and the average surface level is almost 1.4 m above sea level (Karageorgis et al., 2009; Hahladakis et al., 2013). The water depths reach a maximum of 3.3 m, in the North East part of the lake, while in the South East part are less than 1 m (Roussakis, 2003). Within the wider area of the lake there are a marble cutting factory and a military camp; the latter is used as an oil supply depot station and it is located on the east side. Moreover, the lake acts as a recipient of groundwater leachates from the major landfill of Athens (Karageorgis et al., 2009; Conides et al., 1996; Hahladakis et al., 2013).

On the other hand, Elefsis gulf (Fig. 1b) acts as a main passage for tankers, cargo-ships and ferryboats. Along its northern coasts, there are various heavy industry units (such as Hellenic Petroleum Elefsis refineries, EBO-PYRKAL munitions industries, paper mills, cement industries, HALYVOURGIKI steel industry and shipyards), two harbours and two spots with liquid fuel tanks (Sakellariadou et al., 2009).

Consequently, all the aforementioned installations and activities cause a substantial environmental pressure on the surrounding marine area and have been responsible for seawater and sediment contamination of the gulf and the lake for the last 5 decades. A wide variety of PAHs (Polycyclic Aromatic Hydrocarbons), LNAPLs (Light Non-Aqueous Phase Liquids), DNAPLs (Dense Non-Aqueous Phase Liquids) and toxic metals are considered to be permanent contaminants for both Koumoundourou lake and Elefsis gulf. Of course nowadays, a remarkable environmental improvement has been noticed, especially in the water column, mainly due the use of suitable filters, improved waste control systems and decrease in the total amount of wastes produced (Sakellariadou et al., 2009).

Each of the eight sampling sites served for the collection of three samples (n=3) that would finally form one homogenized sample from each sampling site. Hence, eight surficial samples (four from the lake and four from the gulf, were collected (from a 10-15 cm bottom depth), in order to be examined in their toxic metal content and distribution. The aforementioned range of depth was mainly selected, since according to EPA, “for monitoring and assessment studies where historical contamination is not the focus, the upper 10 to 15 cm is typically the horizon of interest” (US EPA, 2001). Generally, “the most recently deposited sediments and most epifaunal and infaunal organisms are found in this horizon” (US EPA, 2001).

Hence, no spatial, horizontal or vertical distribution was assessed, a scientific path that is regularly followed in many recent studies (Gao et al., 2013; Xiao et al., 2013; Xiao et al., 2015).

The samples taken from the gulf were labeled as E1, E2, E3 and E4 (Fig. 1b) and were all collected from the north-western part. On the other hand, lake's samples (labelled as K1, K2, K3 and K4) were taken from two different areas. Two of them from the north side (K2, K4), close to an existing water barrier which prevents further contamination of the water of the lake from petroleum hydrocarbons and two from the east side (K1, K3), close to an existing military camp (Fig. 1a). The selection of the sampling sites, both for the lake as well as for the gulf, was mainly based on a "close to existing contaminant sources" basis.

All samples were collected by the use of a grab sampler and were kept under freezing conditions (-4 °C) for safe transportation to the laboratory. During sampling the weather was fair, with a ground temperature of approximately 23 °C. The sediments were subjected, in turn, to slowly air drying for nearly two days, gently homogenisation and dry sieving using stainless steel sieves of 2 mm. After sequential grinding and sifting, the sub-samples (1 g) were then subjected to five step extraction, as per Tessier's protocol (Tessier et al., 1979).

2.2. Tessier's protocol

In the present study, Tessier's five step SEP was applied for the extraction of the selected metals from all sediment samples, with a few modifications in the last step. The quantities reported below refer to 1 g of sample (dry weight) that was used for the initial extraction. The steps were as follow:

Fraction 1: is the exchangeable fraction (Exch) where contaminants are mostly adsorbed to clays and organics mainly by electrostatic forces. The contaminants are extracted by the use of 8 mL of sodium acetate solution (1 M NaOAc, pH 8.2), under room temperature, with continuous agitation. From a bioavailability point of view, metals bound to fraction 1 are the ones mostly available (Tessier et al., 1979; Patrick et al., 1977)**.**

Fraction 2: It refers to contaminants that are in carbonated form (Carb). These metals/metalloids are quite sensitive to variations in the temperature and/or the pH of the solution, hence, they are the next most easily available (Tessier et al., 1979; Zimmerman and Weindorf, 2010). The residue from the previous step is leached with the use of 8 mL of 1 M NaOAc, this time by adjusting pH to 5.0 using acetic acid (HOAc). Again, room temperature is required, as well as continuous agitation for approximately 1 h, in order to obtain complete extraction.

Fraction 3: in this fraction the contaminants are bound to Fe/Mn colloids. They usually appear in sediments as agglomerates that are rather thermodynamically unstable, especially in anoxic conditions. They also tend to be sensitive to changes in redox potential (ORP or Eh), exhibiting increased availability at low ORP values. They are mostly bioavailable under reducing conditions (Tessier et al., 1979; Patrick et al., 1977; Zimmerman and Weindorf, 2010). The residue from the previous step is extracted using 20 mL of 0.04 M $NH_2OH\cdot HCl$ in 25% (v/v) HOAc. The experiment takes place at 96 ± 3 °C, while the required time for total dissolution of the Fe oxides is estimated between 6-8 h. Occasional agitation is also required.

Fraction 4: this fraction is associated with contaminants bound to the various forms of organic matter (OrgM). These bonds are considered to be strong. These contaminants are most of the time released when changes to the oxidizing environment occur, followed in turn by degradation of the OrgM (Zimmerman and Weindorf, 2010). Contaminants of this fraction are the least biologically available (Tessier et al., 1979). To the residue from the previous step, 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 are added, and the pH is adjusted to 2 by the use of HNO_3. Then, the mixture is heated to 85 ± 2 °C for 2 h with occasional agitation. A second solution (3 mL of 30% H_2O_2, with adjusted pH to 2) is added and the sample is once more heated to 85 ± 2 °C for 3 h; agitation is again required on an occasional basis. After cooling, an additional 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 is added and the sample is diluted to 20 mL and stirred continuously for 30 min. The addition of NH_4OAc is required to prevent the adsorption of already extracted metals onto the oxidized sediment (Gupta and Chen, 1975).

Fraction 5: is the residual fraction which usually involves contaminants that are strongly bound to the structure of the primary and secondary minerals. These contaminants are not available and can only be released by the use of more corrosive acids such as HF (Tessier et al., 1979; Patrick et al., 1977). To 250 mg from the residue of the previous step is added 20 mL of HNO_3 65% and 60 mL of HF 40% (3:1 mixture) heated to 96 ± 2 °C till dryness. The procedure is repeated two more times with the addition of only 5 mL HNO_3 65% and 5 mL HCl 37% (1:1 mixture) with the solution heated to dryness, the first time, and diluted to 50 mL the second time. Finally, the solution is left to evaporate until 35 mL and is then analyzed in its six selected metal content.

2.3. Determination of physicochemical properties of sediment samples

Moisture and organic matter were determined using method ASTM D2974, specific gravity was calculated according to ASTM D854-92, while pH and Eh were measured according to ASTM D4972 by the use of a Crison pH-meter. Furthermore, cation exchange capacity (CEC) was calculated according to EPA 9081 and PZC (zero point of charge) according to a drift method originally developed for activated carbon. The method, however, provides a quick yet reliable PH_{PZC} (Yang et al., 2004).

Finally, an X-ray diffraction technique (XRD), using a Siemens 5000 refractometer model, was performed so as to determine the main minerals that constituted the sediment samples.

2.4. Chemical analyses

All the chemicals used to prepare the necessary reagents were purchased by Sigma Aldrich. Total metal concentrations in all sediment samples were determined according to EPA method 3051A, for total digestion of soil/sediment samples.

For the partitioning of toxic metals, six (Ni, Cr, Pb, Zn, Cu and As) were selected, with regard to their total concentration in samples, to be measured in the solution at the end of each extraction step. Each solution from each step was, in turn, filtered (0.45 μm), acidified with HNO_3 (Merck, Germany) and then taken to the ICP-MS (Agilent 7500-CX) for the determination of metal concentrations. Each measurement was taken as a replicate of three. The extractable percentage of each metal at each step out of the total metal content of each sediment sample was determined by using the following formula:

$$\text{Extractable Percentage (\%)} = \frac{C_i \cdot B_i}{10 \cdot B_0 \cdot C_0}$$

where C_i is the concentration of each examined metal in the solution of each step measured in ppb, B_i is the weight of the solution at each step measured in g, B_0 is the initial weight of the sediment sample measured in g and C_0 is the initial total concentration of the examined metal in the sediment sample measured in ppm. For the aforementioned calculations the density of all solutions was considered to be 1 g/cm^3.

2.5. Quality assurance and quality control (QA/QC)

Quality assurance and control (QA/QC) of the examined sediment samples, as well as of their liquid digestates, (for determining the total metal content) was also performed.

For the sediment samples, procedures included the analysis of a procedural blank, a matrix duplicate and a matrix spike along with every 10 samples processed and surrogate spike compounds. All analytical instruments were calibrated on a daily basis.

For the liquid digestates, samples were measured in triplicate, therefore percent relative standard deviation (RSD %) was calculated. The results were expressed by the use of a calibration curve with at least 5 concentration levels, with a correlation coefficient (r) of 0.99 and by the use of standard solutions of appropriate purity (Merck). Detection limits were calculated by the relevant software existing on the database of the ICP-MS (Chemstation Software by Agilent). QA/QC was based on: a) checking the calibration curve in at least one concentration level with relative standards, maintaining the correction factor of the calibration curve between 0.99-1.01 and of the values of the calibration levels between 0.95-1.05 b) the analysis of spiked samples every 20 samples and c) the analysis of duplicates in 10% of the total daily samples. Recovery for each metal ranged between 90-110 %. Results were deemed satisfactory if RSD % was measured below 10% (RSD % < 10%).

3. Results and discussion

3.1. Physicochemical properties of sediment samples

The physicochemical properties of all sediment samples are presented in Table 1. The results demonstrated that the main minerals present in all sediments were calcite (50% - 54%), quartz (15% - 29%) and dolomite (6% -14%), whereas their classification according to the Unified Soil Classification System (USCS) was found to be clayey sands (SC) for the lake's sediments and sands (S) for the gulf's sediments; quite similar results to other samples collected from the same area and analyzed in another study of the same authors (Hahladakis et al., 2013).

3.2. Partitioning and mobility order of the selected six toxic metals

The results of the partitioning of the selected six metals in all four samples taken from Elefsis gulf are presented in Fig. 2a whereas the respective results from the fractionation of the sediments collected from Lake Koumoundourou are depicted in Fig. 2b. Arsenic is missing in the diagrams of Fig. 2b because, as it is seen from Table 2, its total content in all Koumoundourou samples was below interest and concern level.

As it is clearly shown from Fig. 2a, the results indicated that the examined toxic metals in the sediment samples taken from Elefsis gulf, follow a mobility order of Cu>Zn>As>Pb>Cr>Ni with antagonistic values between Cu and Zn, resulting in changing their aforementioned order in samples E2 and E3. Special consideration must be given to the organic matter in sediments since there is an elevated dissolvingadsorbing balance present in it. Moreover, Cu exhibits a strong affinity to the organic matter with percentages ranging from 65% - 78% of the total while the rest remains bound to the residual fraction (18% - 27%). Considerable Zn (32% - 40%) is bound to Fe-Mn oxides, as it is expected due to their scavenging ability for trace metals. A rather significant percentage of Zn (8% - 13%) is also associated with the exchangeable fraction. The rest of it occurs equally in organic matter (23% - 31%) and in the residual fraction (15% - 31%). Ni and Cr are strongly bound to the residual fraction in considerable high percentages (55% - 75%). Most of the non-residual Cr and Ni (12% - 30%) are associated with the organic fraction; all other examined toxic metals were also found to be present in this fraction, mainly due to the organic content that exist both in sediments as well as in the water.

Regarding the lake's samples, the mobility order for K1 and K3 is Pb>Cu>Zn>Ni>Cr whereas for K2 and K4 is Pb>Zn>Cu>Cr>Ni. Percentages of toxic metals bound to the organic matter are slightly higher in sediments collected from the north area of the lake and Pb is the predominant metal bound to Fe-Mn oxides in percentages of 48% - 51% (Fig. 2b). Moreover, Ni and Cr in samples K2 and K4 are mostly bound to Fe-Mn oxides and organic fraction, in contrast to samples K1 and K3 which they retain their tendency for the residual fraction, an observation also noted in the samples collected from Elefsis gulf. That is mainly due to the existence of more organic matter in K2 and K4, as it can be seen from Table 2. It is also noteworthy the percentage of Zn bound to carbonated fraction (5% - 15%) indicating biological availability and proving once more that total metal concentrations alone are not sufficient and reliable indicators for the estimation of a metal's mobility in the sediments or for the actual toxicity of these sediments (Davidson et al., 1998).

Our findings are close to results found by other researchers that examined sediments from the same or other areas with similar contamination background around the world and are reported as follows: The predominant affiliation of Cu with the organic fraction and of Zn with the reducible (Exch./Carb.) have also been observed by Yu et al. (2001), Tsai et al. (2003), Sakellariadou et al. (2009) and Usero et al. (1998). Moreover, high percentages of Pb in the oxidizable fraction (Fe-Mn) that were observed in sediment samples from Lake Koumoundourou have also been reported by Mester et al. (1998).

3.3 Ecological risk assessment due to presence of toxic metals

3.3.1 Application of Risk Index (RI)

In order to assess the environmental impact by the presence of multiple contaminants in the sediments, both from the lake and the gulf, the approach of the risk index was adopted. According to this method proposed by Hakanson (1980), the risk index (RI) is defined as:

$$\sum_{i=1}^{n} (T_i \cdot \frac{C_i}{C_o})$$

where T_i is the toxic response factor for the metals (for our calculations the factors taken were As=10, Pb=Cu=Ni = 5, Cr=2 and Zn=1), C_i is the total concentration of each metal and C_o is the background reference concentration of each metal in the region of Elefsis. For this study, metal/metalloid reference concentrations proposed by Kokovides et al. (1992) were used as regional background values and were for As=1.5, Pb=48, Cu=17.5, Ni=46, Cr=8.5 and Zn=32 (in ppm).

As it is seen from Fig. 3a, the majority of samples had a risk index below 150 which according to Hakanson's proposal is an indication of low ecological risk of toxic metals for the lake/basin. Only in samples E2 and E3 was the value of 150 surpassed, implying that in some areas of Elefsis gulf there is a moderate ecological risk (Hakanson, 1980).

3.3.2 Application of Risk Assessment Code (RAC)

Another way of assessing the environmental risk of toxic metals being present in the aquatic environment and bound to different physicochemical fractions is the Risk Assessment Code (RAC). According to this approach the percentage of each metal bound to the exchangeable and carbonated fraction is calculated and summed for each metal separately. Then the RAC classification suggests that sediments which could release a percentage of 1% or less for each individual metal in the first two fractions according to Tessier's protocol (exchangeable and carbonated) could be characterized as non-harmful for the environment, whereas metals releasing more than 50% of their total concentration in these aforementioned fractions are considered extremely dangerous (Jain, 2004; Perin et al., 1985; Singh et al., 2005). The detailed classification of the RAC is given below:

Category	Risk	Metal in carbonate and exchangeable fraction (%)
1	No risk	<1
2	Low risk	1-10
3	Medium risk	11-30
4	High risk	31-50
5	Very high risk	>50

Fig. 3b presents the results obtained by the application of RAC for all the sediment samples studied. The results indicated "no risk to low risk" for the majority of the metals (Cr, Ni, Cu, As and Pb) in all sediment samples with values ranging from 0 to 8.59 (with the latter one being the percentage of Pb in K2 sample). However, concentrations of zinc in samples E2, E3 and K1 revealed medium risk for half of the sites in the basin of Elefsis gulf and one station in Koumoundourou lake implicating anthropogenic derived activities and bioavailability of the particular element. Despite the fact that Zn values of RAC fall in the medium risk category for nearly half the samples and in the low risk category for the rest of them, zinc is considered to be less toxic element and therefore poses no threat to the aquatic environment and food chain. To sum up, Zn and Pb were found to be the most abundant and bioavailable toxic metals in all sediment samples, see Fig. 2a and 2b, with significant percentages bound to the first two fractions implying anthropogenic inputs both in the lake and the gulf.

3.3.3 Application of geoaccumulation Index (I_{geo})

The geoaccumulation index (I_{geo}), originally introduced by Muller in 1969 (Abrahim and Parker, 2002), is a way of assessing the contamination levels of an area polluted by toxic metals by comparing current and past concentrations, using the following equation:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 * B_n} \right)$$

where C_n is the total concentration of the selected element in the sediment and B_n the geochemical background reference concentration value. The constant 1.5, which is rather arbitrarily introduced in the equation, enables us to take into account natural fluctuations that may have occurred throughout the years in the environment of the sediment including possible small anthropogenic inputs (Christophoridis et al., 2009). The reference concentrations for the examined elements were adopted from similar studies performed in the same or surrounding area (Kokovides et al., 1992).

The full classification of sediment/soil samples as the I_{geo} proposes comes, then, as follows (Abrahim and Parker, 2008):

I_{geo}	Pollution status
>5	Extremely polluted
4–5	Strongly to extremely strongly polluted
3–4	Strongly polluted
2–3	Moderately to strongly polluted
1–2	Moderately polluted
0–1	Unpolluted to moderately polluted
<0	Unpolluted

The results of the application of the I_{geo} are presented in Table 3. The I_{geo} values for half of the elements (Ni, Cu, Pb) concerning the lake, fall into the first two categories of the I_{geo} classification, characterizing the sediments from "unpolluted to moderately polluted". Zinc and chromium, on the other hand, have higher I_{geo} values indicating a moderate and strong pollution respectively. However, taking into consideration that zinc belongs to the group of less toxic elements and most of the chromium is bound to the residual fraction, no significant concern is arisen. As far as the gulf is concerned, I_{geo} values indicate a moderate pollution regarding arsenic and copper. Most of copper is affiliated to the organic fraction, while the rest of it is bound to the residual fraction. This implies that there is no significant danger, since Cu shall not be released easily in the aquatic environment under naturally derived conditions. Arsenic, on the other hand, is more suspicious of causing any future contamination problems considering its carcinogenic nature and the fact that is almost equally distributed to Fe-Mn oxides, organic and residual fractions. Nevertheless, considering that the I_{geo} arbitrarily introduces the constant 1.5 in its formula, to include any continuous fluctuations in the background reference concentrations which could easily alter the I_{geo} values, it is clear that it should not be used as a unique assessment tool.

4. Conclusions

In general, Elefsis gulf sediments correspond to a moderate pollution level, higher than lake's Koumoundourou with regard to toxic metals. Pb and Ni present in samples collected from Elefsis are less bioavailable than in those taken from the lake, in contrast to Zn and Cu which are more bioavailable. Cu exhibits a strong affinity to the organic matter and considerable Zn is bound to Fe-Mn oxides in all samples. Ni and Cr are mostly affiliated with the residual fraction, a tendency generally observed in all sediments. However, most of the non-residual Cr and Ni are associated either with the organic fraction or with Fe-Mn oxides. It is also noteworthy the percentage of Zn bound to carbonated fraction indicating biological availability.

Judging from the application of RI, for assessing the ecological toxic metal impact in the area (regarding Ni, Cr, Pb, Zn, Cu and As), the results indicated "low to moderate risk" for the basin of Elefsis gulf and "low risk" for Koumoundourou lake, according to Hakanson's classification (Hakanson, 1980).

The application of RAC demonstrated that the majority of samples exhibited low risk for all the examined metals, except that of Zn, in samples E2, E3 and K1 where RAC values fell into the category of "medium risk" (above 11). However, since Zn is considered to be one of the less toxic metals for human health and one of the most bioavailable, this observation dose not raise any concern for the area (Hahladakis et al., 2013).

Finally, an environmentally sound management scheme is always mandatory in such areas that are surrounded by so many contamination sources and its implementation will only be proved to the benefit of everyone.

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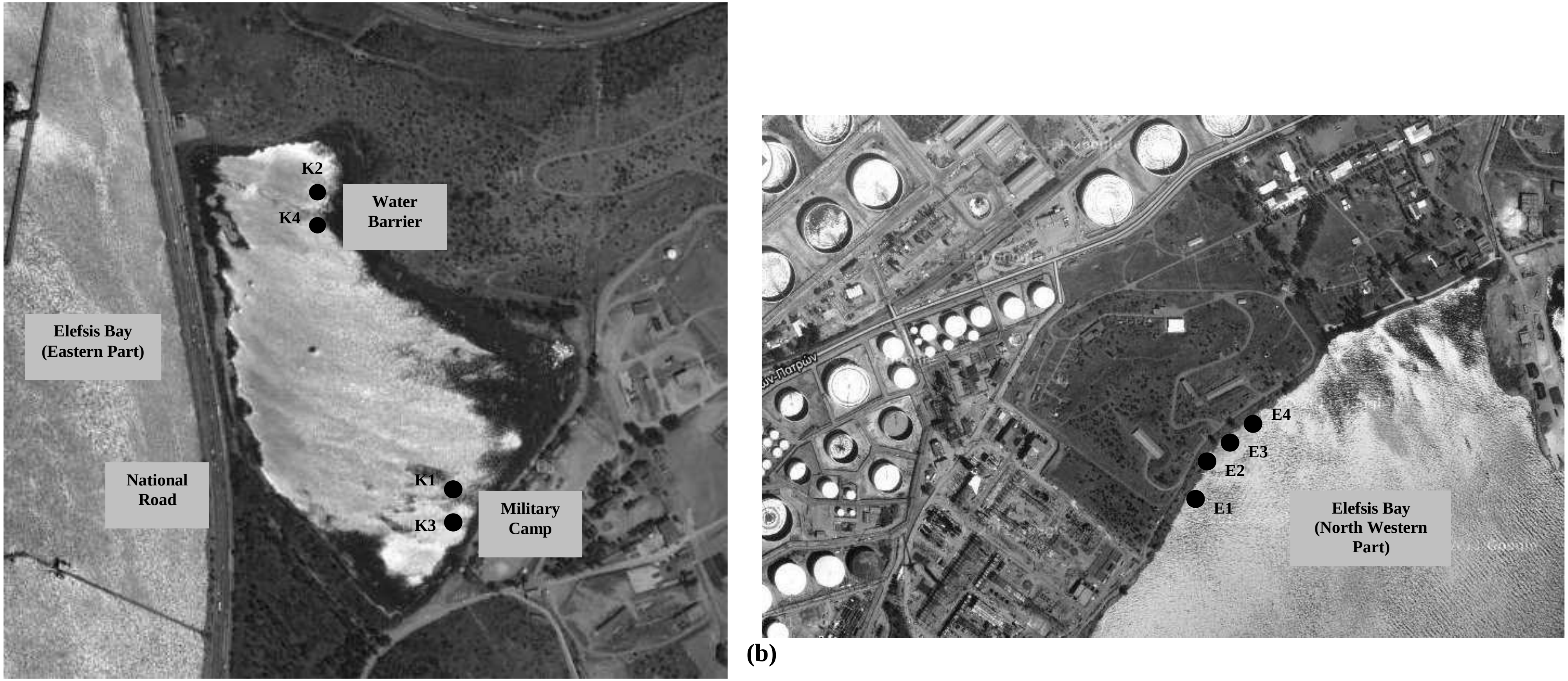
List of Figures

Fig. 1 Google maps taken shots of (a) Koumoundourou Lake and (b) North Western part of Elefsis Bay. Sampling sites are indicated.

Fig. 2 Metal distributions obtained from the sediment samples (a) of Elefsis Bay and (b) of Koumoundourou Lake, using Tessier’s SEP.

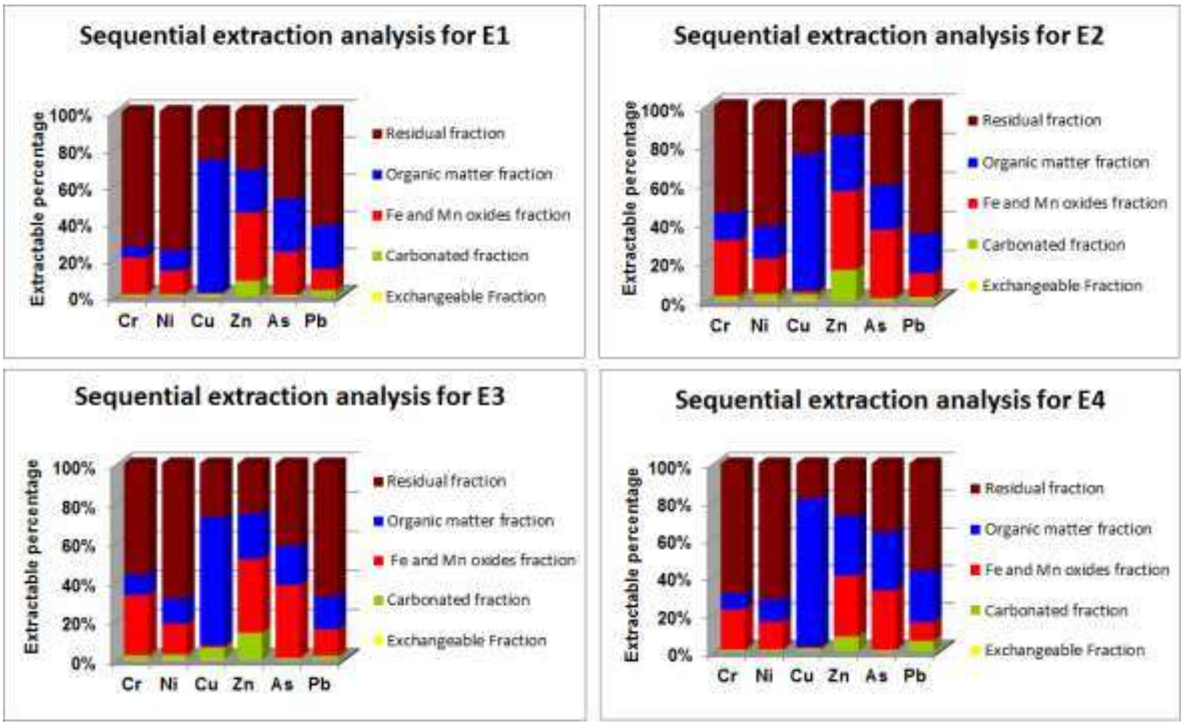
Fig. 3 Potential (a) RI and (b) RAC values calculated for all sediment samples.


K2
K4
Water Barrier
Elefsis Bay (Eastern Part)
National Road
K1
K3
Military Camp
E4
E3
E2
E1
Elefsis Bay (North Western Part)

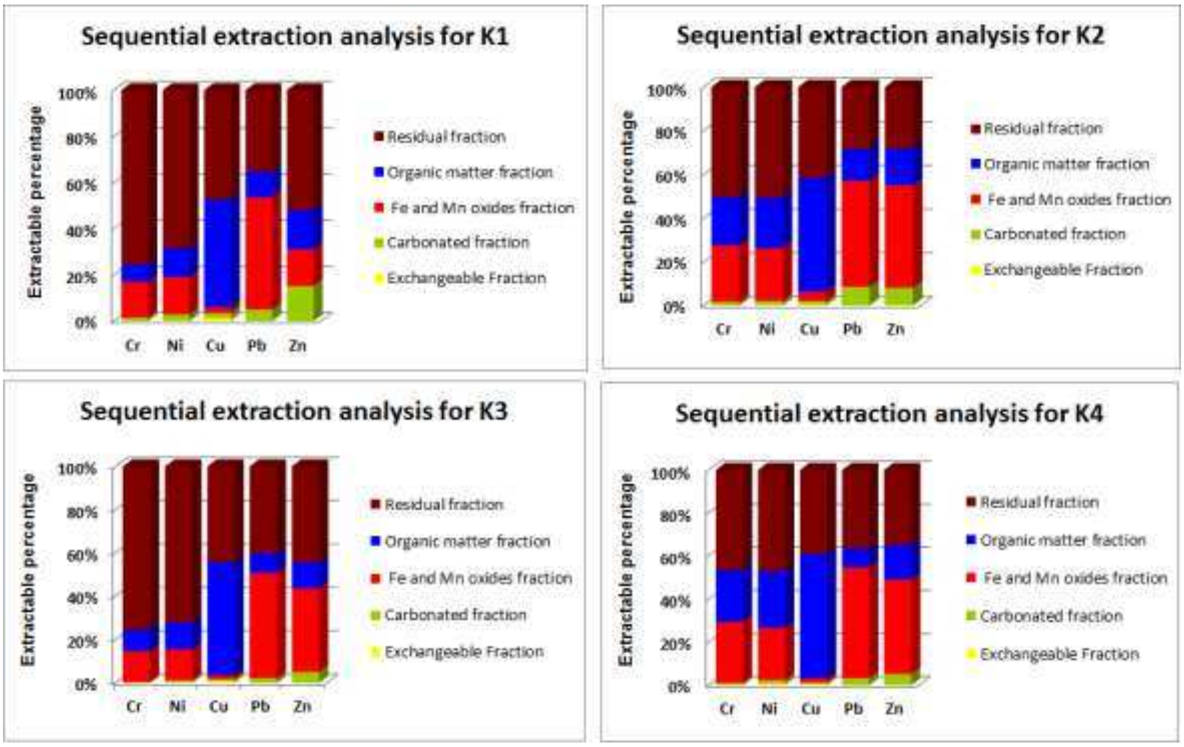
(b)

(a)

Fig. 1

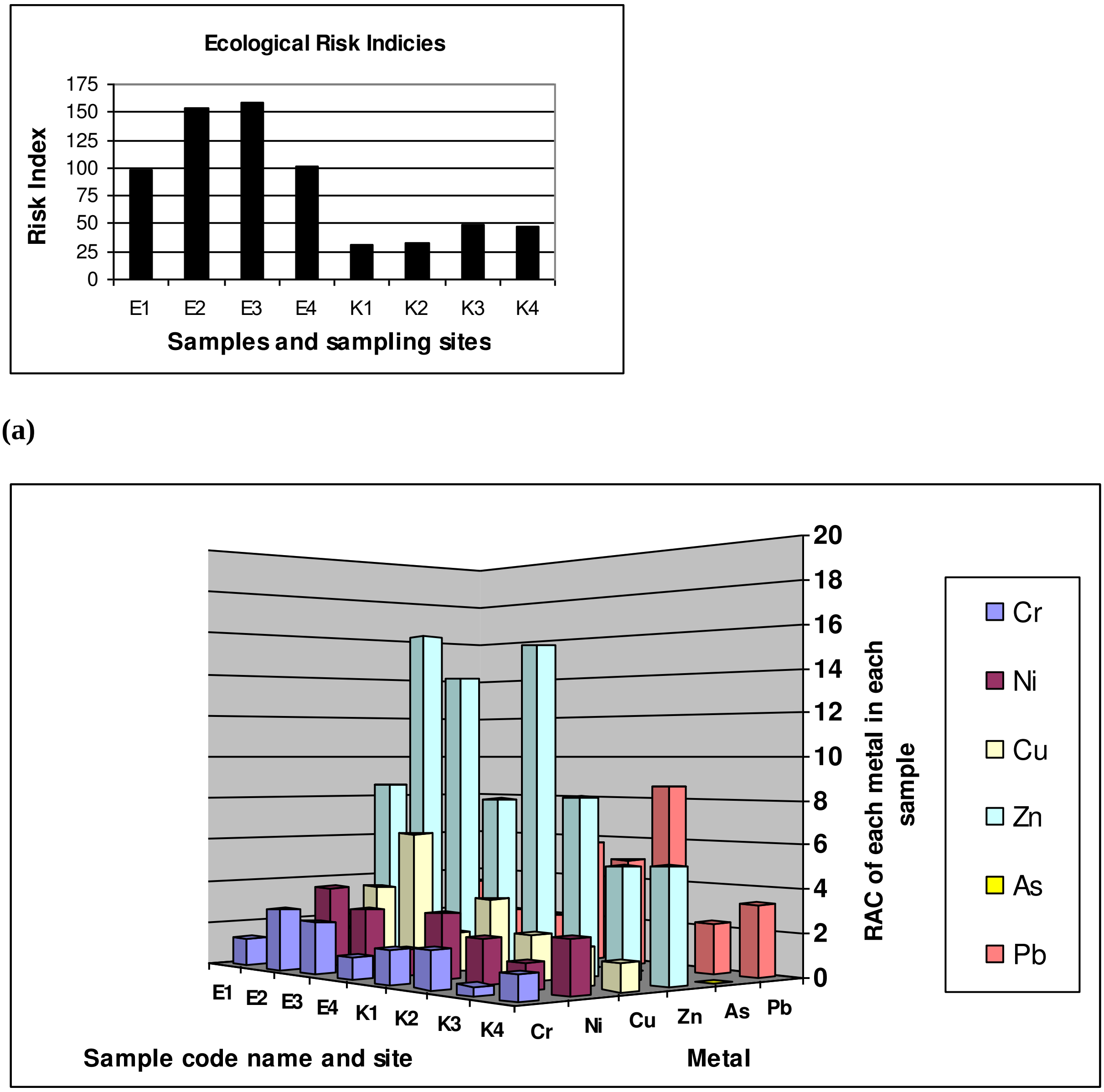

Sequential extraction analysis for E1
Sequential extraction analysis for E2
Sequential extraction analysis for E3
Sequential extraction analysis for E4
Extractable percentage
100%
80%
60%
40%
20%
0%
Cr
Ni
Cu
Zn
As
Pb
Residual fraction
Organic matter fraction
Fe and Mn oxides fraction
Carbonated fraction
Exchangeable Fraction

(a)


Sequential extraction analysis for K1
Sequential extraction analysis for K2
Sequential extraction analysis for K3
Sequential extraction analysis for K4
Extractable percentage
100%
80%
60%
40%
20%
0%
Cr
Ni
Cu
Pb
Zn
Residual fraction
Organic matter fraction
Fe and Mn oxides fraction
Carbonated fraction
Exchangeable Fraction

(b)

Fig. 2


Ecological Risk Indicies
Risk Index
175
150
125
100
75
50
25
0
E1
E2
E3
E4
K1
K2
K3
K4
Samples and sampling sites
20
18
16
14
12
10
8
6
4
2
0
RAC of each metal in each sample
Cr
Ni
Cu
Zn
As
Pb
E1
E2
E3
E4
K1
K2
K3
K4
Cr
Ni
Cu
Zn
As
Pb
Sample code name and site
Metal

(a)

(b)

Fig. 3

List of Tables

Table 1

Physicochemical properties of all sediment samples

Table 2

Total concentrations (mg/kg dw) of the examined metals/metalloids in all sediment samples. Average of three replicates.

Table 3

Geoaccumulation indexes for all sediment samples

Table 1

Physicochemical properties	K1	K2	K3	K4	E1	E2	E3	E4
Moisture (%)	22.4	38.5	19.5	34.8	27.2	17.4	21.7	23.9
pH	7.51	7.82	7.31	7.88	6.92	6.84	7.23	6.88
Redox (mV)	-16	-28	-15	-27	-8	-12	-6	-7
Organic matter (%)	4.31	7.47	3.98	7.32	5.64	7.13	6.63	6.17
Specific gravity	1.43	0.91	1.45	0.98	1.82	1.78	1.83	1.91
Cation Exchange Capacity CEC (meq/100g)	3.6	3.9	3.7	4.1	1.18	1.23	1.38	1.35
PZC (Zero point of charge)	7.83	7.98	7.81	7.95	7.64	7.58	7.86	7.63

Table 2

Element	K1	K2	K3	K4	E1	E2	E3	E4
Cr	65.08	31.26	86.81	38.79	52.49	158.46	143.12	64.17
Ni	53.19	20.61	90.17	30.29	22.41	71.23	48.49	34.13
Cu	16.35	13.82	31.59	29.46	38.76	145.36	169.32	49.56
Zn	47.28	111.39	121.28	181.97	128.52	251.78	363.78	159.78
As	0.85	0.35	0.53	0.34	9.92	6.90	7.65	8.98
Pb	37.38	156.01	51.12	201.28	26.72	123.57	85.45	32.13

Table 3

Igeo Table

	Samples								**Mean I_{geo} from samples K1-K4**	**Mean I_{geo} from samples E1-E4**	**Mean I_{geo} from all sediment samples**
Element	**K1**	**K2**	**K3**	**K4**	**E1**	**E2**	**E3**	**E4**			
Cr	2.35	1.29	2.77	1.61	2.04	3.64	3.49	2.33	2.12	3.04	2.58
Ni	-0.38	-1.74	0.39	-1.19	-1.62	0.05	-0.51	-1.02	-0.51	-0.65	-0.58
Cu	-0.68	-0.93	0.27	0.17	0.56	2.47	2.69	0.92	-0.20	1.94	0.87
Zn	-0.02	1.21	1.34	1.92	1.42	2.39	2.92	1.73	1.27	2.23	1.75
As	0.34	-2.68	2.01	1.67	2.14	1.62	1.77	2.00	1.11	1.89	1.50
Pb	-0.95	1.12	-0.49	1.48	-1.43	0.78	0.25	-1.16	0.63	-0.10	0.26