HEAVY METAL POLLUTION RECORDED IN THE SEDIMENTS OF KOUMOUNDOUROU LAKE, GREECE

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ABSTRACT

Lake Koumoundourou is a shallow (maximum depth 2.3 m) lake located ~11 km NW of Athens. It communicates through a narrow weir with the Elefsis Bay. This study focuses on the geochemistry of surface (25 samples) and core (14 samples) sediments recovered from the lake and two coastal marine sediments. The sediments were analyzed for their grain-size properties, organic carbon, as well as major and minor elements using standard analytical techniques. The surface sediments of the lake are rich in sand, which is of biogenic origin and it is composed by shells and their fragments, resulting in a mean carbonate content of 70.7 wt%. The organic carbon content is between 2.04 and 7.50 wt%, indicating anthropogenic inputs and/or temporary anoxic conditions in the lake. Heavy metal and metalloid levels (V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Pb) appear to be low, when compared (as absolute values) directly to other polluted lake, river, and marine sediments from Greece. However, in our study we calculated enrichment factors (EFs) taking as a reference sediment a pre-industrial core sample from the neighboring Saronikos Gulf. The calculated EFs revealed that the surface sediments of the lake have been substantially contaminated by heavy metals and metalloids in the order V, Mn, Ni, Co, Cr, Cu, Pb, Zn, As, Mo. Vanadium exhibited the lowest EF (1.73) and Mo the highest (19.9). Similar results were obtained when EFs were calculated using the 'average shale' as a reference unpolluted sediment. Core sediments were characterized by high EFs for the same elements.

1. INTRODUCTION

Koumoundourou Lake is located inshore of Elefsis Bay (Saronikos Gulf, Greece; Fig. 1) and it is surrounded by many land-based pollution sources, mainly oil refineries. The Elefsis Bay in particular, is a heavily polluted marine area because it receives industrial effluents and water renewal is weak (Scoullos and Riley, 1978; Scoullos, 1983, 1986, Scoullos and Pavlidou, 1997). The Lake receives groundwater leaching from the major landfill of Athens which is situated ~7 km north of the Lake (Dimitriou *et al.*, 2008). Previous investigations have reported that the Lake is heavily polluted by crude oil (Conides *et al.*, 1996; Conides and Parpoura, 1997; Dimitriou *et al.*, 2008) but not by heavy metals. Hatzianestis (2003), reported that both the waters and sediments of the Lake are heavily contaminated by aliphatic and polycyclic aromatic hydrocarbons (PAHs).

The aim of this study is to investigate whether surface and sub-surface sediments collected from the Lake exhibit enrichment in heavy metals, based on the calculation of enrichment factors (EFs) against local (Saronikos Gulf) pre-industrial sediment and the average shale (Turekian and Wedepohl, 1961).
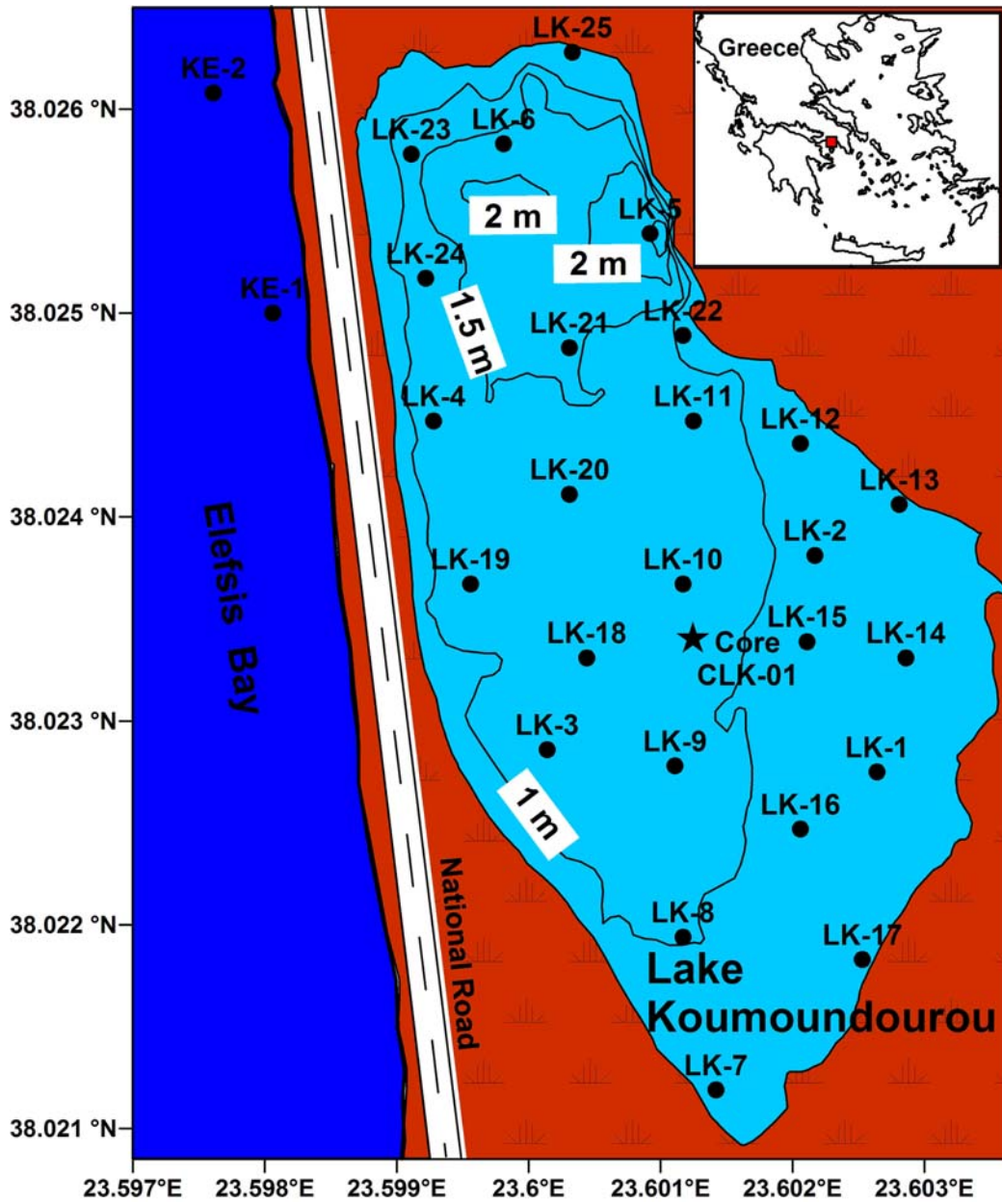
Fig. (1): Koumoundourou Lake location map and sampling station locations.

2. REGIONAL SETTING

The Lake is separated from the adjacent Elefsis Bay by the Athens-Corinth national road, but it communicates with the sea through a narrow weir and a pipeline. It covers an area of 147,000 m^2, and it is approximately 600 m long and 400 m wide. The shoreline perimetry is ~1,700 m and the surface elevation is 1.4 m above sea level (Dimitriou *et al.*, 2008). Water depths do not exceed 3.3 m in the NE sector of the Lake, whilst in the SE sector water depths are less than 1 m, with a mean of 1.5 m (Roussakis, 2003). The Lake receives freshwaters from underground discharges in the NE sector, as well as from rainfall. The annual precipitation is about 410 mm, the maximum precipitation (about 65 mm per month) occurring during the period November-January (Conides *et al.*, 1996). Freshwater inputs, due to the surface elevation, outflow towards the Elefsis Bay with a rate of 30 m^3 per hour (Conides *et al.*, 1996). However, seawater intrusion is often observed and results in a brackish environment with low salinities. In the period December 2002, April, August, and November 2003, salinity varied from 10.25 to 13.1 psu, and temperature from 10 to 28.15 °C (Papadopoulos, 2003).

Koumoundourou Lake hosts within its catchment area oil refinery companies, a marble cutting factory, and a military camp, which serves as an oil supply depot station, the latter located on the east side of the lake (Conides *et al.*, 1996). Also shipyards and Halyvourgiki steel industry are situated within a range of few kilometers from the Lake. Underground crude oil leaks from a national oil refinery have been reported and floating oil traps were installed in the northern sector of the Lake to contain pollution. However, a thin film of oil is formed periodically by the oil leaks, and it moves towards the western sector of the lake and outflows into the Elefsis Bay through the narrow weir, following the freshwater circulation. Pavlidou (1998) reported that during 1994-1996 crude oil leaks in the Lake were very high, particularly in its NW sector.

Another pollution source is related to the main landfill of Athens, which operated from 1960 to 1998 without any impermeable lining to prevent possible groundwater contamination. Since 1998 the new landfill is well managed and prevents groundwater pollution. However, during the former period, and due to the generally permeable lithology of the Lakes' catchment (Dimitriou *et al.*, 2008), it is possible that the Koumoundourou Lake has been contaminated by leachates originating from the landfill.

3. MATERIALS AND METHODS

3.1. SEDIMENT SAMPLING

During December 2002, twenty five surface sediment samples were collected from the Lake and two samples from the Elefsis Bay (Fig. 1), using a rubber-boat and an Ekman-Birge grab (weight 8 kg and surface 225 cm^2). A short (70 cm) core (CLK-01) was recovered from the center of the lake and fourteen core subsamples were analyzed similarly to the surface sediments. During sampling, the weather conditions were: calm winds, cloudiness, and rain, whilst atmospheric temperature was about 15 °C. Plastic tools and containers were used, and sediment (0-1 cm) was collected from the inner part of the grab in order to avoid contact with the metal parts of the grab and to avoid contamination of the samples. A part of the sediment dedicated for organic carbon determination was stored in aluminum foil.

3.2. GRAIN-SIZE ANALYSIS

Grain-size analysis and classification followed Folk's (1974) methodology. The sand fraction was separated by wet sieving using a 63 µm pore size sieve. The fine silt and clay fractions were analyzed in a

Micromeritics Sedigraph 5100 X-ray grain-size analyzer. The dry percentages of sand (>63 μm), silt (2 μm <Ø <63 μm), and clay (<2 μm) were determined (Table 1).

Table (1): Station coordinates, water depth, sand, silt, and clay percentages, and sediment grain-size classification after Folk (1974).

Station	Latitude N deg.dec	Longitude E deg.dec	Depth m	Sand %	Silt %	Clay %	Classification
LK-1	38.02275	23.60264	1.0	50	20	30	sandy silt
LK-2	38.02381	23.60217	1.1	53	16	32	clayey sand
LK-3	38.02286	23.60014	1.2	66	9	25	clayey sand
LK-4	38.02447	23.59928	1.6	61	11	28	clayey sand
LK-5	38.02539	23.60092	2.3	55	13	32	clayey sand
LK-6	38.02583	23.59981	1.6	67	7	26	clayey sand
LK-7	38.02119	23.60142	0.6	70	8	22	clayey sand
LK-8	38.02194	23.60117	1.1	60	11	29	clayey sand
LK-9	38.02278	23.60111	1.2	65	7	28	clayey sand
LK-10	38.02367	23.60117	1.3	63	9	28	clayey sand
LK-11	38.02447	23.60125	1.3	58	14	28	silty sand
LK-12	38.02436	23.60206	1.1	58	10	32	clayey sand
LK-13	38.02406	23.60281	1.0	48	13	39	clayey sand
LK-14	38.02331	23.60286	0.9	59	13	29	clayey sand
LK-15	38.02339	23.60211	1.1	60	11	29	clayey sand
LK-16	38.02247	23.60206	1.1	67	6	28	clayey sand
LK-17	38.02183	23.60253	0.6	12	55	33	sandy silt
LK-18	38.02331	23.60044	1.2	68	10	22	clayey sand
LK-19	38.02367	23.59956	1.1	68	6	27	clayey sand
LK-20	38.02411	23.60031	1.2	69	7	24	clayey sand
LK-21	38.02483	23.60031	1.8	70	4	27	clayey sand
LK-22	38.02489	23.60117	1.0	54	9	37	clayey sand
LK-23	38.02578	23.59911	1.2	71	5	24	clayey sand
LK-24	38.02517	23.59922	1.3	67	11	22	clayey sand
LK-25	38.02628	23.60033	0.8	71	6	24	clayey sand
KE-1	38.02500	23.59806	0.9	95	1	4	sand
KE-2	38.02608	23.59761	0.9	97	0	3	sand

3.3. ORGANIC CARBON AND CARBONATE CONTENT

Sediment samples were thoroughly ground in an agate mortar and very well homogenized to reduce variability between replicates. Splits of 10-20 mg of powdered homogenized sample were weighed accurately (0.01 mg) into specially designed silver containers. Organic carbon was determined after removal of inorganic carbon by acidification of samples with 20 μL of 6N HCl at 60 °C (this treatment was conducted five times in 12 hours intervals). After the inorganic carbon removal, the samples were dried at 60 °C overnight. After drying, the containers were pinched closed, compacted, and formed into a ball. The balls then were placed in the auto-sampler of a Fisons Instruments CHN elemental analyser type EA-1108 to determine organic carbon contents. The operating parameters were very similar to those reported by Verardo (1990), Cutter and Radford-Knoery (1991) and Nieuwenhuize *et al.* (1994). The precision of the method is within 5%. For the analysis of the sediment samples for total carbon, separate splits (10-15 mg) of the samples were transferred into tin cups that were sealed and analyzed without any pre-treatment. Inorganic carbon was calculated by subtracting organic carbon from the total carbon, and subsequently carbonate content was calculated. Summary results are given in Table 2.

Table (2): Summary results (min, max, standard deviation, mean, and median) for organic carbon, carbonate content, major/minor elements in surface sediments from the Koumoundourou Lake (*n* = 25).

Component	Unit	minimum	maximum	SD	mean	median
org. carbon	%	2.04	7.50	1.10	4.71	4.69
carbonate	%	52.6	79.9	7.2	70.7	73.9
SiO_2	%	3.95	26.13	6.16	9.12	6.99
Al_2O_3	%	0.64	6.47	1.61	1.64	1.05
TiO_2	%	0.030	0.360	0.089	0.086	0.060
Fe_2O_3	%	0.360	3.120	0.750	0.831	0.580
K_2O	%	0.170	1.150	0.260	0.364	0.270
Na_2O	%	1.05	3.14	0.50	1.88	1.84
CaO	%	28.4	43.1	4.42	37.1	39.7
MgO	%	0.740	3.410	0.704	1.143	0.910
P_2O_5	%	0.031	0.108	0.025	0.054	0.043
V	μg/g	12	70	16	23	17
Cr	μg/g	29	186	42	58	40
Mn	μg/g	97	399	83	155	125
Co	μg/g	3	9	2	5	5
Ni	μg/g	16	84	19	28	21
Cu	μg/g	10	46	11	21	17
Zn	μg/g	57	176	36	83	68
As	μg/g	13	26	3	20	20
Rb	μg/g	1	53	19	14	8
Sr	μg/g	54	341	75	225	241
Zr	μg/g	44	108	17	53	48
Mo	μg/g	1	53	19	14	8
Ba	μg/g	445	4489	1037	3475	3818
Pb	μg/g	44	108	17	53	48

3.4. MAJOR AND MINOR ELEMENTS

Bulk (not sieved and unwashed) samples were oven dried, ground to a fine powder in a twin swinging motorized mill with agate mortar and balls and were analyzed for their chemical composition in a Philips PW-2400 wavelength X-Ray fluorescence analyzer, equipped with Rh-tube. Major elements were determined in fused beads (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, K_2O, Na_2O, CaO, MgO, P_2O_5). Fused bead preparation involved a complete fusion of 0.6 g of sample, with 5.4 g of flux (50:50 lithium meta-borate, lithium tetra-borate) and 0.5 g of lithium nitrate, the latter being used as an oxidizer. Minor elements were determined according to the following procedure: 5 g of powdered sample were mixed with 0.5 g of wax and subsequently pressed in a 31 mm aluminium cup. The powder pellets were analyzed in the XRF to determine minor element contents (V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Ba, Pb). Analytical accuracy was checked by parallel analysis of certified sediment standards (MESS-2, PACS-2, MAG-1) and was found to be satisfactory for all elements analyzed (for details see Karageorgis *et al.*, 2005). Analytical precision was checked in sample replicates and was always better than 0.5%. Summary results are given in Table 2.

4. RESULTS AND DISCUSSION

4.1. SEDIMENT GRAIN SIZE

The surface sediments of the Koumoundourou Lake are characterized by high percentages of sand (12-71 wt%, mean 59 wt%; Table 1) and are classified mostly as clayey sands. The spatial distribution of sand content exhibits lowest values along a narrow strip in the SE sector of the Lake (Fig. 2a). Sand contents increase gradually towards the NW, where they reach their highest values. Silt contents show an inverse spatial distribution pattern, with low values in the NW sector of the Lake and highest values in

the SE sector (Fig. 2b). Clay contents range from 22 to 39 wt% (mean 29 wt%) and their spatial distribution is more uniform, with high values in the eastern sector of the Lake, and decreasing gradually towards the west (Fig. 2c). The two coastal samples from the Elefsis Bay are classified as sands, with sand content >95 wt%.

4.2. ORGANIC CARBON AND CARBONATES

Bulk organic carbon contents are generally high (Table 2). They range from 2.04 to 7.50 wt% (mean 4.71 wt%) and suggest accumulation of organic material possibly related to pollution by petroleum hydrocarbons which has been identified by previous investigations (Conides *et al.*, 1996; Conides and Parpoura, 1997; Dimitriou *et al.*, 2008) as well as the decomposition of various aquatic plants, which are abundant around and inside the Lake. The spatial distribution of organic carbon contents exhibits highest values in the NE sector of the Lake (Fig. 2d), which is the area where oil leaks have been recorded. Hence, organic carbon accumulation should be attributed mostly to anthropogenic sources. Zeri (2003) reported that the total organic carbon (TOC) concentrations in the Lake waters are 10 times higher than those determined in the water of the Elefsis Bay, and suggests that potential sources of DOC are residues of petroleum and products of terrestrial and aquatic plants decomposition. The preservation of elevated organic carbon contents in the surface sediments suggests that occasionally the Lake encounters dysoxic or even anoxic conditions, particularly at the NE sector, where organic carbon contents exhibited their highest values.

Bulk carbonate contents (52.6-79.9 wt%, mean 70.7 wt%; Table 2) show high values allover the Lake and mostly in the central sector (Fig. 2e). According to Conides and Parpoura (1997) the zoobenthos is rich in large-sized Polychaeta, whilst Oligochaeta and Mollusca have been also reported. The

benthic community is characterized by the predominance of pollution tolerant species and the overall diversity of the fauna is very limited (Dimitriou *et al.*, 2008). Often sediments were dominated by shells and fragments of bivalves. The presences of numerous organisms in the surface sediments, which build their shells by calcium carbonate, suggest that carbonates in the Koumoundourou Lake have primarily biogenic origin. This is also supported by the marked correlation between carbonate and Sr ($r = 0.89$; Table 3), which results from the geochemical similarities between Ca and Sr (Shankar *et al.*, 1987).
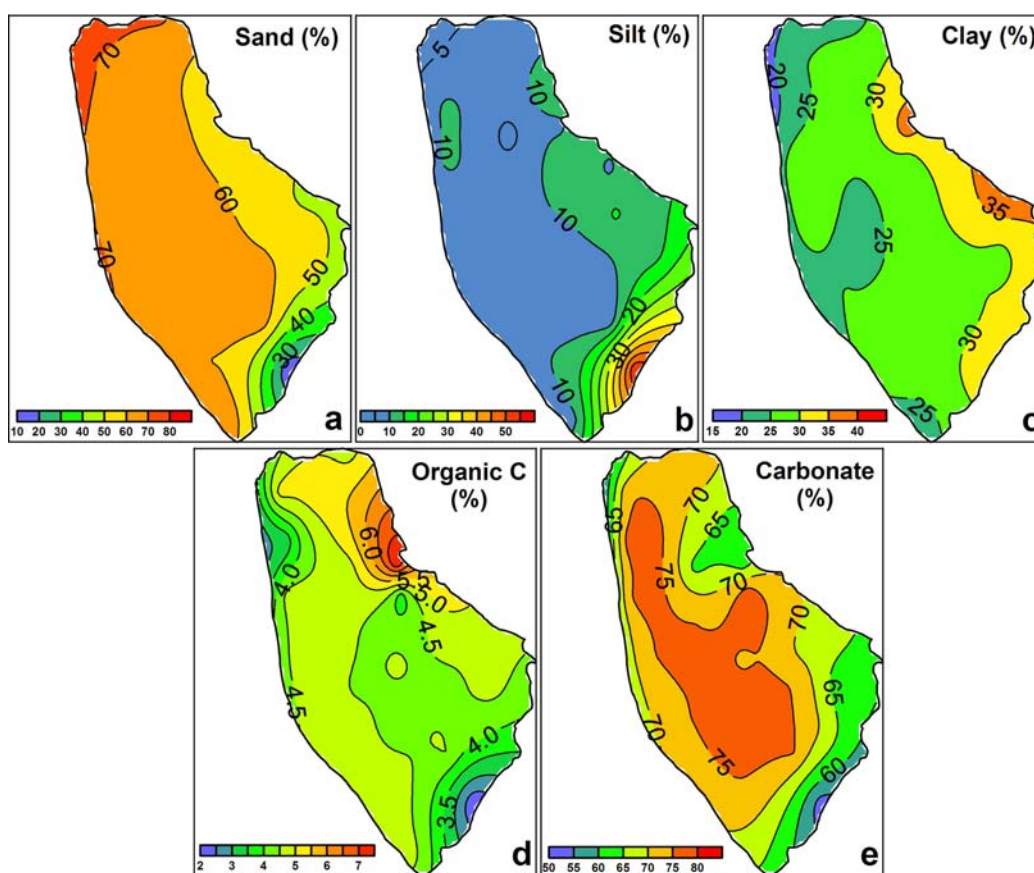

Fig. (2): Contour maps of the Koumoundourou Lake showing (a) dry weight percentage of sand (Ø>63 μm), (b) dry weight percentage of silt, (63 μm<Ø<2 μm), (c) dry weight percentage of clay (Ø<2 μm), (d) dry weight percentage of organic carbon, (e) dry weight percentage of carbonate content.

Table (3): Correlation coefficient matrix of organic carbon, carbonate content, major/minor elements in surface sediments from the Koumoundourou Lake ($n = 25$).

	Org. Carbon	Carbonate	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	K_2O	Na_2O	CaO	MgO	P_2O_5	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Ba
Carbonate	-0.08																							
SiO_2	-0.20	-0.91																						
Al_2O_3	-0.46	-0.79	0.85																					
TiO_2	-0.49	-0.79	0.85	1.00																				
Fe_2O_3	-0.43	-0.83	0.87	0.99	0.99																			
K_2O	-0.42	-0.80	0.85	0.99	0.99	0.99																		
Na_2O	0.87	-0.11	-0.11	-0.38	-0.41	-0.36	-0.33																	
CaO	-0.10	0.96	-0.92	-0.75	-0.74	-0.78	-0.76	-0.16																
MgO	-0.47	-0.78	0.84	0.96	0.98	0.97	0.97	-0.38	-0.73															
P_2O_5	0.25	-0.85	0.69	0.61	0.60	0.66	0.62	0.28	-0.89	0.61														
V	-0.37	-0.86	0.86	0.96	0.96	0.98	0.95	-0.31	-0.82	0.95	0.71													
Cr	-0.24	-0.67	0.88	0.88	0.90	0.92	0.89	-0.14	-0.86	0.92	0.80	0.93												
Mn	-0.49	-0.61	0.68	0.90	0.90	0.90	0.90	-0.40	-0.58	0.91	0.48	0.90	0.79											
Co	-0.44	-0.86	0.64	0.77	0.79	0.78	0.76	-0.41	-0.56	0.78	0.45	0.78	0.74	0.69										
Ni	-0.33	-0.82	0.84	0.96	0.96	0.98	0.96	-0.28	-0.81	0.96	0.74	0.98	0.95	0.89	0.76									
Cu	0.24	-0.77	0.68	0.52	0.54	0.59	0.53	0.25	-0.84	0.56	0.91	0.66	0.82	0.41	0.48	0.69								
Zn	0.08	-0.49	0.63	0.49	0.51	0.58	0.49	0.05	-0.73	0.51	0.73	0.68	0.74	0.49	0.52	0.66	0.88							
As	0.26	-0.73	0.38	0.34	0.32	0.34	0.33	0.13	-0.47	0.26	0.54	0.35	0.35	0.22	0.21	0.41	0.50	0.41						
Rb	-0.71	0.89	0.78	0.99	0.99	0.99	0.99	-0.53	-0.69	0.96	0.50	0.95	0.85	0.95	0.83	0.95	0.35	0.32	0.08					
Sr	0.31	0.89	-0.92	-0.93	-0.94	-0.96	-0.93	0.22	0.87	-0.96	-0.75	-0.96	-0.96	-0.84	-0.75	-0.96	-0.72	-0.66	-0.30	-0.93				
Zr	-0.44	-0.83	0.89	0.99	0.99	0.99	0.98	-0.35	-0.79	0.98	0.64	0.96	0.92	0.88	0.78	0.96	0.58	0.53	0.34	0.97	-0.96			
Mo	0.51	-0.64	0.45	0.15	0.16	0.23	0.17	0.44	-0.61	0.17	0.63	0.30	0.45	0.06	0.12	0.32	0.74	0.72	0.39	-0.10	-0.33	0.21		
Ba	-0.45	-0.68	0.74	0.93	0.92	0.92	0.92	-0.35	-0.69	0.90	0.61	0.88	0.83	0.85	0.66	0.88	0.49	0.40	0.31	0.94	-0.85	0.91	0.11	
Pb	0.49	-0.72	0.50	0.30	0.30	0.37	0.31	0.45	-0.74	0.33	0.88	0.47	0.61	0.20	0.29	0.49	0.93	0.81	0.60	0.05	-0.50	0.36	0.79	0.27

4.3. GEOCHEMISTRY OF MAJOR AND MINOR ELEMENTS

Summary data of the sediments' chemical composition are given in Table 2. The Lakes' surface sediments are a mixture mainly of biogenic carbonates and terrigenous components. In order to investigate element interrelations as well as possible sediment enrichment in heavy metals, elements were normalized to Al, assuming that Al is held exclusively in terrigenous aluminosilicates (Loring and Rantala, 1992). This normalization procedure is considered particularly useful in the present study because it compensates for grain-size variations and dilution by carbonates, which are the prevailing component of the Lakes' sediments (for more details see Karageorgis et al., 2005). The spatial distribution of selected major and minor elements is therefore expressed as element to Al ratio.

A correlation coefficient matrix (Table 3) was used in order to group elements for discussion, based on their common geochemical behavior. This analysis revealed that a suite of major and minor elements are strongly correlated to Al_2O_3, suggesting their common origin, i.e. terrigenous aluminosilicates. This groups SiO_2, TiO_2, Fe_2O_3, K_2O, and MgO (Table 3; correlation coefficients r: 0.85, 0.99, 0.99, 0.99, and 0.96, respectively) among the major elements, and V, Cr, Mn, Co, Ni, Rb, Zr, and Ba (Table 3; correlation coefficients r: 0.96, 0.88, 0.90, 0.77, 0.96, 0.99, 0.99, and 0.93, respectively) among the minor elements. Silt is also positively correlated to Al ($r = 0.86$), showing that aluminosilicates are mostly found in the fine silt fraction. Representative spatial distributions of Si/Al, Al, and Ni/Al (Figs. 4a, b, c) reveal an increase from the SE to the NW, which is very similar to the spatial distribution of silt (Fig. 2b). The Si weight ratio to Al is much larger than the average shale (Si/Al = 3.41; Turekian and Wedepohl, 1961). This pattern suggests that there are additional sources of Si, which

could be either detrital quartz and/or siliceous diatoms.

Carbonate content, Ca and Sr exhibit strong relationships ($r >0.89$) revealing their biogenic origin (Shankar et al., 1987). High strontium contents (Table 2) imply that carbonates are probably rich in aragonite. Strontium spatial distribution (Fig. 4d) exhibits elevated contents towards the central sector of the Lake, and it is similar to the spatial distribution of the carbonate content (Fig. 2e).

Another group of elements (P, Cu, Zn, As, Mo, and Pb) show weak correlations to aluminium and relatively high correlations between them. However, their spatial distribution patterns of the elements weight ratios to Al (e.g. Cu, Mo, and Pb illustrated in Figs. 5a, b, c) show considerable similarities. The predominant feature is the consistent maxima in the NE sector of the lake, where the oil leaks occur, as well as where the highest organic carbon contents are recorded (Fig. 2d). These observations imply that this group of elements is related to industrial activities, and it will be studied in more detail by means of enrichment factors (EFs) calculations.

4.4. CORE GEOCHEMISTRY

The short core CLK-01 geochemical analysis provided information about the downcore variability of major and minor elements, which were also determined in the surface sediments. The core samples exhibited elevated carbonate contents (calculated from total Ca contents and assuming that all Ca is in the form of $CaCO_3$; range 61.8-79.4 wt%, mean 66.6 wt%). The aluminosilicates group of elements is represented by Si, Ti, Fe, K, Cr, Ni, Rb, and Zr, whilst the biogenic component is represented by Ca and Sr.

The other elements do not show marked downcore similarities, which could lead to grouping and subsequently to similar geochemical behavior. This patchiness is

illustrated in the downcore variability of major and minor elements (Fig. 6). The weight ratio Si/Al is very high, when compared to the average shale, and therefore implies additional sources of Si, similarly to the surface sediments. Aluminium contents show from top to bottom small decrease, constant values, and small increase near the bottom of the core. Relatively similar downcore variability to Al is also observed for the ratios Ti/Al, K/Al, and Cr/Al (Fig. 6). Some element to Al ratios exhibit generally decreasing trends from the top to the bottom of the core, i.e. Fe/Al, Ca/Al, V/Al, Mn/Al, Co/Al, Ni/Al, Cu/Al, As/Al, Sr/Al, Zr/Al, Ba/Al, and more clearly the same pattern is observed for the ratio Pb/Al (Fig. 6). On the other hand, Zn/Al and Rb/Al increase constantly with depth. Many minor similarities can be observed in the downcore variability of the elements, but a complete understanding is difficult. For example, at ~14.5 cm a marked increase appears for Mn/Al, Co/Al, and Mo/Al, which could be attributed to redox changes, as well as increase in productivity (>Ba/Al), although these conditions can not be satisfied simultaneously (Gallego-Torres *et al.*, 2007). Another alternative could be that certain heavy metal peaks could be related to accidental release of industrial effluents.

4.5. HEAVY METAL POLLUTION ASSESSMENT

Previous studies on the geochemistry of surface sediments of Koumoundourou Lake have concluded that sediments are not enriched in heavy metals (Conides *et al.*, 1996; Conides and Parpoura, 1997; Dimitriou *et al.*, 2008). However, the authors simply compared heavy metal contents of the Lake sediments against other sediment analyses from various Hellenic sites, including lake, river, and marine sediments. This simple comparison may be misleading, because the analytical methods, size fractions, and other parameters may differ, thus making a direct comparison based on absolute heavy metal contents doubtful. Moreover, autocthonous components (in this case biogenic carbonates) can dilute considerably sediment's heavy metal contents, giving an overall impression that measured values are generally low.

Enrichment factors (EFs) are commonly used in the literature as a means of identifying and quantifying human interference with global element cycles. The concept of normalizing element concentrations to an average crustal value is subject to various flaws, which are discussed in detail by Reimann and de Caritat (2000, 2005). A better approach is to use as reference local, non-contaminated sediment, often collected from a sediment core, and representing pre-industrial conditions (Loring and Rantala, 1992; Angelidis and Aloupi, 1995). In the present work we use as reference sediment a core sample collected from the neighboring Saronikos Gulf and represents non-contaminated sediment (see also Karageorgis and Hatzianestis, 2003). Enrichment factors (EFs, median values of 25 surface sediment samples) were calculated from:

$$EFs=(element/Al)_{sample}/(element/Al)_{ref. sed.}$$

where reference sediment is the core sample from Saronikos Gulf and also the average shale, for comparison. The results are illustrated in Fig. 7. According to the EFs, all heavy metals and metalloids (As) are enriched in the surface sediments of Koumoundourou Lake, either using the average shale or Saronikos Gulf core sediment as reference. Based on the latter reference, it may be induced that elements analyzed can be grouped as follows:

(1)   V, Mn, and Ni are slightly enriched by a factor <2
(2)   Cr, Co, and Cu are moderately enriched by a factor of 2 to 5
(3)   Zn, As, Mo, and Pb are strongly enriched by a factor of 6 to 20.

The highest EFs are observed for Mo (median 19.8), As (median 15.6), and Zn (median 7.5). Geographically, the highest EFs are located in the NE sector of the Lake, where contamination by oil has been identified. The available evidence therefore suggest that the surface sediments of Koumoundourou Lake are enriched in heavy metals and metalloids in the series Mn<V<Ni<Co<Cr<Cu<Pb<Zn<As<Mo.

Enrichment factors calculated for the core sediments (Fig. 7; median value of 14 samples) show also enrichment classified in the following groups:

(1)   Mn, V, and Ni are Ni are slightly enriched by a factor <2
(2)   Cr, Pb, Co, and Cu are moderately enriched by a factor of 2 to 5
(3)   As, Zn, and Mo are strongly enriched by a factor of 6 to 20.

The groups are very similar to those formed for the surface sediments, with the exception of Pb, which seems to be less enriched. The enrichment series is Mn<V<Ni<Cr<Pb<Co<Cu<As<Zn<Mo.

As far as it concerns the two coastal sediments, they appear to be uncontaminated, with the exception of Cr, As, and Mo, which exhibit slight to moderate enrichment. This evidence implies that heavy metal pollution is contained within the Lakes' sediments and does not influence the Elefsis Bay to great extent, at least nearby the coast.

Combining all observations, it may be concluded that pollution by leaking of petroleum hydrocarbons recorded in the NE sector of the Lake is accompanied by heavy metal and metalloid contamination, originating from the same sources, i.e. groundwater inputs and oil leaching.

5.   CONCLUSIONS

The surface and subsurface sediments of Koumoundourou Lake are coarse grained carbonate sands mostly of biogenic origin. Although heavy metal and metalloid contents of the sediments were considered low by previous investigations, the use of enrichment factors revealed that sediments are contaminated by heavy metals and metalloids several times above background levels. Underwater karstic springs, which discharge into the NE sector of the Lake, are the most probable pathways of the metals originating in industrial activities in the broader heavily industrialized area which surrounds the Lake.

ACKNOWLEDGEMENTS
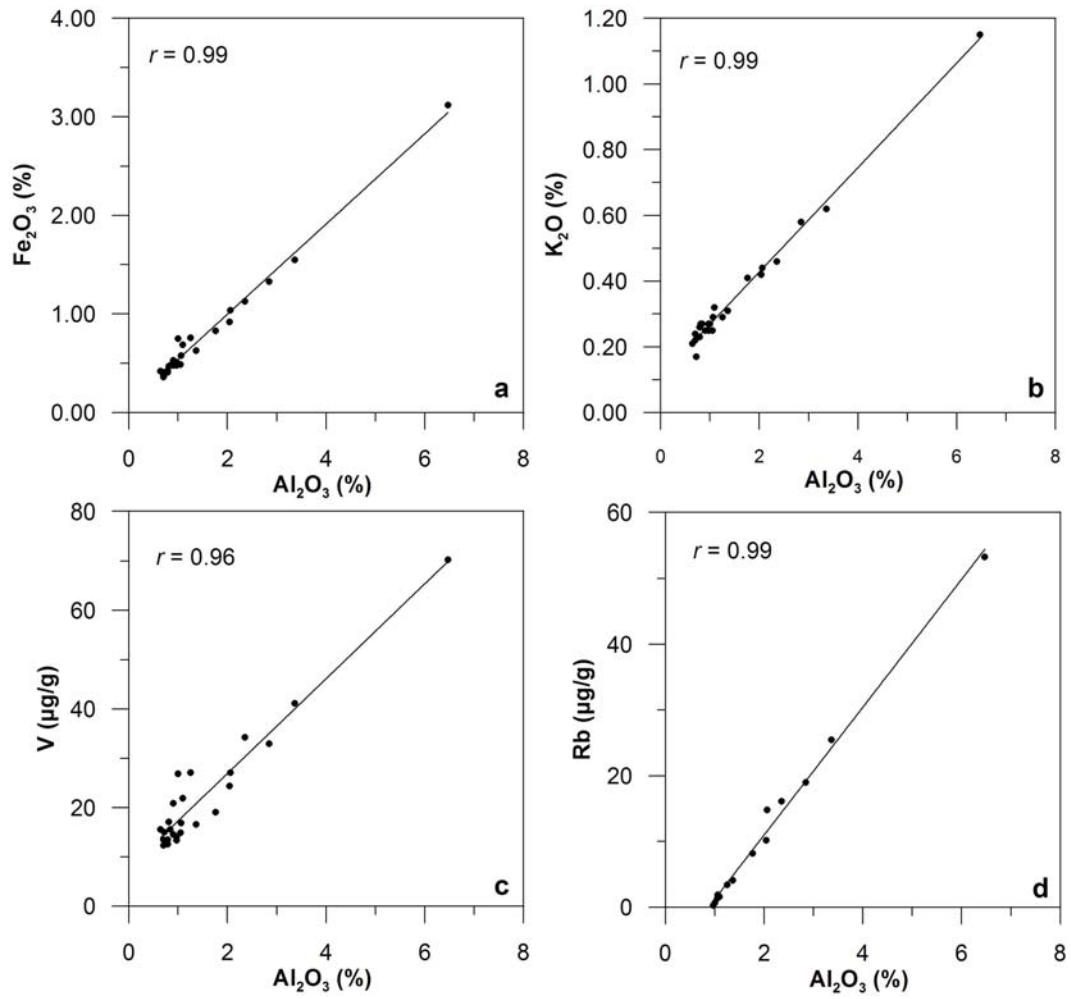
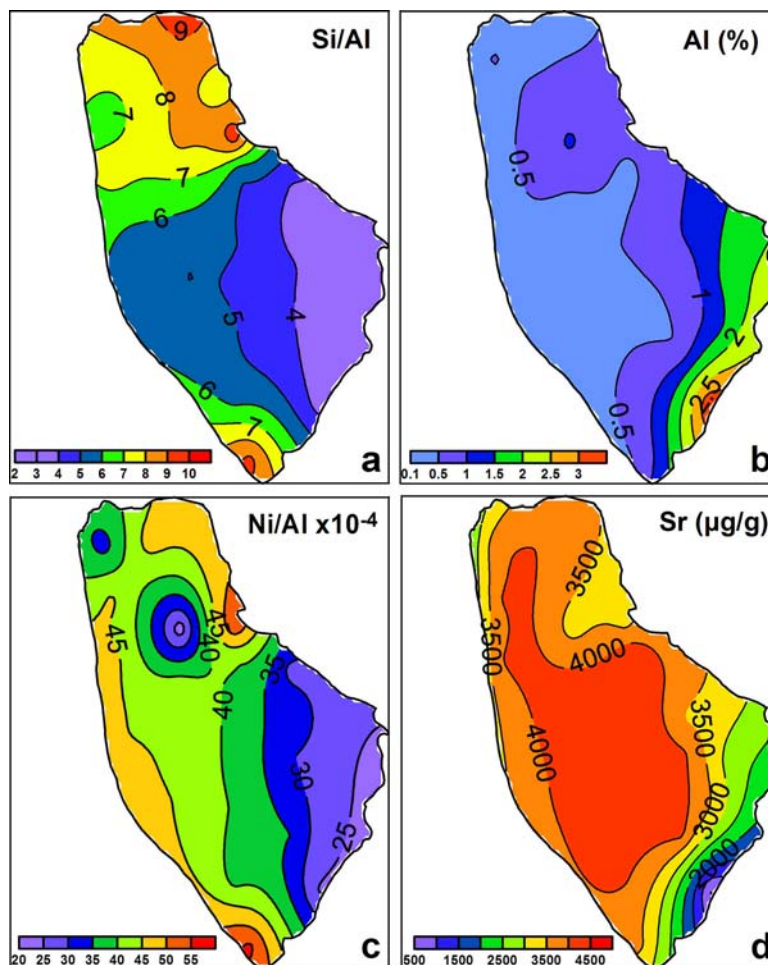**Fig. (3): Correlation plots of selected major and minor elements versus aluminium.**

Fig. (4): Spatial distribution of Si/Al, Al (%), Ni/Al (x10^{-4}), and Sr (µg/g).
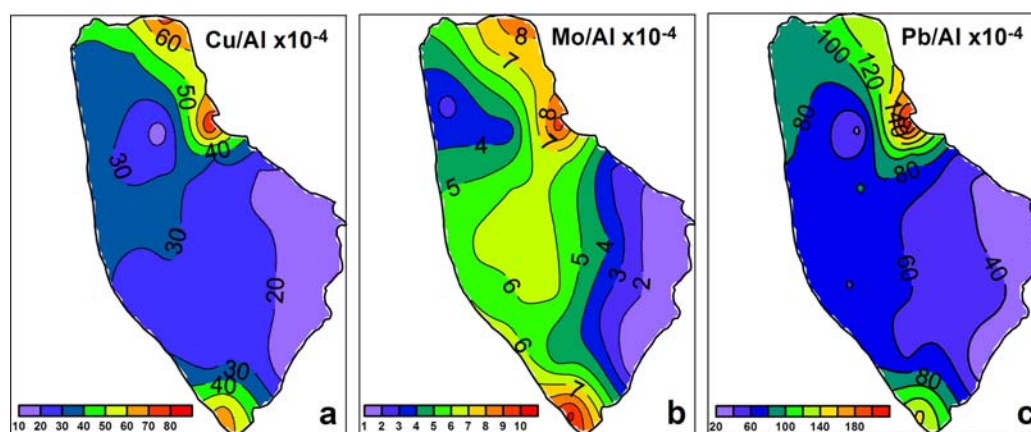

Fig. (5): Spatial distributions of Cu, Mo, and Pb weight ratios to Al. Note: minor element/Al ratios x10^{-4}.
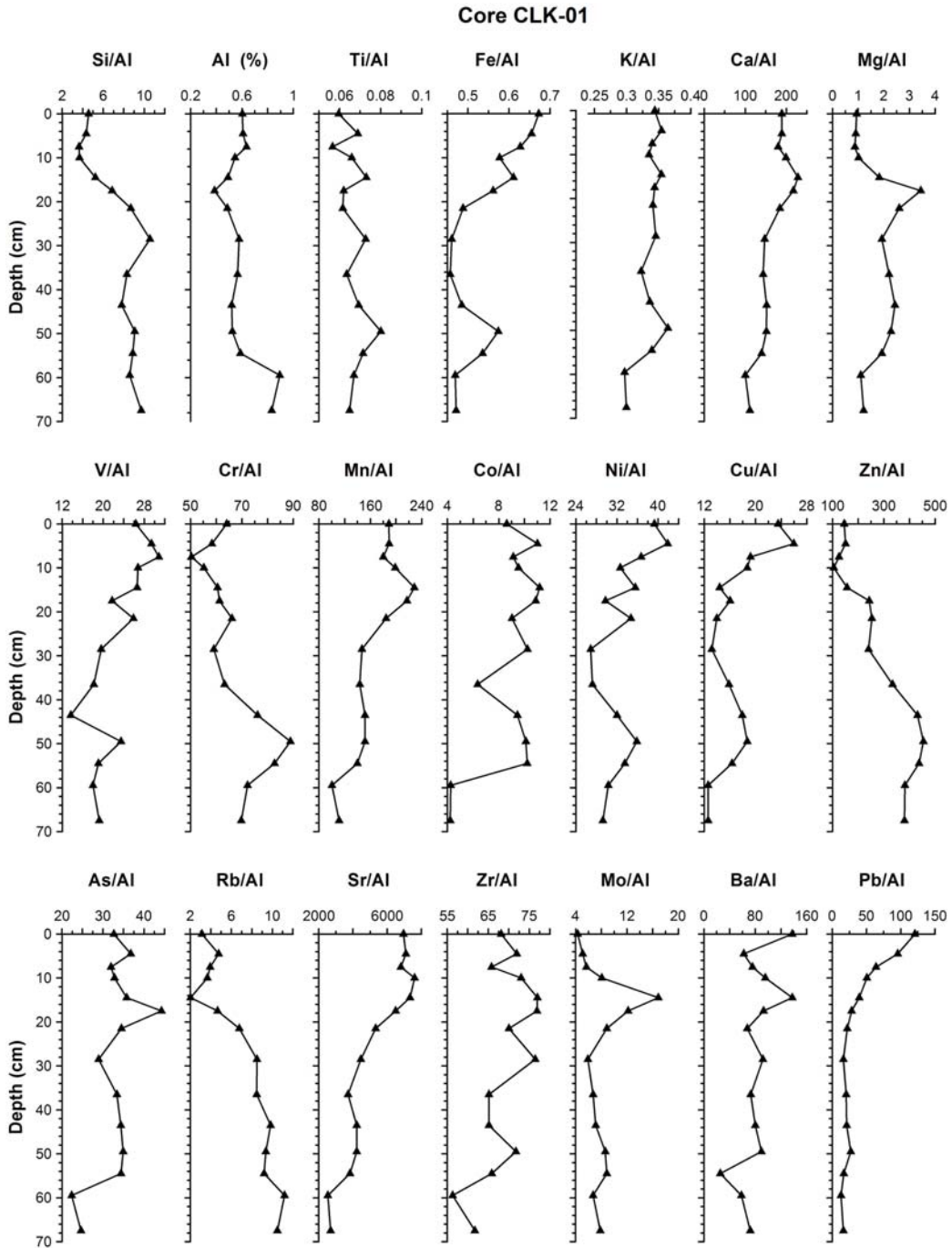
Core CLK-01

Fig. (6): Vertical distribution of major and minor elements weight ratios to Al along Core CLK-1. Note: minor element/Al ratios x10⁻⁴.
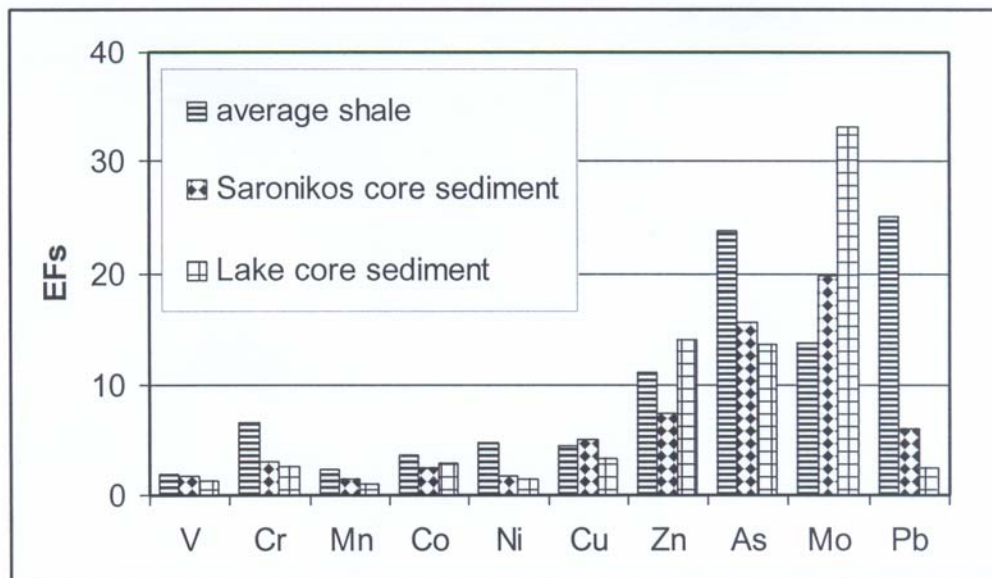
Fig. (7): Enrichment factors versus average shale (Turekian and Wedepohl, 1961) and the Saronikos Gulf pre-industrial core sediment for V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, and Pb analyzed in surface sediments (median values from 25 samples) and core samples (median values of 14 samples from the Koumoundourou Lake.

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