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WATER-LEVEL FLUCTUATIONS

Patterns, origin and possible effects of sediment pollution in a Mediterranean lake

Nikolaos Skoulikidis · Helen Kaberi · Dimitrios Sakellariou

Abstract Vegoritis is a large, deep, mesotrophic, karstic lake in NW Greece, located in Ptolemais basin. Dramatic lowering of the lake's level has occurred during the last half century due to human pressures. The Ptolemais Basin and the lake itself are subjected to serious human pressures. Pollutants are carried into the lake through both, the atmosphere and surface runoff. In order to identify the levels, and assess the origin of heavy metals in surface lake sediments, 24 samples were collected and analyzed for their grain size, as well as for their mineral, organic matter, major element and heavy metal content. The origin of heavy metals has been attributed to specific geogenic and anthropogenic sources. Despite the anthropogenic disturbance, the levels of micropollutants were low, possibly due to the low retention time of lake water and the recent increase of sedimentation rates. Only Cr, Ni, Co As, and Ba were present in relatively high concentrations. Ba is derived from the erosion of acid silicate rocks, Cr primarily from mafic rocks and secondarily from pollution, whereas for Ni and Co the opposite is true, while As is primarily attributed to fly ash deposition. The lowering of the lakes' water level exposes sediments, which are then being oxidized. Mobilization of As and Cr could impair humans' and ecosystems' health.

Keywords Lake Vegoritis · Sediments · Heavy metals · Fly ash · Toxicity

Introduction

Pollutant levels in lake sediments can be a firm criterion for the evaluation of degradation in water bodies; sediments reveal higher pollutant concentrations than the overlying waters and stable surplus levels over time (Salbu & Steiness, 1995), while lake sediments are the final recipients of anthropogenic activities within the lake-basin, operating as pollutants storage tanks and reflecting long-term impacts (e.g., Maltby, 1992). Since lakes are essentially closed, or nearly closed systems with respect to sediment transport, metals are amassed through atmospheric deposition and/or watershed leaching and are then potentially adsorbed onto the organic or clay fraction in sediments (e.g., Salomons & Förstner, 1984). Through water-level fluctuations lake sediments are periodically either exposed to the

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atmosphere or inundated. In sediments that undergo periodic flooding there may be considerable variation of oxidation-reduction states, and as the oxidation condition of the sediments changes, redox-active inorganic constituents are affected (Maltby, 1992). Inorganic and/or microbially mediated redox reactions transform the physicochemical forms and valency of metals affecting their bioavailability and toxicity.

Due to water management practices, the water level of Vegoritis Lake experienced a gradual long-term diminishing (see Section "Hydromorphological aspects and sedimentation rates"). Due to the presence of significant pollution sources in the basin, the lake became subject for research concerning heavy metals in sediments (Katsanos et al., 1987; Fytianos et al., 1994; Skoulikidis, 2001a, b). This article present the levels and possible origin of heavy metals found in lake sediments and attempts an assessment of the environmental risk caused by water level change. The article is part of a greater research funded by the Prefecture of Florina and West Macedonia Region in order to assess the causes of the lakes' level drop and to evaluate the quality of lake sediments.

Materials and methods

Study area

The Vegoritis is a karstic lake in West Macedonia without any surface run-off. Apart from the southern flat part of its basin (1,853 km^2), where the Ptolemais plain extends, the lake is surrounded by high mountains, i.e., Mount Voras (2,524 m), at the northern and north-eastern boundary, and mounts Vermio (2,052 m) and Vernon (2,128 m) at the east and west respectively (Fig. 1). The geochemically important rock formations in the basin are acid metamorphic siliceous rocks (mica schist and gneiss) and calcareous formations (marbles/sipolines, limestones, and dolomites) of Mount Voras (Fig. 1). In the east and northeastern part of the catchment dominate marbles/sipolines, with schist and serpentinite intercalations, and ophiolites. The Ptolemais plain is filled with Holocene deposits (alluvium, lacustrine sediments, and peat), Pleistocene fluvio-lacustrine, lake-bog, and fluvial conglomerate sediments, with gneiss-schist material, as well as Upper-Pliocene lake/lake-bog deposits with lignite ores. The lake is supplied by the permanently flowing river Soulou (Pentavrisos), that crosses the Ptolemais plain, and the small temporary streams Panagitsa and Zervi, which drain the northern part of the basin. In addition, overflow waters from the lake system Zazari–Chimaditida–Petron (Fig. 1) enter the lake. Moreover, a great amount of karstic waters supplies the lake contributing to the low retention time of the lake's water (9.5 times/year) (Papakonstantinou et al., 1989). In Vegoritis basin, and especially in Ptolemais plain, urban development, extensive agriculture, and industrial activities (agro-industries and lignite mining and combustion) comprise major environmental pressures. Surface water flowing in the southern part of the lake is loaded with partly treated urban and hydropower plant wastewaters, wastes from agricultural manufacturing units, erosion effluents of lignite mines, agrochemicals, and leachates from landfills. In addition, atmospheric pollution from the hydropower stations heavily impacts the area making the city of Ptolemais one of the most-polluted cities in Europe. A heavy metal pollution source in the study area is the excavation and combustion of lignite. The combustion procedure releases particulates rich in heavy metals, such as As, B, Ni, Se, Cu, Cd, Cr, Pb, Hg, Mo, Fe, Mn, and Zn (Kagey & Wixson, 1983; Gerouki et al., 1997; Fytianos and Tsaniklidi, 1998; Zevenbergen et al., 1999; Samara, 2005). In the north part of the basin, agriculture and urban development are limited. As a result of intense human activity, a degradation of the terrestrial and aquatic status of Ptolemais basin is apparent. The Soulou River is highly mineralized due to elevated carbonate dissolution, caused by sulfuric acid that originates from lignite, and exhibits low oxygen levels and high nutrient concentrations (e.g., average $N–NH_3$ levels by 2 mg/l) due to the impact of organic effluents. Thus, the river reveals a moderate to bad biological status (Skoulikidis, 2001a). The waters of the lake show seasonally toxic ammonia levels (Diamandithis & Andonopoulos, 1984), which have probably caused massive deaths of fish (Fotis et al., 1984). The lake experiences summer stratification, with very low oxygen concentrations in the meta- and hypo-limnion (Diamandithis, 1984), while its trophic status changed from oligotrophic in 1977 to mesotrophic in 1983 (Nikolaidis et al., 1985).

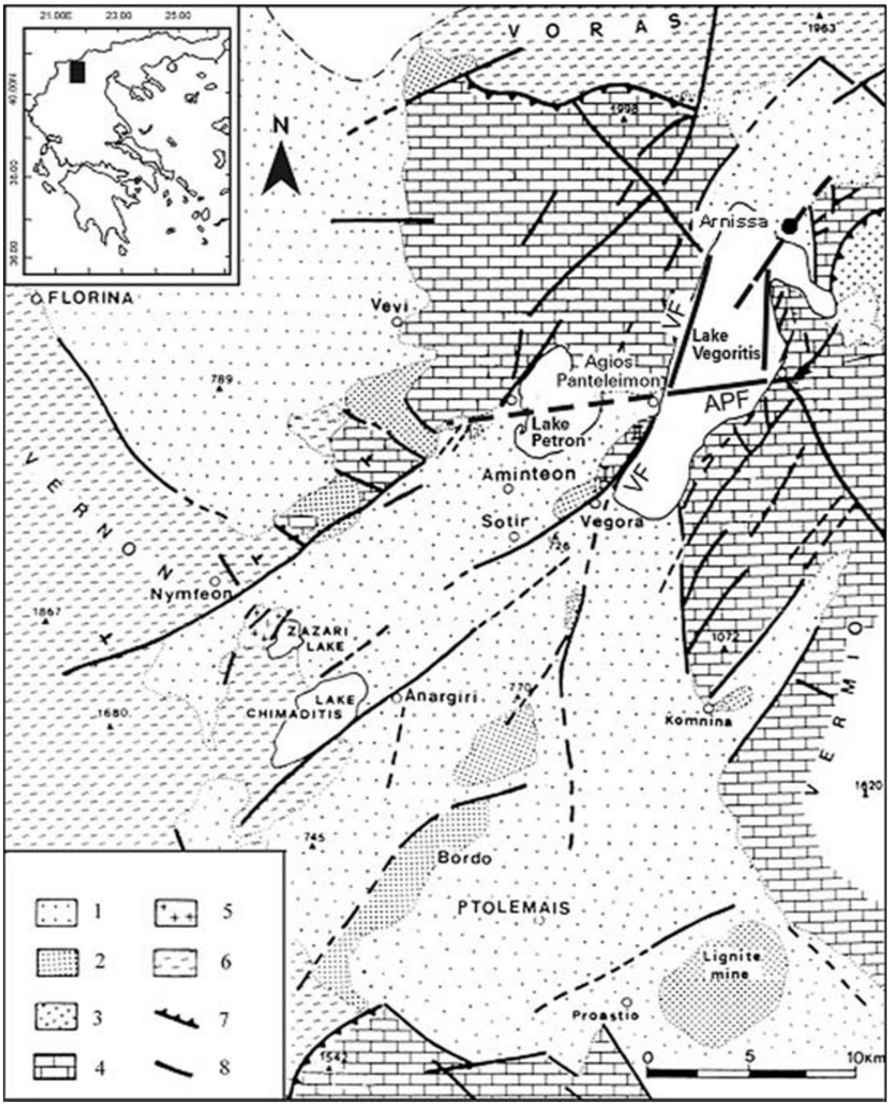

Fig. 1 Location and geological map of Vegoritis Lake basin (after Pavlides and Moundrakis, 1987; modified after Sakellariou et al., 2001). 1: Quaternary, 2: Neogene, 3: Ophiolites, 4: Marbles (Mesozoic), 5: Gneiss (U. Carboniferous), 6: Metamorphics (L. Palaeozoic), 7: Overthrust, 8: Fault, APF: Agios Panteleimon fault, VF: Vegoritis fault

Sampling and analysis

A sampling network was designed (Fig. 2), according to the distribution of active and potential pollution sources around the lake (villages, streams, agricultural areas, industrial units). 22 sediment samples were collected in September 2001 on a boat with the use of a VAN VEEN sampling device from depths ranging from 2 to 18 m and additional samples were taken from the river bed of Soulou and from the lignite field. All samples designated for chemical analysis were kept and maintained under low temperature (portable refrigerators). Grain-size analysis was carried out by wet sieving, for the sand fraction, while a SEDIGRAPH 5100 device was used for the resolution of silt and clay. Mineral composition was determined by a PHILLIPS X-ray diffraction (XRD) of CuNa radiation and 0.8 KW (40 KV–20 mA) maximum operation power. Concentrations of main elements (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, K_2O, Na_2O, CaO, MgO, P_2O_5, MnO, and S) and heavy metals (V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Ba, and Pb) were determined with the use of a PHILLIPS X-ray fluorescence (XRF) device. Total and organic carbon, total nitrogen and sulfur were determined with a Fisons Instruments CHN EA-1108-type element analyzer. Data were statistically processed with the use of multivariate statistical analysis (Principal

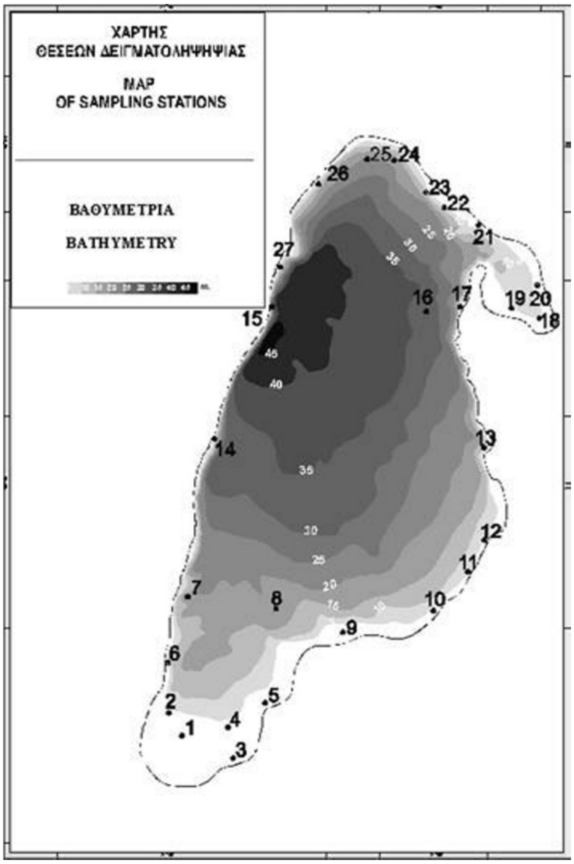

Fig. 2 Batymetric map of Vegoritis Lake with sampling sites (the sediment core is marked with triangle) (GIS Department of HCMR)

Component Analysis, Statistica Release 6.0). A 70 cm long core, recovered from the southern shallow part of the lake (which presents highest sedimentation rates and shows direct and more visible response to any changes in sedimentation processes) was used to calculate the actual sedimentation rate with the ^{210}Pb geochronological method. The core was collected from a water depth of 1.5 m, a few meters from the outflow of Soulou River. The corer, actually a 3-m long and 70 mm in diameter plastic tube with a core catcher at the lower edge, was pressed vertically into the lakebed and was pulled out by hand. The sediment core was sealed and transferred to the lab, where it was cut lengthways. 11 samples, every 1–2 cm from the upper part of the core and every 8–10 cm below 23 cm depth, were taken for XRD and XRF analyses. In addition, about 20 samples were taken every 1 cm until 10 cm depth and then every 5 cm to the lower end of the core. The down-core activity of ^{210}Pb was determined through the measurement of it's a-emitting granddaughter ^{210}Po, assuming secular equilibrium with ^{210}Pb. For the total dissolution of the dried-sediment samples the analytical method described by Sanchez-Cabeza et al. (1998) was followed, whereas the ^{210}Po activities were counted on a total a- counter (Ortec EG&C, Oak Ridge, TN, USA) (Radakovitch, 1995). The supported ^{210}Pb activity, which corresponds to sediment layers deposited earlier than the last 100–120 years, was determined in sediments old enough to accept that all the excess ^{210}Pb has decayed and assuming that parent-supported ^{210}Pb is constant.

Results

Hydromorphological aspects and sedimentation rates

In September 1999, when the present survey was conducted, the Vegoritis Lake level was at about 513–515 m asl. At that time, the area covered by the lake water was estimated to be approximately 50 km^2, with a maximum length of 12 km in NNE-SSW direction and maximum width of 5 km. The lake constitutes the northward prolongation of the southern flat part of the Ptolemais plain. Thus, the southern part of the lake, up to Agios Panteleimon village, is very shallow and characterized by the rapid accumulation of sedimentary material carried into the lake by the Soulou River. The lake-bed deepens gradually to the north and reaches a maximum depth of 48 m (about 465 m asl). The deepest part of the lake-bed is located at the base of the steep slope at the western lakeside, which is formed along the trace of Vegoritis fault. On the contrary, towards the east the lake-bed shallows very gently, indicating a significant morphological asymmetry.

Lake Vegoritis lacks any surficial outflow. Nevertheless, the strongly karstified Triassic-Jurassic marbles, which outcrop at the margins of the lake, allow the underground discharge of lake water to the Voda springs, a few kilometers NE of Arnissa village (Fig. 1). The lake level used to fluctuate normally, following climatic patterns, until 45 years ago (Fig. 3), and in 1956 it was measured at 542 m asl (Stamos, 1996). In this year, a water tunnel was set in

Fig. 3 Water-level fluctuations in Vegoritis Lake during the last century (Stamos, 1996)

operation at the NE side of the lake, through which huge quantities of lake water were abstracted to cover the needs of Agras hydro-electric power station. 34 years later (1990), the lake level was lowered by almost 30 m and fell below the operational level of the tunnel (515.5 m asl), which is abandoned since then, while the lake has lost about 65% of its water (Antonopoulos & Gianniou, 2003).

Figure 4 presents the vertical distribution of ^{210}Pb activity. From the sediment surface until 30 cm depth, the ^{210}Pb activity increases with depth, whereas from this depth to the lower end of the core the activity exponentially decreases, showing an almost theoretical pattern. The cause for this unusual distribution is attributed to the enormous lowering of the lake level since 1956. Hence, two separate sedimentation rates have been calculated. The CRS (Constant Rate of Supply) model was used (Appleby & Oldfield, 1978) for the calculation of the sedimentation rate in the lower part of the core. According to our assumption, this part of the core represents the period before 1956, and the apparent maximum sedimentation rate was calculated to about 0.4 cm/year. Consequently, the upper 30 cm of the sediment core have been accumulated during the last 45 years, after 1956, at a significantly higher sedimentation rate of 0.6 cm/year. Therefore, the rapid increase of the sedimentation rate in the upper 30 cm of the sediment core is attributed to the dramatic lowering of the lake level since 1956.

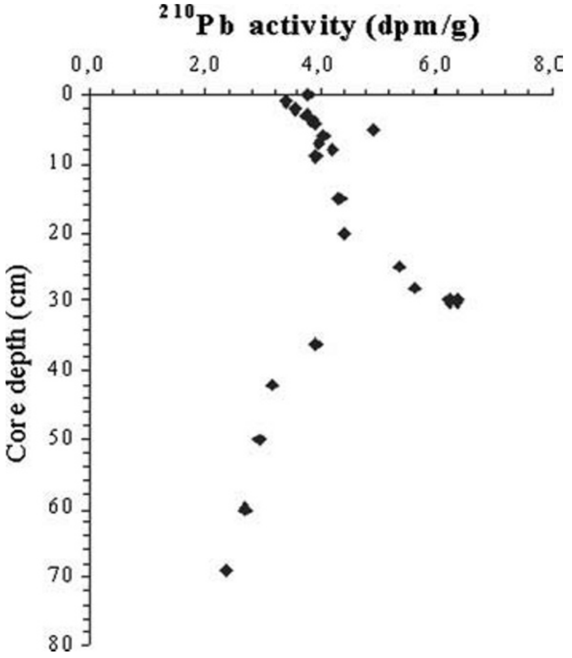

Fig. 4 ^{210}Pb distribution along the sediment core recovered from Vegoritis Lake bed. The depth of ca. 30 cm corresponds to year 1956 (for details see Section "Hydromorphological aspects and sedimentation rates")

Physico-chemical characteristics of lake sediments

Tables 1 and 2 present the physical and chemical properties of the sediments in Vegoritis Lake and Soulou River and the metal concentrations in lignite. In average, lake sediments are composed by clayey silt, i.e., silt (51.7%), clay (33.6%) and sand (14.7%). The northern and, especially, the eastern parts of the lake reveal higher percentage in coarse grain material (33% and 15% sand, respectively), while the southern part is covered by finer grained material (96% silt/clay) as a result of fluvial inputs from the Neogene-Quaternary deposits of Ptolemais basin. The mineralogical assemblage of the sediments is made up by silica, calcite, dolomite, plagioclase, montmorillonite, illite, and chlorite. The north part of the lake is particularly enriched with illite. Organic carbon in lake sediments ranges between 0.65% and 2.26%, whereas Soulou River sediments are more enriched (3.76%). During the field study, a large part of lake sediments was covered by gas bubbles, indicating anaerobic decomposition of sediment organic matter (Sakellariou et al., 2001). The sediments' gray/black color and smell also indicate anoxic conditions.

Table A1 (Supplementary material) illustrates heavy metal concentrations in surface lake sediments, according to the present and previous research in Vegoritis Lake, and undisturbed lakes. It also includes heavy

Table 1 Concentrations of organic and total carbon, total nitrogen and sulfur and major elements in Lake Vegoritis and Soulou River sediments (28) and of major elements in lignite (29) (units in %)

Station ID	OC	TC	TN	TS	Sand	Silt	Clay	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	K_2O	Na_2O	CaO	MgO	P_2O_5	MnO
1	1.05	3.83	0.14	0.029	0.8	58.5	40.7	40.25	12.63	0.68	7.05	1.95	0.7	13.81	4.59	0.17	0.11
2	1.2	4.28	0.16	0.04	1	68	31	40.14	11.6	0.67	6.56	1.79	0.87	15.25	4.53	0.16	0.11
3	0.89	3.33	0.12	0.017	11	53	36	42.81	12.9	0.72	7.32	1.96	0.83	12.39	4.52	0.16	0.11
4	0.99	3.71	0.14	0.035	0.35	55.85	43.8	39.5	13.02	0.71	7.47	1.95	0.69	13.5	4.57	0.16	0.11
5	1.75	4.7	0.21	0.095	0.54	64	35.5	38.28	12.32	0.68	7.06	1.84	0.71	14.49	4.58	0.17	0.11
6	1.47	5.43	0.19	0.058	4.25	48.8	47	33.64	11.44	0.59	6.34	1.73	0.48	18.9	4.47	0.18	0.09
7	1.46	5.84	0.18	0.038	11	42.3	46.7	31.9	10.86	0.55	5.95	1.71	0.44	20.69	4.51	0.18	0.1
8	1.91	4.84	0.21	0.493	1.3	52	46.8	36.78	12.26	0.65	7.58	1.84	0.51	14.4	5.06	0.16	0.12
9	1.77	4.28	0.19	0.087	3.8	61.6	34.6	42.46	11.44	0.65	6.77	1.73	0.74	12.75	5.42	0.16	0.11
10	0.65	3.59	0.07	0.026	55.7	30	14.3	51.27	7.35	0.66	4.24	0.97	0.88	13.96	5.34	0.13	0.08
11	0.95	4.32	0.1	0.025	53	32	15	46.05	7.81	0.54	4.28	1.07	0.87	15.82	5.2	0.14	0.08
12	1.74	5.36	0.21	0.056	15.3	53.4	31.3	40.33	9.57	0.58	5.26	1.58	0.71	16.52	5.34	0.16	0.09
13	2.2	6.33	0.26	0.175	8.6	50	41.5	32.99	10.24	0.55	5.88	1.49	0.47	19.28	5.21	0.18	0.09
18	1.88	5.69	0.22	0.178	3	52.5	44.5	36.15	10.86	0.52	5.33	1.85	0.55	18.66	3.97	0.18	0.09
19	1.63	5.59	0.2	0.093	11	48.2	40.8	33.79	11.16	0.52	5.44	2.01	0.64	19.71	3.87	0.19	0.08
20	2.26	5.55	0.28	0.241	2.3	65.5	32.2	38	12.47	0.53	5.16	2.49	0.88	15.81	3.96	0.18	0.09
21	1.74	4.3	0.23	0.195	7.2	64	28.7	43.1	14.34	0.55	5.09	3.32	1.31	12.04	3.56	0.19	0.09
22	1.32	2.36	0.09	0.054	40.8	44.6	14.6	51.89	17.88	0.54	4.88	4.73	1.93	4.43	3.12	0.18	0.08
23	0.96	3.08	0.1	0.066	13	51.5	35.5	45.79	15.24	0.59	5.44	3.43	1.42	10.25	3.49	0.18	0.09
24	0.95	2.66	0.11	0.09	32.7	51.7	15.6	48.47	16.08	0.56	5.22	3.99	1.7	8.98	3.14	0.19	0.09
26	1.51	5.39	0.18	0.076	6.3	55.7	38	34.79	12.01	0.55	5.35	2.25	0.82	18.12	4.28	0.17	0.09
27	1.65	8.92	0.21	0.086	40	35	25	20.87	6.15	0.32	2.84	1.06	0.63	31.38	5.49	0.14	0.07
Average	1.45	4.70	0.17	0.10	14.68	51.73	33.60	39.51	11.80	0.59	5.75	2.12	0.85	15.51	4.46	0.17	0.09
Median	1.49	4.51	0.185	0.071	7.9	52.25	35.5	39.82	11.805	0.57	5.44	1.845	0.73	14.87	4.525	0.17	0.09
% StDev	30.8	30.6	33.6	106.4	119.7	20.0	32.2	17.9	23.1	15.1	20.7	44.5	46.3	33.7	16.4	9.9	14.1
Max	2.26	8.92	0.28	0.49	55.7	68	47	51.89	17.88	0.72	7.58	4.73	1.93	31.38	5.49	0.19	0.12
Min	0.65	2.36	0.07	0.02	0.35	30	14.3	20.87	6.15	0.32	2.84	0.97	0.44	4.43	3.12	0.13	0.07
28	3.75	5.98	0.38	0.04	21.3	45.3	33.4	41.43	9.36	0.56	6.07	1.27	0.67	13.07	6.72	0.37	0.08
29								46.59	16.7	0.77	8.33	3.13	2.11	5.44	4.58	0.13	0.14

OC: Organic carbon, TC: total carbon, TN: total nitrogen, TS: total sulfur, % StDev: Standard Deviation * 100/average

metal concentrations estimated in fly ash of the area, background heavy metal concentrations in rock types found in the basin and recommended heavy metal limits in soils. As it is stemmed from comparisons with concentrations found in reference lakes, typical concentration levels of different types of rocks and soils and recommended thresholds in soils, only Cr, Ni, Co, As, and Ba exhibited relatively high concentrations in the lake.

A Principal Component Analysis (PCA) was performed on the parameters investigated in lake sediments in order to reveal their relationships (Table 3). Three principal components interpreting 75% of the total variability were distinguished. The first PCA component, which accounted for the one-thirds of the total variance, was more heavily weighted on V, Co, Ni, Cu, Mn, and Fe. The second component, which accounted for the $^1/_4$ of the total variance, was characterized by Rb, Ba, Ti, Si, Al, K (positive loadings) and Sr, Ca, and total C (negative loadings). Factor 3 (16.4% of the observed variance) involves Cu, Zn, As, Pb, clay, organic C, total N and total S (positive loadings) and Cr, sand (negative loadings).

A next PCA was performed on the 24 samples from the study area for major elements and heavy metals (Fig. 5) in order to differentiate groups of sites with similar composition, and thus, to allocate the main factors determining the differentiation of these groups. Three core groups of sites were distinguished,

Table 2 Heavy metal concentrations in the sediments of Lake Vegoritis and Soulou River sediments (28) and in lignite (29) (units in ppm)

Station ID	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Mo	Ba	Pb
1	118.9	323.1	897.7	33.9	309	42.6	97.5	10.5	116.7	170.9	1.7	412.7	24.4
2	111.7	297.8	947.1	30	260	40.6	87.6	12.4	104.1	196.9	2.2	387.6	23.3
3	124.9	324.4	910.8	31.8	283	44.1	97.1	13.4	113.2	164.4	1.8	426.1	23
4	127	318.2	896.9	33.6	292.5	46.7	100.9	12.1	116.6	165.1	1.7	422.5	23.9
5	116.6	308.6	977.4	31.6	271.8	44.7	98.6	8.5	111.6	187.7	2.2	417.3	25.6
6	114.4	262.7	825.6	28.1	247.5	42.6	93.5	11.8	111	199.6	2.4	403.3	25.7
7	109.2	241.5	863.3	26.3	233.5	42.3	86.8	12.1	110.4	212.1	1.5	423	26.7
8	124.7	348	1,018	33.1	306.7	48.2	102.6	13.5	114.3	161.9	3.4	404.8	26
9	113.1	380.4	933.3	33.2	321.9	40.9	93	12.4	99.7	159.7	2.3	374.7	23.2
10	88.7	706.1	713.3	25.5	261.4	16.4	51.9	8.5	47.3	227.9	2.2	231.3	11.6
11	87.1	424.3	712.3	23.8	255.4	22.1	58.5	9.5	59.8	238.9	2.3	263.9	14.2
12	99.5	299.5	832.1	26.7	244.5	34.3	76.7	11.6	87.1	201.6	2.2	332.8	19.6
13	109.9	291.3	838.2	29.1	257.1	43.3	82	13.6	94.5	223	2.1	372.3	23.4
18	99.1	207.5	754.5	23	201.5	41.2	85.2	13.3	118	228.6	2.1	410.4	27.3
19	99.6	210.1	716.2	25.2	203.8	39.9	87	13	124.1	256.5	3.6	443.8	28.2
20	93.6	164.3	795.2	21.3	156	37.7	90.8	15.6	152.8	242.3	1.6	513.4	32.5
21	92.5	139.9	754.9	20	121.6	33.3	97.2	12	188	241.8	3	605.4	33.4
22	90.6	61.7	692.5	14	37.7	29.8	111.2	11.9	256.3	204.7	2	963.6	40.3
23	96.7	149.4	738.3	19.4	135.4	30.4	99.1	10.4	195.5	218.5	2	610.4	32.5
24	90.7	114	736.2	16.2	97.8	23.7	98.2	8	214.7	221.3	2.1	667.4	29.7
26	101.3	176	792.2	22	162.4	39.7	93.6	10.9	139.9	246.5	2.5	485.1	33.4
27	68.3	104.1	681.6	13.3	86.4	21.4	49.8	15	67.9	345.3	3.9	365.2	20.6
Average	104	266	819	25.5	215.8	36.6	88.1	11.8	124.7	214.3	2.3	451.7	25.8
% StDev	14.3	51.8	12.2	24.9	37.3	24.6	18.2	16.9	40.4	19.5	27.5	34.0	25.0
Max	127	706	1018	33.9	322	48.2	111.2	15.6	256.3	345.3	3.9	964	40.3
Min	68.3	61.7	681.6	13.3	37.7	16.4	49.8	8	47.3	159.7	1.5	231	11.6
28	–	447	–	–	200	40	87.5	7	93.5	142	–	–	53
29	100.4	494.1	729.6	35.6	430.8	70.1	242.5	8.9	78.1	176.1	3	334.6	30.5

% StDev: Standard Deviation * 100/average

denoting that the distribution of metals in lake sediments follows a geographical pattern: sites in the south part of the basin (sites 1–9), sites in the east part of the basin (sites 10–13) and sites in the north part of the basin (sites 18–27). Sites in the south and east parts of the lake revealed stronger geochemical associations since they are closely located. Sites situated in the north part of the lake presented strong dissimilarities, possibly due to the heterogeneity of heavy metal sources. Especially site 27 differs greatly from the others since its composition depends on the erosion of carbonate formations of Mt. Voras. Soulou River sediments and lignite are obviously enriched in major elements and heavy metals; however, they present strong dissimilarities in their composition. This facilitates the heavy metal sources apportion. According to basic statistics in each one of the distinguished site-groups (Table 4), the following results can be depicted: (a) the south part of the basin is enriched in V, Mn, Co, Ni, Cu, Zn, (b) the east part of the basin is characterized by high Cr concentrations, (c) Pb, Rb, Sr, and Ba dominate in the north part of the basin and (d) As and M*o* present a, more or less, homogenous distribution.

Figure 6 presents a comparison of heavy metals levels in lignite and in the sediments of Soulou River and Vegoritis Lake. Cu, Zn, Cr, Ni, and Co exhibit maximum concentrations in river sediments, whereas

Table 3 The three main components of sediment quality in Lake Vegoritis according to a Principal Component Analysis carried out on the whole data set (bold numbers: significant loadings, italics numbers: significant negative loadings)

%	PC1 33.2	PC2 25.3	PC3 16.4
V	**0.230**	0.197	0.001
Cr	0.184	−0.074	*−0.276*
Mn	**0.221**	0.146	0.007
Co	**0.294**	0.067	−0.054
Ni	**0.288**	−0.007	−0.086
Cu	**0.230**	0.088	**0.215**
Zn	0.107	0.101	**0.158**
As	0.004	−0.072	**0.2419**
Rb	−0.197	**0.242**	0.136
Sr	−0.190	*−0.247*	0.091
Mo	−0.020	−0.182	0.148
Ba	*−0.208*	**0.214**	0.1326
Pb	−0.114	0.188	**0.298**
Si	−0.081	**0.201**	*−0.256*
Al	−0.110	**0.317**	0.092
Ti	0.170	**0.233**	−0.1969
Fe	**0.223**	**0.228**	0.0278
K	−0.208	**0.242**	0.0921
Na	*−0.236*	0.177	−0.065
Ca	0.049	*−0.295*	0.122
Mg	**0.206**	−0.197	−0.068
P	0.076	0.025	0.186
Sand	−0.162	−0.149	*−0.246*
Silt	0.074	**0.211**	0.184
Clay	0.193	0.039	**0.224**
Organic carbon	0.107	−0.077	**0.292**
Total carbon	0.064	*−0.285*	**0.226**
Total nitrogen	0.128	−0.098	**0.318**
Total sulfur	0.022	0.0191	**0.212**
φ	*−0.264*	−0.016	0.145
λ	*−0.211*	−0.0219	0.005

PC1, PC2, PC3: Components, φ/λ: coordinates

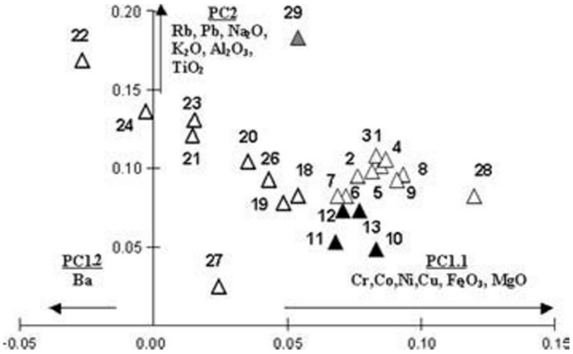

Fig. 5 Distribution of sampling sites according to the first and second axes of a PCA carried out on major elements and heavy metals (1–9: sites at the southern part of the lake, 10–13: sites at the eastern part of the lake, 18–26: sites at the northern part of the lake, 28: Soulou River, 29: lignite. For sampling site location see Fig. 1)

Mn, As, Pb, and Sr are maximum in lignite. Compared to the river and to lignite, the lake is enriched only with Ba and presents average concentrations of Cr, Mn, Co, Ni, As, Rb, Sr, and Mo and low concentrations of V, Cu, Zn, and Pb.

Elements in the sediment core did not differ substantially from those in surface sediments. Nevertheless, element concentrations derived from fly ash (Table A1—Supplementary material); show a slight increase in the upper ~30 cm (from 1956 up today) of the sediment core. The upper section of the sediments was enriched with sulfur, As, Mn, Sr, and Pb compared to the lower sediment section. Enrichment factors ranged between 1.12 and 1.36. However, the application of a *t*-test showed a statistically accepted variation only for Mn. Figure 7 shows the depth distribution of a selected example.

Discussion

The Soulou River comprises a significant source for lake organic matter of anthropogenic origin. In fact, organic carbon and total nitrogen are several times higher in river sediments compared with sediments of other Greek rivers, included polluted ones (Skoulikidis, unpublished data). On the other hand, sulfur concentration in river sediments is 2.5 times lower compared to the lake's average and similar to other Greek rivers, suggesting that lignite combustion is the main sulfur source for the lake. The association of V, Co, Ni, Cu, Mn and Fe in lake sediments, as derived from the PCA, suggests the adsorption of trace metals on Fe and Mn oxyhydroxides, as these minerals constitute significant sinks of trace metals through the effect of sorption/co-precipitation (Salomons & Förstner, 1984; Nikolaidis et al., 2004). The relationship of Rb–Ba with silicate, aluminum and potassium is due to the fact, that these metals are constituents

Table 4 Range, Median and Standard Deviation (S.D.) of heavy metal concentrations (ppm) in the sediments of the southern, eastern and northern parts of Lake Vegoritis (s: sampling site)

	South part (s. 1–9)			East part (s. 10–13)			North part (s. 18–26)		
	Min–Max	Median	S.D.	Min–Max	Median	S.D.	Min–Max	Median	S.D.
V	109–127	116.6	6.4	87–110	94.1	10.6	91–101	95.2	4.2
Cr	242–380	318	41.7	291–706	362	194	62–210	156.9	49.2
Mn	826–1,018	911	58.1	712–838	773	70.7	693–795	746	35
Co	26–34	31.8	2.6	24–29	26	2.2	14–25	20.7	3.6
Ni	234–322	283	29.9	245–261	256	7.2	38–204	145.7	55.1
Cu	41–48	42.6	2.6	16–43	28	12.1	24–41	35.5	6.2
Zn	87–103	97	5.5	52–82	67.6	14.4	85–111	95.4	8.2
As	8.5–13.5	12.1	1.5	8.5–14	10.6	2.3	8–15.6	12	2.2
Rb	100–117	112	5.7	47–95	73.5	22.3	118–256	170.4	48.3
Sr	160–212	171	19.5	202–239	225	15.6	205–257	235.2	17.2
Mo	1.5–3.4	2.2	0.6	2.1–2.3	2.2	0.1	1.6–3.6	2.1	0.6
Ba	375–426	412.7	17.4	231–372	298	64	410–964	559	176
Pb	23–27	24.4	1.4	12–23	16.9	5.3	27–40	32.5	4.1

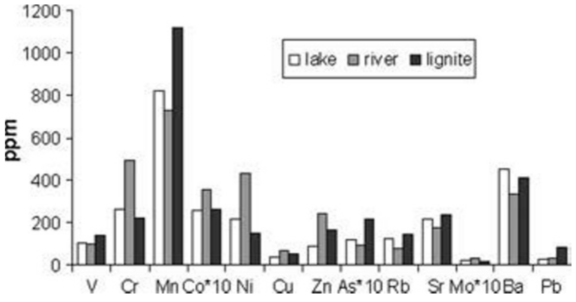

Fig. 6 Comparative concentrations of heavy metals in the sediments of Lake Vegoritis and Soulou River and in lignite

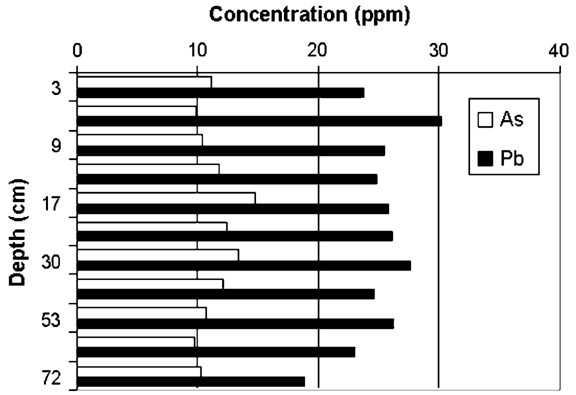

Fig. 7 Depth distribution of As and Pb in the sediment core

of potassium minerals, including illite [$KAl_3Si_3O_{10}(OH)_2$]. The association between calcium, total carbon and Sr is typical for calcite, where Sr replaces Ca since they present similar chemical behavior (Hem, 1985). The relation of Cu, Zn, As, Pb with clay, organic carbon, total nitrogen, and sulfur reveals metal adsorption on rich in organic matter clay material.

For the assessment of the origin of heavy metals in the lake, apart of the aforementioned associations, their spatial distribution in lake sediments and their relative concentrations in lake and river sediments and in lignite were used. Ba and Rb reach maximum concentrations in the north part of the lake as a result of the presence of metamorphic rocks and the dominance of illite in the mineralogical fraction of the sediments. Sr shows highest levels at the north and east parts of the lake due to the predominance of carbonate geology. In the south part of the lake, lignite may account as an additional source for Rb and Sr. The latter may also be derived from fly ash (Table A1—Supplementary material). The main source of Cu, Zn, Ni and Co for the lake is Soulou, which carries, partly treated, industrial and municipal wastewaters, agrochemicals, landfill leachates and geogenic material. Solid and liquid wastes resulting from urban areas are enriched with Cu, Pb, Zn, and Ni (DVWK, 1998), while Cu, Pb, Zn, Cr, Ni, and Co are constituents of agrochemicals (Förstner & Wittmann, 1981). High Pb and Zn concentrations at the north part of the lake are attributed to metal sulfides found in metamorphic rocks. Maximum Ni concentrations in the southern part of the lake suggest a prevalence of anthropogenic Ni-sources over geogenic ones, i.e., ophiolites found at the eastern part of the lake. In contrast, mafic rock erosion is the dominant Cr source for lake sediments, since Cr is associated with sand and maximum Cr concentrations occur at the eastern part of the lake. The east part of the lake illustrates minimum concentrations of Mn, Cu, Zn, As, and Pb probably due to the lack of important pollution sources, and minimum Rb and Ba levels, due to the low abundance of K-minerals (Skoulikidis, 2001a). Mn and V, which show higher concentrations at the southern part of the lake, may be derived from lignite weathering/erosion and combustion. The As distribution in lake sediments does not facilitate the partition of its sources. Application of arsenical compounds as pesticides and herbicides are band. Fly ash from Ptolemais area contains high As concentrations (Table A1—Supplementary material), while river sediments revealed lower concentrations than lake sediments. Therefore, it is assumed that the main As source in Lake Vegoritis is fly ash.

Despite the prolonged anthropogenic pressures on the lake, the majority of metal concentrations in sediments are below the health standard limits. Only arsenic and chromium will be considered hereafter, since their concentrations in the lake may pose toxic hazards to the environment and to humans. Concerning As, the concentration in lake sediments did not exceeded the limits for undisturbed soils, according to Eikmann & Kloke (1993) and VROM (1988). Nevertheless, over 80% of the samples surpassed the 10 ppm threshold for residential areas according to the State of Connecticut regulations (1996). Regarding Cr, all, except one, sites exceeded 100 ppm, indicating disturbance. The State of Connecticut (1996) sets distinct limits for Cr(III) and Cr(VI). The Cr(VI) limit for residential areas soils is 100 ppm.

As described before, the water level of the lake underwent a dramatic diminishing in the past half century. Only between 1981 and 1993, the surface area of the lake reduced by 13 km^2 (Antonopoulos & Gianniou, 2003). As a result, huge sediment amounts were exposed to the atmosphere. Although there is an incomplete understanding of the biogeochemical controls on arsenic transformation among reservoirs (sediment—aqueous—atmosphere) (Nicholas et al., 2003), an attempt will be made to assess its toxicity in exposed sediments. Arsenic is a toxic and well known human carcinogen (IARC, 1987). In environmental media, arsenic exists as As(III) (arsenite) or As(V) (arsenate). Arsenite is considered as more toxic (Morton & Dunnette, 1994; Yamauchi & Fowler, 1994). Human exposure to As, includes ingestion of food and water and inhalation of airborne particulates. As sediments shift to anoxic sulfidic environments, a repartition of bound arsenic from iron and manganese compounds to the sulfide phase is possible (Moore et al., 1988). Anoxic sediments can, therefore, become an arsenic sink. The likelihood for arsenic to appear as sulfide in the lake is high, since waters inflowing to the lake are rich in sulfate (average sulfate concentration of Soulou river amounts 245 mg/l), lignite combustion cause high SO_2 emissions and sediment conditions are anoxic. Moreover, there is an association between As and sulfur in the sediments of the lake (Table 3). Exposure of the sediments due to the lake level drop results in the re-establishing of oxic conditions and sulfides can be oxidized releasing arsenic. In that case, arsenic could pass in the trophic chain of the terrestrial ecosystem. The microbial activity of soils alters causing hazards to biota (Luh et al., 1973). Arsenic could also be transported with dust and, acting cumulatively to fly ash, may pose adverse effects to humans, e.g., cardiovascular disease, peripheral vascular disease, developmental effects, neurologic and neurobehavioral effects, diabetes, hearing loss, portal fibrosis of the liver, lung fibrosis, hematologic effects and carcinogenic effects (Chen & Linn, 1994).

The stable forms of chromium are the trivalent Cr(III) and the hexavalent Cr(VI) species. Cr(VI) is a potent, extremely toxic carcinogen (SRC, 1993), 10–100 times more toxic than Cr(III) (Katz & Salem, 1994). Human exposure to chromium includes ingestion of food and water and inhalation of airborne particulates. Under oxic conditions, Cr(III) may be oxidized to Cr(VI), which can lead to serious environmental consequences (Bartlett, 1991). What happens when wetted sediments gradually dry out? Masscheleyn et al. (1992) found out that Cr(III) in floodwater may be oxidized to Cr(VI) by iron and manganese oxyhydroxides, while if any Cr(VI) is present in floodwater it will not be reduced to Cr(III). However, the oxidation of Cr(III) to Cr(VI) is restricted by the availability of mobile Cr(III)

(Bartlett, 1991), it is a very slow process (Eary & Rai, 1987) and is expected to decrease when sediments dry out (Zayed & Terry, 2003). Hence, when sediments are exposed to the atmosphere, it is assumed that if any Cr(VI) is present it will remain as that, while only a small part of Cr(III) will be oxidized to Cr(VI). Only if over one-thirds of chromium concentration found in lake Vegoritis sediments is present as Cr(VI), could pose hazards to humans (e.g., lung carcinogenesis, toxicity through oral or dermal exposure) and to the environment, e.g., toxic effects in terrestrial and aquatic plants (Dirilgen, 1998; Shanker et al., 2005) and amphibians (Calevro et al., 1998).

Conclusions

In the late 1950s, the area started to develop industrial and agricultural activity, which gradually became intense. At the same time the first thermal power stations started operating. Since the lakes sediments were ~30 cm below their present level, it was expected that this sediment fraction should be more impacted with anthropogenic elements. Nevertheless, it was found that there was only a slight enrichment in the upper section of the sediments for selected elements (S, As, Mn, Sr, and Pb). In addition, heavy metal levels in surface sediments are generally low compared to concentrations found in reference lakes, typical concentration levels of different types of rocks and soils and recommended thresholds in soils. It is assumed, that the increase of the sedimentation rate during the last half century, in combination with the low retention time of the lake water, cause a "dilution" of pollutants, and positively affects the environmental state of the lake. Only Cr, Ni, Co, As, and Ba exhibited relatively high concentrations in lake sediments, whereas only As and Cr presented concentrations that could be regarded as toxic. The main source for arsenic is considered to be fly ash, while chromium mainly derives from mafic rocks. Since 1956, when lake water started to be used for hydropower production, the lake level was lowered by almost 30 m and large lake sediment surfaces were exposed to the atmosphere. Exposure of sediments results in re-establishing of oxic conditions causing oxidation of As-sulfides and of Cr(III) to Cr(VI). These metals may then pass in the trophic chain of the terrestrial ecosystem or may be transferred with dust particles. Regarding chromium, it is estimated that only when over one-thirds of Cr found in lake sediments is present as Cr(VI), could pose hazards to the environment and to humans. In order to secure humans and ecosystem health, future research should focus on the valency of chromium and arsenic, their bioavailable fraction, as well as the biogeochemical processes that control their mobility.

References

Antonopoulos, V. Z. & S. K. Gianniou, 2003. Simulation of water temperature and dissolved oxygen distribution in Lake Vegoritis, Greece. Ecological Modelling 160: 39–53.

Appleby, P. G. & F. Oldfield, 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported lead-210 to the sediment. Catena 5: 1–8.

Bartlett, R. J., 1991. Cromium cycling in soil and water: links, gaps and methods. Environmental Health Perspectives 92: 31–34.

Calevro, F., S. Campani, M. Ragghianti, S. Bucci & G. Mancino, 1998. Tests of toxicity and teratogenicity in biphasic vertebrates treated with heavy metals (Cr^{3+}, Al^{3+}, Cd^{2+}). Chemosphere 37: 3011–3017.

Chen, C. J. & L. J. Linn, 1994. Human carcinogeneicity and athirogenicity induced by chronic exposure to inorganic arsenic. In Nriagu, J. O. (ed.), Arsenic in the environment, Part II: human health and ecosystem effects. Wiley & Sons, Inc., New York: 109–131.

Diamandithis, G.Ch., 1984. Seasonal variations of primary productivity and biomass in Lake Vegoritis. Geotechnica 4: 93–107. (in Greek).

Diamandithis, G.Ch. & B. Z. Antonopoulos, 1984. Distribution of nitrogen, total phosphorus and some other qualitative variables in Lake Vegoritis. Geotechnica 6: 37–47. (in Greek).

Dirilgen, N., 1998. Effects of pH and chelator EDTA on Cr toxicity and accumulation in Lemna minor. Chemosphere 37: 771–783.

DVWK (Deutsche Verband für Wasserwirtschaft und Kulturbau e.V.), 1998. Hydrogeochemische Stoffsysteme. Heft 117, Teil II.

Eary, L. E. & D. Rai, 1987. Kinetics of Cr(III) oxidation by manganese dioxide. Environmental Science & Technology 21: 1187–1193.

Eikmann, Th. & A. Kloke, 1993. Nutzungs- und schutzbezogene Orientierungswerte für (Schad-) Stoffe in Boeden–Eikmann–Kloke Werte. 2. Überarbeitete und erweiterte Fassung. Nutzungs- und schutzbezogene. Orientierungswerte 3590: 1–26.

Faure, G., 1991. Inorganic Chemistry – A Comprehensive Textbook for Geology Students. Macmillan Publishing Company, New York.

Förstner, U. & G. T. W. Wittmann, 1981. Metal Pollution in the Aquatic Environment. Springer, Berlin, Heidelberg, New York.

Fotis, G., S. Kilikidis & A. Kamarianos, 1984. Study of the pollution and productivity of Lake Vegoritis. Geotechnica 3: 74–79. (in Greek).

Fytianos, K., S. Bovolenta & H. Muntau, 1994. Assessment of metal mobility from sediments of lake Vegoritis. In Varnavas, S. P. (ed.), Environmental Contamination 6th International Conference, Delphi, Edinburgh, 343 pp.

Fytianos, K. & B. Tsaniklidi, 1998. Leachability of heavy metals in Greek fly ash from coal combustion. Environment International 24: 477–486.

Gerouki, F., A. H. Foskolos, M. Dimitroula & E. Vasileiadis, 1997. Environmental impacts from the trace metals of fly ash coming from the burning of lignite in the electric stations of the greater area of Ptolemais – first results. Technical time reports, lignite and other solid fuels of our country: present status and potentials (2nd part), 6: 128–136.

Hem, J. D., 1985. Study and interpretation of the chemical characteristics of natural waters. US Geological Survey Water Supply Paper 1473, 2nd edn.

Henkin, R. I., 1984. Zink. In Merian, E. (ed.), Metalle in der Umwelt. Verlag Chemie, Weinheim: 597–630.

Horn, M. K. & J. A. S. Adams, 1966. Computer-derived geochemical balance and element abundances. Geochimica et Cosmochimica Acta 30: 279–298.

IARC (International Agency for Research on Cancer), 1987. Monographs on the evaluation of carcinogenic risks of chemicals to humans. Supplement F. Overall Evaluation of Carcinogenicity. World Health Organization, Lyon, France: 29–57.

Kagey, B. T. & B. G. Wixson, 1983. Health implications of coal development. In Thornton, I. (ed.), Applied Environmental Geochemistry. Academic Press, London: 463–480.

Katsanos, A. A., N. Panayotakis, M. Tzoumezi, E. Papadopoulou-Mourkidou & G. A. Mourkides, 1987. Elemental analysis of water and sediments by external beam PIXE Part2. Industrial zone of ptolemais, Greece. Chemistry and Ecology 3: 75–100.

Katz, S. A. & H. Salem, 1994. The Biological and Environmental Chemistry of Chromium. VCH Publishers Inc., New York.

Luh, M.-D., R. A. Baker & D. E. Henley, 1973. Arsenic analysis and toxicity – a review. The Science of the Total Environment 2: 1–12.

Maltby, E., 1992. Soil and wetland functions. In Gerakis, P. A. (ed.), Conservation and Management of Greek Wetlands. The IUCN Wetlands Programme: 9–60.

Masscheleyn, P. H., J. H. Pardue, R. D. DeLanue & J. W. H. Patrick, 1992. Chromium redox chemistry in a lower Mississippi Valley bottomland, hardwood wetland. Environmental Science & Technology 26: 1217–1226.

Moore, J. N., W. H. Ficklin & C. Johns, 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environmental Science & Technology 22: 432–437.

Morton, W. E. & D. A. Dunnette, 1994. Health effects of environmental arsenic. In Nriagu, J. O. (ed.), Arsenic in the Environment, Part II. Human Health and Ecosystem Effects. Wiley & Sons Inc., New York: 17–34.

Nicholas, D. R., S. Ramamoorthy, V. Palace, S. Spring, J. N. Moore & F. Rosenzweig, 2003. Biogeochemical transformations of arsenic in circumneutral freshwater sediments. Bioremediation 14: 123–137.

Nikolaidis, N. P., Th. Koussouris, G. Fotis & E. Papachristou, 1985. Trophic status assessment of Lake Vegoritida, Greece. ISEM Journal 7: 11–25.

Nikolaidis, N. P., G. M. Dobbs, J. Chen & J. A. Lackovic, 2004. Arsenic mobility in contaminated lake sediments. Environmental Pollution 129: 479–487.

Papakonstantinou, A., I. Meladiotis & C. Demiris, 1989. Karsthydrologische Untersuchungen in den südoestlichen Randbereichen des Amyndeon-Braunkohlen-beckens, Griechenland. Braunkohle 41: 44–50.

Pavlides, S. B. & D. Moundrakis, 1987. Extensional tectonics of northwestern Macedonia, Greece, since the late Miocene. Journal of Structural Geology 9: 385–392.

Radakovitch, O., 1995. Étude du transfert et du dépôt du matériel particulaire par le ^{210}Po et le ^{210}Pb. Application aux marges continentales du Golfe de Gascogne (NE Atlantique) et du Golfe du Lion (NW Méditerranée). Ph.D. Thesis, University of Perpignan.

Salbu, B. & E. Steiness, 1995. Trace Elements in Natural Waters. CRC Press, Boca Raton, Ann Arbor, London, Tokyo.

Sakellariou, D., G. Rousakis, Ch. Kranis, E. Kamberi, P. Georgiou & N. Skoulikidis, 2001. Neotectonic movements and water level fluctuations of Lake Vegoritis during the Upper Quaternary. Bulletin of the Greek Geological Society Greece XXXIV: 207–216. (in Greek).

Salomons, W. & U. Förstner, 1984. Metals in the Hydrosphere. Springer, Berlin, Heidelberg, New York, Tokio.

Samara, K., 2005. Chemical mass balance source apportionment of TSP in a lignite-burning area of Western Macedonia, Greece. Atmospheric Environment 39: 6430–6443.

Sanchez-Cabesa, J. A., P. Masque & I. Ani-Ragolta, 1998. ^{210}Pb and ^{210}Po analysis in sediments and soils by microwave acid digestion. Journal of Radioactivity and Nuclear Chemistry 227: 19–22.

Shanker, A. K., C. Cervantes, H. Loza-Tevera & S. Avudainayagam, 2005. Chromium toxicity in plants. Envitonmental International 31: 739–753.

Skoulikidis, N., 2001a. Environmental state of the bottom of Vegoritis lake, Northern Greece. In Skoulikidis, N., G. Rousakis, D. Sakellariou & P. Georgiou (eds), Investigation of the Morphological and Geophysical Structure and Environmental State of the Bottom of Vegoritis Lake, Northern Greece. Final Report, HCMR.

Skoulikidis, N., 2001b. Levels and possible origin of heavy metals in the sediments of Lake Vegoritis. Bulletin of the Greek Geological Society XXXIV: 1123–1130. (in Greek).

SRC (Syracuse Research Corporation), 1993. Toxicological profile for chromium. U.S. Dept. Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Contract No. 205–88–0608.

Stamos, A., 1996. Lake Vegoritis: Basic hydrogeologic – hydrologic characteristics of the lake and the adjacent area. Institute of Geological & Mineral Research, Kozani, Greece (in Greek – unpublished report).

State of Connecticut Regulation, 1996. Remediation standard. State of Connecticut. Department of Environmental Protection.

Ure, A. M., & M. L. Berrow, 1982. The chemical constituents of soils. In Bowen, H. J. M. (ed.), Environmental

Chemistry, Vol. 2. R. Soc. Chem., Burlington House, London: 94–202

VROM, 1988. Niederländische Liste: Testtabelle für die Beurteilung verschiedener Stoffe im Boden für die Nutzungsformen Wohngebiete.

Yamauchi, H. & B. A. Fowler, 1994. Toxicity and metabolism of inorganic and methylated arsenicals. In Nriagu, J. O. (ed.), Arsenic in the Environment, Part II: Human Health and Ecosystem Effects. Wiley & Sons Inc., New York: 35–43.

Wedepohl, K. H., 1978. Handbook of Geochemistry. Springer, New York.

Zayed, A. M. & N. Terry, 2003. Chromium in the environment: factors affecting biological remediation. Plant and Soil 249: 139–156.

Zevenbergen, C. S., J. Bradley, L. P. Van Reeuwijk, A. K. Shyam, O. Hjelmar & R. N. J. Comans, 1999. Clay formation and metal fixation during weathering of fly ash. Environmental Science & Technology 33: 3405–3409.