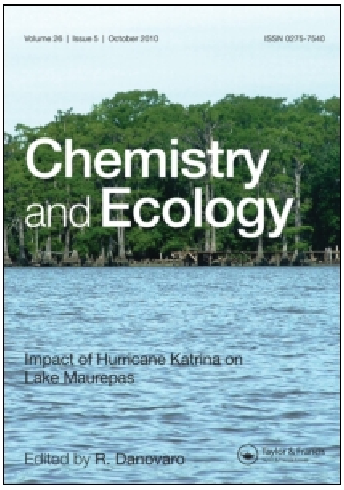

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ELEMENTAL ANALYSIS OF WATER AND SEDIMENTS BY EXTERNAL BEAM PIXE PART 4. ALIAKMON RIVER, GREECE†

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The Aliakmon River originates in the North Western part of Greece, traverses the Western part of Macedonia, and discharges into the Thermaikos Bay in the North Aegean Sea. Proton induced X-ray emission (PIXE) method with external beam was used for the determination of the metallic elements in the waters and sediments of the Aliakmon River. The pH, dissolved oxygen, conductivity, and total phosphate and nitrate concentrations were also monitored in the water samples. Data collected for a 20-month period indicate that the Aliakmon River can be still considered as an unpolluted river.

KEY WORDS Proton induced X-ray emission, trace elements, water pollution, sediment, Aliakmon River, Greece

INTRODUCTION

The Aliakmon River is the longest river of Greece with a total length approximating of 310 km. It originates from the North West part of Macedonia, Greece and after traversing mountainous terrain, agricultural plains, and urban areas, discharges into the Thermaikos Bay in the North Aegean Sea (Figure 1).

The population of the natural water bodies of Northern Greece has been studied and monitored for the last 10 years (Mourkides *et al.*, 1978, 1983, Papadopoulou-Mourkidou *et al.*, 1986). Research on the water quality of the Aliakmon River has been conducted for a 20-month period from September, 1982 to April 1984. This study is of major importance for Greece since for the first time background information on this river water quality has been obtained and its different pollution sources have been tentatively identified.

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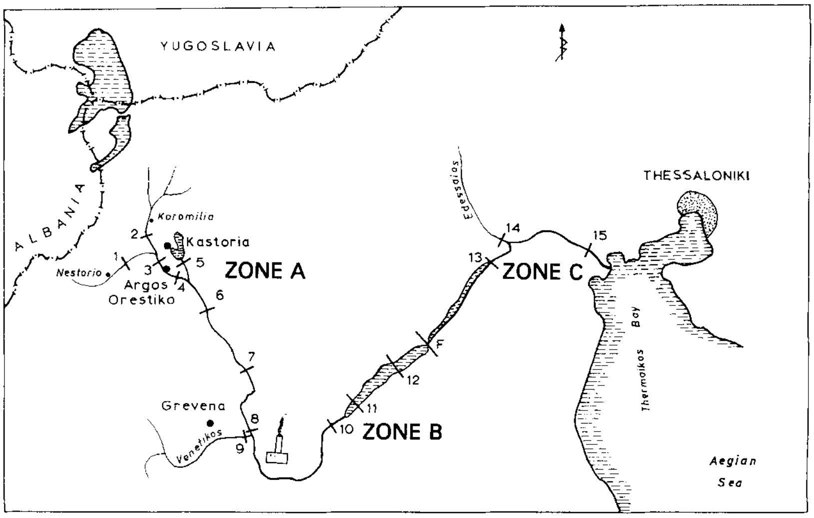

Figure 1 Geographical area transversed by Aliakmon River.

EXPERIMENTAL

Site Description

To assist the discussion, the Aliakmon River has been divided into three sections, A, B, and C, respectively. There are two main tributaries to the Aliakmon River; the one called Venetikos discharges into section A, while the other, Edessaios, discharges to section C. Fifteen water sampling sites (SS) have been selected along the course of the Aliakmon River, its tributaries, and the other water bodies discharging into this river (Figure 1).

Section A: This section is a stretch of 200 km and the sampling sites (SS) 1 through 10 are located on this section. The river originates in the form of two streams which collect the runoff and spring waters from two separate areas of an altitude of 1000 m and located, respectively, close to two villages called Nestorio (1200 people) and Koromilia (350 people). The SS 1 and 2 are located each on one of these streams, respectively (Figure 1). These two streams join to give rise to the Aliakmon river. In the area before the river enters the small town of Argos-Orestico (6000 people), the SS 3 is located, while SS 4 is located three km downstream from Argos-Orestico. The SS 5 is located on a canal which brings the overflow waters from the Orestias Lake (Kastorias Lake) into the Aliakmon River. The SS 6 is located on the Aliakmon River and 33 km downstream from SS 4. Further south from SS 6 are located SS 7, 8 and 10. Near SS 8 is the town of Grevena with 8000 people. The SS 9 is located on the tributary Venetikos close to its discharge point into the Aliakmon River, 0.5 km south from SS 8. The river basin in section A includes mostly mountainous areas with an altitude of 600–800 m. A chromium mine is located in the loop (Figure 1) between the SS 8, 9 and 10. Within this section of the river basin small villages are scattered, with a total population of 12,000 people. The land is used mainly for the cultivation of cereals (15,000 ha) and a population of 6500 cows and 13,000 sheep graze the area.

Section B. This section is a stretch of 68 km and includes SS 11, 12, and 13. It flows in a south to north direction and from SS 10 the river bed becomes very wide, with a maximum width of approximately 1200 m. At the end of this wide part (30 km length) of the river there is a dam (F) and some fish farming activities exist in this area, producing 80 tons of fish per year. The altitude of this area is 350–450 m. The rest of this section of the river traverses a woody mountainous area with small scattered villages with a total of 12,000 people. The land (6000 ha) is also used for cereal cultivation and 2000 cows and 50,000 sheep graze the land.

Section C. From SS 13 and up to the discharge point of the Aliakmon River into the Thermaikos Bay in the Aegean Sea, a section of 42 km length, the river traverses an agricultural area and its water is used for irrigation of the low land of Thessaloniki plain. The SS 15 is located close to the river discharge point while SS 14 is located on a tributary named Edessaios (Figure 1). This tributary drains an area of intensive agriculture with fruit trees and vegetable crops, (5000 ha). The population of the area amounts to 30,000 people; cows (15,000) and sheep (250,000) graze the area. Fish production of 60 tons per year is reported. The river stretch from the dam (F) and up to the SS 13 traverses an area of 400–800 m altitude while the rest of the section C traverses a low plain with an altitude below 100 m.

The Aliakmon river originates from two areas differing in geology. One is made from sandstones and other conglomerates (Koromilia) and the other (Nestorio) from limnological deposits, sands, and clays. The geological composition of the latter area persists up to SS 7 while in the area of SS 8, 9, 10 ofiolites predominate and later on at SS 10 to 12 the area is again made from limnological deposits, clays and sands. The section B of the Aliakmon River traverses areas underlain by gneisses, amphibolites, schists and ofiolites while the last section, Section C, traverses areas made of limnological deposits, clays and sandstones.

MATERIALS AND METHODS

Water samples were collected from the middle of the river bed, or the tributaries and other water bodies discharging to the Aliakmon River, and were transported to the laboratory in an insulated ice chest filled with crushed ice. The proton induced x-ray emission (PIXE) method with external beam was used for the elemental analysis of all samples (Mourkides, *et al.*, 1983). Samples of the river sediment were collected from four SS located on the sections B and C. The sediment core samples were taken with the Phleger corer (Kahlsico International), sectioned and analyzed by the PIXE method, as previously reported (Katsanos *et al.*, 1987). In addition, the core layers were also subjected to particle size analysis by the pipette method (Black, *et al.*, 1965). The minimum detection limit (MDL) for all the metallic elements was 0.3 ppb (μg/kg, dry) for the water samples (soluble materials), 0.1 ppb (related to the water volume) for the particulate-associated forms (filtration cakes), and 1–5 ppm (dry wt) for the sediments. The relative standard deviations were 10% for those elements present at least 10 times above the MDL levels and 20–50% for those with concentrations close to the MDL levels.

Measurements *in situ* and in the laboratory were performed as previously reported (Papadopoulou-Mourkidou *et al.*, 1986). The flow of the Aliakmon River was regularly monitored by personnel from a unit of the Greek Electricity Power Supply Co. located at the Ptolemais City, Greece.

RESULTS AND DISCUSSION

The data showing the ranges of recorded pH values, dissolved oxygen expressed as % saturation, conductivity measured as mmho/cm, nitrates as mg N l^{-1}, and total phosphates as μg of total P l^{-1}, are presented for a 20-month period and for each of the sampling sites in Table 1.

The pH values ranged from 7.0 to 8.8 with the exception of SS 12 where pH values up to 9.3 were recorded. The dissolved oxygen levels ranged mostly from 80 to 125%. Supersaturation in oxygen was recorded in a number of SS where % saturation up to 140% was recorded. However, very low levels of oxygen saturation, as low as 40%, were recorded but during the summer at SS 14 located on the tributary Edessaios. The conductivity ranged mainly between 0.23 to 0.48 mmho/cm. The lowest values of conductivity (0.16 to 0.33 mmho/cm) were recorded at SS 2 and the highest (0.36 to 0.65 mmho/cm) at SS 14.

The nitrate nitrogen concentrations were rather low, ranging from 0.1 to 1.2 mg l^{-1} except for SS 14 and 15 where considerably higher levels ranging from 0.5 to 2.5 and 0.4 to 2.2 mg l^{-1}, respectively, were measured. The total phosphate concentrations were generally low in the upper part of the river (Sections A and B). Low levels, as low as 5 or 10 μg l^{-1} were found at SS 1, 2, 6, and 12. In the

Table 1 Quality of the waters of the Aliakmon River

SS	*pH*	*Oxygen saturation K%*	*Conductivity mmho/cm*	*NO_3-N mg l^{-1}*	*P-total μg l^{-1}*
1	8.2–8.4	87–107	0.31–0.48	0.3–1.2	8–150
2	8.0–8.6	80–108	0.16–0.33	0.3–1.2	5–200
3	7.8–8.2	90–900	—	0.3–0.6	10–230
4	7.0–8.4	87–140	0.28–0.43	0.3–0.6	40–300
5	7.4–8.5	88–100	0.23–0.50	—	—
6	8.1–8.7	98–125	0.29–0.42	0.4–0.7	8–90
7	7.9–8.8	84–107	0.27–0.47	0.3–0.6	50–250
8	8.3–8.8	88–115	0.28–0.48	0.4–0.8	32–220
9	7.8–8.7	89–110	0.23–0.45	0.1–0.6	34–100
10	8.3–8.8	89–106	0.23–0.42	0.3–1.2	10–100
11	8.3–8.8	88–95	0.28–0.45	0.3–0.8	15–200
12	7.9–9.3	83–116	0.28–0.43	0.1–1.0	5–350
13	7.5–8.3	87–120	0.32–0.41	0.1–1.2	30–500
14	7.2–8.4	40–140	0.36–0.65	0.5–2.5	80–700
15	7.6–8.3	90–108	0.36–0.47	0.4–2.2	55–650

lower section of the river (Section C) the concentrations of the total phosphates were much higher, ranging from 0.03 to 0.70 mg l^{-1}, only slightly exceeding the concentration of 0.5 mg l^{-1} which is considered as the lower limit for river waters to pose a risk of eutrophication. Lower values of pH, conductivity, and total phosphate concentrations were recorded during the winter time, while higher values were found during the summer. However, for the nitrate and the dissolved oxygen contents, the reverse was true.

The concentrations of metallic elements found at the different sampling sites are presented in Tables 2 and 3, for the particulate-associated and the water soluble constituents, respectively. In these Tables, the mean and respective standard deviation for the 20-month sampling period are given for each element and for each sampling site the concentration. Table 2 also shows the mean and standard deviation values of the river flow (FR) measured at some of the sampling sites during the same period. Generally, the standard deviations of the

Table 2 Concentrations[a] of the particulate-associated elements in the waters of the Aliakmon River

SS		*FR*[b]	*Ca*	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*	*Rb*
1	x[c]	4.93	345	15.2	0.8	2.4	4.8	281	2.2	0.4	2.6	0.8	ND[f]
	s[d]	4.67	180	8.2	0.8	1.1	3.6	206	1.6	0.5	1.3	1.3	ND
2	x	4.77	98	14.4	1.0	1.2	15.0	221	0.4	0.6	2.6	0.2	ND
	s	5.06	61	9.9	0.2	0.4	20.7	162	0.5	0.5	0.9	0.4	ND
3	x	—	295	31.5	2.5	3.0	10.0	494	2.0	0.6	2.5	0.6	ND
	s	—	189	30.4	2.1	2.8	8.5	386	1.4	0.6	2.1	0.6	ND
4	x	15.92	480	40.0	2.0	3.8	14.0	644	2.1	0.7	3.3	0.9	ND
	s	14.10	512	50.0	2.2	5.0	18.7	763	2.4	0.9	2.5	1.4	ND
5	x	—	68	2.2	0.5	1.5	8.5	59	ND	0.2	1.8	ND	ND
	s	—	42	2.8	0.5	1.4	8.2	43	ND	0.40	1.2	ND	ND
6	x	—	496	41.4	2.8	4.8	14.6	650	2.6	0.6	3.6	ND	ND
	s	—	290	32.4	2.4	4.7	11.9	481	2.5	0.5	1.5	ND	ND
7	x	31.69	455	41.9	3.0	4.0	13.7	721	2.4	0.7	3.3	1.2	ND
	s	26.56	564	47.9	3.7	4.5	14.9	815	2.7	0.7	2.0	1.1	ND
8	x	—	920	65.5	4.0	9.0	26.2	1371	8.5	1.3	4.8	1.3	2.7
	s	—	735	65.0	5.1	7.0	23.4	1250	6.0	1.0	2.9	1.4	3.2
9	x	27.03	561	85.0	4.3	12.7	30.7	1839	13	2.0	5.5	1.5	2.5
	s	19.24	486	88.0	4.7	11.5	28.8	1854	12	2.4	2.9	1.5	3.8
10	x	60.00	515	27.0	1.7	27.0	12.3	715	9.0	1.3	4.3	ND	0.3
	s	58.28	516	9.0	1.2	23.1	6.8	358	6.9	1.5	1.2	ND	0.6
11	x	—	479	28.0	1.6	7.7	10.9	635	6.6	0.6	3.6	1.1	ND
	s	—	762	31.3	2.1	3.4	11.7	742	8.0	0.5	1.3	1.1	ND
12	x	—	350	14.7	0.9	5.9	7.6	359	4.3	1.0	2.7	0.7	ND
	s	—	463	27.1	1.2	9.9	11.0	768	9.3	2.3	1.7	0.9	ND
13	x	—	375	36	4.2	3.5	11.0	399	3.3	0.5	2.7	1.1	ND
	s	—	428	51	9.4	3.6	10.7	466	3.9	0.7	1.5	1.3	ND
14	x	—	612	39	1.7	12.3	24.0	911	11.5	1.2	5.5	2.8	ND
	s	—	759	39	2.3	17.7	24.9	1008	21.4	0.4	2.5	2.7	ND
15	x	—	356	21.4	1.6	4.1	12.4	416	3.0	1.7	2.7	1.4	0.5
	s	—	184	12.8	1.5	2.9	6.7	277	1.9	3.1	1.0	1.3	0.7

[a] All concentrations are expressed as $\mu g\, l^{-1}$ (ppb) on a dry weight basis.
[b] FR denotes flow rate expressed as m^3 per second.
[c] x denotes concentration mean values measured over a 20-month period.
[d] s denotes concentration standard deviation values during a 20-month period.
[e] —denotes not measured.
[f] ND denotes not detectable.

Table 3 Concentrations[a] of the water soluble elements in the waters of the Aliakmon River

		TDS	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Pb	As
1	x	358	69.40	3.0	1.0	11.0	23.4	3.4	2.4	16.6	289	2.8	ND
	s	56	9.24	4.5	1.7	8.5	9.9	0.9	1.7	9.3	52	1.8	ND
2	x	221	37.00	2.4	0.6	6.6	75.6	1.4	2.2	18.6	58	2.8	ND
	s	88	15.57	2.5	0.9	3.9	35.4	0.6	1.1	16.1	11	1.3	ND
3	x	263	50	3.0	1.0	8.5	30.5	2.0	2.5	17.5	168	2.5	ND
	s	18	2	2.8	1.3	3.5	12.0	0.2	0.7	13.4	32	0.7	ND
4	x	309	57.78	2.8	6.2	22.8	48.6	4.2	3.6	22.9	196	3.4	ND
	s	59	8.00	3.3	8.5	27.3	41.3	2.6	2.2	15.1	63	2.7	ND
5	x	355	52.67	4.8	12.3	22.3	68.2	2.7	3.2	20.2	120	2.5	3.3
	s	128	13.29	5.8	15.9	16.4	43.3	1.2	1.7	5.2	26	2.0	0.8
6	x	308	55.60	8.6	1.8	7.8	28.0	2.2	3.0	15.6	194	2.6	1.0
	s	24	8.41	4.5	2.7	3.0	11.4	0.8	1.9	3.8	48	0.6	0.7
7	x	298	56.89	7.6	2.3	21.3	55.6	3.8	3.0	17.2	190	2.4	0.8
	s	28	11.83	5.9	3.2	40.8	35.4	2.5	0.9	10.6	39	1.7	0.8
8	x	309	47.67	7.8	5.2	7.3	30.7	4.0	2.5	13.8	182	1.8	1.0
	s	33	15.46	5.9	6.3	3.1	15.3	0.9	0.8	7.1	33	1.5	0.6
9	x	284	29.33	ND[b]	6.5	5.7	53.7	4.5	2.7	15.0	115	1.8	0.8
	s	37	4.46	ND	5.9	3.6	36.7	1.9	0.8	4.5	24	1.5	0.4
10	x	304	36.00	5.7	3.3	2.7	31.3	4.3	2.3	14.3	138	3.0	0.7
	s	18	10.39	5.1	1.5	0.6	4.5	0.6	0.6	4.5	12	1.7	0.6
11	x	328	43.22	7.4	4.3	8.6	74.3	7.7	3.9	26.3	102	4.2	0.9
	s	66	17.43	4.3	3.5	5.5	59.7	4.1	1.6	22.0	48	2.4	0.6
12	x	298	40.11	8.6	4.3	3.3	42.3	5.2	3.8	44.9	150	2.7	0.8
	s	53	15.18	3.2	3.7	2.7	51.2	2.5	1.6	66.3	36	1.4	0.8
13	x	334	45.00	5.4	3.5	4.6	85.2	5.0	4.4	61.0	154	2.7	1.0
	s	63	9.84	4.6	4.5	2.4	115.9	2.3	1.8	84.3	30	1.9	0.8
14	x	400	62.83	6.8	6.0	19.0	45.2	5.7	9.5	108.8	161	4.5	4.2
	s	52	11.57	8.6	4.0	30.5	47.6	3.6	15.1	127.6	20	2.7	1.3
15	x	333	51.7	8.7	4.7	6.7	51.4	5.5	3.9	56.5	152	3.9	2.0
	s	37	11.0	4.7	3.5	2.2	50.1	3.4	2.1	75.9	23	3.0	1.2

[a] Concentrations of all the elements are expressed as $\mu g\, l^{-1}$ (ppb) except for TDS and Ca which are expressed as $mg\, l^{-1}$ (ppm).
[b] ND denotes not detectable.

reported metal concentration means are relatively high, and in many cases, especially for the particulate-associated forms of metals, they are even higher than the respective mean values indicating a high seasonal variation in the particulate-associated metallic elements in the waters of this river. However, the concentrations of the particulate-associated forms of zinc (Table 2) and the soluble forms of nickel and strontium (Table 3) exhibit relatively smaller standard deviations at all the sampling sites. The particulate-associated elements generally peak during July with a secondary peak occurring during January, while their soluble forms peak only during January (data not shown).

The two streams giving rise to the Aliakmon River (Figure 1) have similar flow rates (Table 2); however, the composition of their waters, in so far as the metal content is concerned, is quite different (Tables 2 and 3, SS 1 and 2). The concentrations of the particulate-associated forms (Table 2) of calcium, chromium, iron, nickel and lead are substantially higher at SS 1 than at SS 2 and only manganese is present at higher concentrations at SS 2 than SS 1. Also the patterns of the correlation matrices among the particulate-associated elements are quite different between these two streams (Tables 4 and 5). At SS 1 here is good

Table 4 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 1

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.86	1.00								
V	−0.46	−0.46	1.00							
Cr	0.81	0.92	−0.16	1.00						
Mn	0.85	0.97	−0.27	0.95	1.00					
Fe	0.77	0.98	−0.31	0.95	0.98	1.00				
Ni	0.56	0.88	−0.15	0.88	0.91	0.96	1.00			
Cu	0.40	0.26	−0.87	0.08	0.05	0.09	−0.11	1.00		
Zn	−0.51	−0.49	0.13	−0.69	−0.44	−0.48	−0.41	−0.41	1.00	
Pb	0.94	0.66	−0.50	0.57	0.63	0.53	0.26	0.49	−0.34	1.00

correlation among chromium, manganese, iron, nickel, calcium and titanium. This correlation also extends to the downstream sites 4, 6, and 7. At SS 2 (Table 5), however, only the correlation coefficients of titanium with nickel and iron, and calcium with zinc are high. Also the correlation coefficient of calcium with manganese is negative and there is no correlation between iron with managese (Table 5) at SS 2. At SS 1, the concentrations of the total dissolved solids (TDS) and the soluble forms of calcium are 358.0 ± 56.0 and $69.4 \pm 9.2\,mg\,l^{-1}$, respectively, while at SS 2 the respective concentrations are 221.0 ± 88.0 and $37.0 \pm 15.6\,mg\,l^{-1}$, (Table 3). These latter values are characteristic of areas with dolomite minerals (Drever, 1982). The concentrations of the soluble forms of strontium and manganese are much higher at SS 1 than at SS 2. In contrast, the water soluble forms of iron are present at higher concentrations at SS 2 than at SS 1, although the sum of the concentrations of the particulate-associated and the water soluble forms of iron is approximately the same at both sampling sites (Tables 2 and 3).

The correlation matrices for the water soluble forms of the different elements (data not shown in table) present at SS 1 and 2, respectively, also exhibit different patterns. At SS 1, correlation coefficients >0.90 are found only between strontium and calcium ($r = 0.93$), iron and manganese ($r = 0.96$), and zinc and copper ($r = 0.91$). However, at SS 2 correlations between these elements are very

Table 5 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 2

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	−0.20	1.00								
V	0.00	0.00	0.00							
Cr	−0.07	0.26	0.00	1.00						
Mn	−0.66	0.16	0.00	−0.19	1.00					
Fe	−0.27	0.99	0.00	0.35	0.21	1.00				
Ni	−0.04	0.88	0.00	0.61	−0.20	0.89	1.00			
Cu	0.69	0.50	0.00	0.41	−0.49	0.47	0.67	1.00		
Zn	0.91	−0.06	0.00	−0.37	−0.38	−0.15	−0.10	0.61	1.00	
Pb	−0.07	0.26	0.00	1.00	−0.19	0.35	0.61	0.41	−0.38	1.00

low while strontium is correlated with TDS ($r = 0.93$), nickel with vanadium ($r = 0.95$), and lead with zinc ($r = 0.92$).

Since the water flow rates of the two streams giving rise to the Aliakmon river are approximately the same, it was expected that the levels of the different elements at the downstream SS 3 (Figure 1) would be similar to the mean of their respective concentrations at SS 1 and 2. Any subsequent increase in the content of elements at SS 4 would indicate a possible enrichment in metals contributed by the municipal wastes of the small town of Argos Orestiko. Indeed, as shown in the Tables 2 and 3, at SS 3 there is no source of elements other than what is carried by the waters of the two original streams. At SS 4 the concentrations of all the measured elements have been slightly increased compared to their respective concentrations at SS 3. The concentration profiles of all the metallic elements in both the particulate-associated and the water soluble forms present in the waters of SS 3 will be considered as background levels of metallic elements in the waters of the Aliakmon River. Any changes in these levels during passage of this river can be considered as being caused by some form of contamination or pollution.

In Table 6 the correlation matrix of the particulate-associated elements at SS 4 is shown. The correlation coefficients between the different elements are high except for that between zinc and lead. However, the correlation coefficients between all the water soluble forms of the elements (data not shown in Table) are generally poor (<0.80); correlation coefficients of the level of 0.80 are only found between zinc and lead with TDS, lead with nickel, and copper with zinc.

The metal content of the waters at SS 5 provides an indication of the water quality of the Orestias Lake and a measure of the load of metallic elements carried by its overflow waters into the Aliakmon River. At SS 5 the concentrations of the particulate-associated elements are much lower than their values at SS 4 (Table 2). However, water soluble forms of vanadium, chromium, iron and arsenic are present at higher concentrations at SS 5 than at SS 4 while other water soluble elements are present at the SS 5 at approximately the same levels as at SS 4. In general the correlation coefficients between most of the particulate-associated elements present at SS 5 are relatively small (Table 7). The correlation coefficients among most of the water soluble elements are also small (<0.80) (data not shown in Table). Correlation coefficients over 0.90 are found only between manganese and strontium with TDS and over 0.80 between manganese with nickel and strontium.

Table 6 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 4

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.95	1.00								
V	0.91	0.97	1.00							
Cr	0.98	0.97	0.94	1.00						
Mn	0.95	1.00	0.97	0.97	1.00					
Fe	0.91	0.99	0.95	0.92	0.98	1.00				
Ni	0.97	0.93	0.88	0.94	0.94	0.92	1.00			
Cu	0.76	0.87	0.90	0.76	0.86	0.89	0.74	1.00		
Zn	0.60	0.75	0.74	0.65	0.74	0.76	0.51	0.81	1.00	
Pb	0.45	0.69	0.61	0.51	0.68	0.76	0.53	0.71	0.67	1.00

Table 7 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 5

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*
Ca	1.00								
Ti	0.79	1.00							
V	−0.22	−0.07	1.00						
Cr	−0.12	0.29	0.66	1.00					
Mn	0.67	0.76	−0.55	−0.22	1.00				
Fe	0.96	0.86	−0.32	−0.04	0.71	1.00			
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Cu	−0.31	0.15	0.45	0.89	−0.09	−0.22	0.00	1.00	
Zn	0.28	0.32	0.16	0.06	−0.13	0.37	0.00	−0.35	1.00

The overall contribution of the municipal wastes from the town of Argos Orestiko and the Orestias Lake on the water quality of the Aliakmon River is demonstrated by the analytical results from SS 6. The concentrations of all the particulate-associated and some of the water soluble forms of elements have been increased at SS 6. The correlation coefficients between the particulate-associated elements are high except for those involving copper and zinc (Table 8), although the correlation coefficient between copper and zinc is high. The lack of correlation of copper and zinc with the other elements present at SS 6 is probably due to an incoming load from the lake Orestias which is enriched in these elements due to the discharge to this lake of municipal wastes from the town of Kastoria, a town of 30,000 people. Copper and zinc are generally considered of domestic origin (Forstner and Wittman, 1979). However, the correlation coefficient between the water soluble forms of copper and zinc is poor ($r = 0.59$) (data not shown in Table). Correlation coefficients >0.90 are not found while between TDS and iron, copper and zinc, vanadium and arsenic, chromium and nickel, and iron and strontium are at the level of 0.80. The correlation coefficient between strontium and iron is −0.94.

The concentrations of the particulated-associated forms of iron and lead and the soluble forms of manganese, iron, and nickel are increased at SS 7 compared to SS 6 (Tables 2 and 3). However, the pattern of the correlation matrix (Table 9) of the particulate-associated elements present at SS 7 is similar to that for the

Table 8 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 6

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*
Ca	1.00								
Ti	0.90	1.00							
V	0.81	0.95	1.00						
Cr	0.84	0.98	0.98	1.00					
Mn	0.92	1.00	0.94	0.97	1.00				
Fe	0.91	1.00	0.93	0.96	1.00	1.00			
Ni	0.82	0.93	0.94	0.98	0.92	0.92	1.00		
Cu	0.57	0.50	0.31	0.45	0.51	0.51	0.58	1.00	
Zn	0.52	0.51	0.39	0.52	0.50	0.51	0.67	0.96	1.00

Table 9 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 7

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.95	1.00								
V	0.95	0.92	1.00							
Cr	0.95	0.96	0.97	1.00						
Mn	0.97	0.99	0.94	0.97	1.00					
Fe	0.95	1.00	0.92	0.96	1.00	1.00				
Ni	0.99	0.98	0.96	0.97	0.99	0.98	1.00			
Cu	0.70	0.80	0.72	0.71	0.75	0.78	0.74	1.00		
Zn	0.55	0.75	0.65	0.69	0.71	0.75	0.67	0.77	1.00	
Pb	0.61	0.75	0.62	0.64	0.70	0.74	0.68	0.92	0.74	1.00

elements present at SS 6 (Table 8). The correlation coefficients between all the water soluble forms of elements present at SS 7 are very small (data not shown in Table). At SS 8 the concentrations of particulate-associated forms of the elements are further increased (Table 2) while water soluble forms of chromium are increased, concentrations of manganese and iron are decreased and that of other elements are almost unchanged (Table 3). Also the correlation coefficients involving nickel with the rest of the elements are changed at SS 8 (Table 10) compared to those between the elements at SS 7 (Table 9). These changes may be due to the domestic discharges into the river from the town of Grevena (Figure 1). Correlations among the water soluble elements are very poor (data not shown in Table) except for those involving TDS with calcium ($r = 0.94$) and strontium ($r = 0.89$), and between strontium and zinc ($r = -0.85$).

The SS 9 is located on the tributary Venetikos which appears to be richer in some of the metallic elements than the waters of the Aliakmon River at SS 8, upstream from the discharge point of this tributary (Figure 1). The concentrations of the water soluble forms of the elements calcium, manganese, and strontium (Table 3) and the particulate-associated forms of calcium (Table 2) are lower at SS 9 than at SS 8. Correlation coefficients among the concentrations of all particulate-associated elements present in the waters at SS 9 (Table 11) are

Table 10 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 8

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Rb*	*Pb*
Ca	1.00										
Ti	0.70	1.00									
V	0.68	0.96	1.00								
Cr	0.91	0.91	0.90	1.00							
Mn	0.79	0.96	0.98	0.97	1.00						
Fe	0.78	0.99	0.97	0.96	0.99	1.00					
Ni	0.88	0.41	0.45	0.75	0.60	0.54	1.00				
Cu	0.72	0.98	0.91	0.91	0.94	0.97	0.48	1.00			
Zn	0.48	0.78	0.69	0.63	0.69	0.73	0.19	0.84	1.00		
Rb	0.51	0.91	0.84	0.74	0.80	0.86	0.15	0.83	0.58	1.00	
Pb	0.08	0.58	0.60	0.36	0.52	0.53	−0.10	0.61	0.84	0.40	1.00

Table 11 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 9

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Rb*	*Pb*
Ca	1.00										
Ti	0.85	1.00									
V	0.88	0.95	1.00								
Cr	0.87	0.99	0.95	1.00							
Mn	0.91	0.99	0.97	0.99	1.00						
Fe	0.87	1.00	0.96	0.99	0.99	1.00					
Ni	0.88	0.99	0.97	0.99	1.00	1.00	1.00				
Cu	0.86	0.99	0.91	0.99	0.98	0.99	0.98	1.00			
Zn	0.84	0.92	0.88	0.93	0.90	0.91	0.90	0.91	1.00		
Rb	0.74	0.96	0.83	0.94	0.92	0.94	0.93	0.97	0.82	1.00	
Pb	0.70	0.74	0.59	0.77	0.71	0.73	0.70	0.81	0.87	0.75	1.00

relatively high. However, the correlation coefficients between concentrations of the water soluble elements (data not shown in Table) are small except for those involving nickel and calcium ($r = 0.98$) and nickel and chromium ($r = 0.93$).

At SS 10, concentrations of all the particulate-associated forms of most metallic elements are decreased while the concentration of chromium is almost 3 times higher than its concentration at SS 8 (Table 2). This increase can be associated with a chromium mine located in the area between SS 8 and 10. At SS 10, the concentrations of the water soluble forms of calcium, chromium, manganese, and strontium are decreased and there is only a slight increase in the concentration of lead. Also at this SS, the correlation coefficients among all particulate-associated elements are high (Table 12). The correlation coefficients involving zinc and rubidium are negative. Also the correlation coefficients among the water soluble elements are better at SS 10 in comparison with those among elements at other sampling sites (data not shown in Table). Correlation coefficients equal to 1.00 are found between the concentrations of the water soluble forms of nickel and copper and lead and −1.00 between arsenic and calcium.

In the lower and wider section B of the Aliakmon River (SS 11, 12, and 13) there is a progressive decrease in the concentrations of the particulate-associated forms of chromium, iron, nickel and copper (Table 2) and the soluble forms of

Table 12 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 10

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.83	1.00								
V	0.99	0.90	1.00							
Cr	0.84	1.00	0.90	1.00						
Mn	0.94	0.97	0.98	0.97	1.00					
Fe	0.91	0.99	0.95	0.99	1.00	1.00				
Ni	0.99	0.90	1.00	0.90	0.98	0.95	1.00			
Cu	0.90	0.99	0.94	0.99	0.99	1.00	0.94	1.00		
Zn	−0.99	−0.90	−1.00	−0.90	−0.98	−0.95	−1.00	−0.94	1.00	
Rb	−0.39	−0.83	−0.50	−0.83	−0.68	−0.74	−0.50	−0.76	0.50	1.00

Table 13 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 11

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.94	1.00								
V	0.73	0.75	1.00							
Cr	0.58	0.73	0.51	1.00						
Mn	0.95	0.99	0.71	0.68	1.00					
Fe	0.94	1.00	0.72	0.76	0.99	1.00				
Ni	0.92	0.97	0.64	0.79	0.97	0.98	1.00			
Cu	0.41	0.67	0.60	0.69	0.62	0.67	0.60	1.00		
Zn	0.42	0.54	0.51	0.90	0.49	0.56	0.59	0.57	1.00	
Pb	0.59	0.65	0.25	0.47	0.69	0.66	0.70	0.33	0.40	1.00

vanadium, manganese and nickel (Table 3) while concentrations of the particulate-associated forms of titanium and vanadium and the soluble forms of iron, copper, zinc, and strontium are slightly increased. At SS 11 the correlation coefficients between the particulate-associated elements are relatively small (Table 13) while correlation coefficients higher than 0.90 are found only between some elements. The correlation matrix are found only between some elements. The correlation matrix for the particulate-associated elements present at SS 12 indicates that correlation coefficients between all the pairs of elements are slightly increased and in some cases are relatively high (>0.96) (Table 14). However, at SS 13 those correlation coefficients are decreased except for those involving calcium and chromium, manganese, iron, and nickel, titanium and vanadium, chromium and manganese, iron, and nickel, manganese and iron and nickel, and iron and nickel (Table 15). Correlation coefficients between the concentrations of pairs of water soluble elements present at all the stations of the section B are very small. At SS 11 only strontium was correlated with calcium ($r = 0.93$), at SS 12 lead with iron ($r = 0.91$) and at SS 13 Strontium with calcium (0.90) and lead with chromium (0.91). This section is surrounded by mountains and obviously the run-off waters draining to the river dilute the metallic elements while there is a continuous non-point source of geological contamination.

Table 14 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 12

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.97	1.00								
V	0.62	0.71	1.00							
Cr	0.98	0.97	0.64	1.00						
Mn	1.00	0.97	0.64	0.99	1.00					
Fe	0.96	1.00	0.70	0.97	0.96	1.00				
Ni	0.96	0.99	0.67	0.98	0.96	1.00	1.00			
Cu	0.92	0.97	0.70	0.96	0.92	0.98	0.98	1.00		
Zn	0.46	0.51	0.56	0.50	0.48	0.50	0.54	0.53	1.00	
Pb	0.11	0.88	0.82	0.11	0.13	0.17	0.14	0.19	0.35	1.00

Table 15 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 13

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.36	1.00								
V	0.04	0.94	1.00							
Cr	0.96	0.45	0.13	1.00						
Mn	0.96	0.33	0.02	0.96	1.00					
Fe	0.97	0.33	−0.01	0.99	0.97	1.00				
Ni	0.99	0.38	0.05	0.98	0.97	0.99	1.00			
Cu	0.82	0.55	0.32	0.86	0.85	0.80	0.82	1.00		
Zn	0.56	0.62	0.39	0.74	0.65	0.68	0.66	0.58	1.00	
Pb	0.33	−0.19	−0.28	0.21	0.31	0.30	0.32	0.18	−0.10	1.00

The section C of Aliakmon River includes the final site (SS 15) located close to the river discharge to Thermaikos Bay and SS 14 located on the tributary Edessaios. At SS 14 the waters are richer in all the elements compared to their levels either upstream or downstream from the discharge point of the tributary Edessaios. Apparently the Aliakmon River is not significantly affected by the loads carried by the Edessaios so that concentrations of the different metallic elements at SS 15 are only slightly increased compared to their respective levels at SS 13 (Tables 2 and 3). At SS 14 there is good correlation among the particulate-associated forms of the elements calcium, chromium, titanium, vanadium, manganese, iron, and nickel and between lead and titanium and lead and zinc (Table 16). However, at SS 15 (Table 17) only the correlation coefficients between titanium and chromium, manganese, and iron and between manganese and iron are >0.90. For the water soluble elements at SS 14 correlation coefficients >0.90 are found between iron and manganese (0.97), manganese and copper (0.98), and iron and copper (0.99) while at SS 15 the correlation coefficients between all the elements are small (data not shown in Table).

The river flow rate is highly correlated ($r > 0.90$) only to chromium, both soluble and particulate forms, while it is slightly correlated to both forms of calcium ($r = 0.60$) and the particulate-associated form of zinc ($r = 0.60$).

Table 16 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 14

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Ca	1.00									
Ti	0.78	1.00								
V	0.92	0.90	1.00							
Cr	0.98	0.86	0.98	1.00						
Mn	0.94	0.95	0.97	0.97	1.00					
Fe	0.86	0.99	0.95	0.93	0.98	1.00				
Ni	0.99	0.82	0.96	1.00	0.95	0.90	1.00			
Cu	−0.19	0.45	0.07	−0.06	0.14	0.32	−0.13	1.00		
Zn	0.57	0.83	0.60	0.60	0.75	0.77	0.55	0.49	1.00	
Pb	0.62	0.94	0.74	0.69	0.83	0.88	0.64	0.57	0.95	1.00

Table 17 Correlation matrix for the particulate-associated elements in the waters of the Aliakmon River at the sampling site 15

	Ca	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Rb*	*Pb*
Ca	1.00										
Ti	0.84	1.00									
V	0.38	0.29	1.00								
Cr	0.70	0.91	0.49	1.00							
Mn	0.79	0.93	0.21	0.80	1.00						
Fe	0.74	0.98	0.20	0.88	0.93	1.00					
Ni	0.89	0.84	0.42	0.81	0.68	0.73	1.00				
Cu	0.07	−0.05	−0.34	−0.13	0.16	−0.08	−0.05	1.00			
Zn	0.20	0.36	0.59	0.49	0.33	0.35	0.31	−0.22	1.00		
Rb	0.44	0.77	0.08	0.83	0.70	0.80	0.61	−0.12	0.20	1.00	
Pb	0.71	0.76	0.23	0.68	0.66	0.69	0.82	0.05	0.01	0.70	1.00

The measured metal concentrations in the Aliakmon River are not considered toxic and they are at acceptable concentrations for potable waters as proposed by the World Health Organization, except for the concentration of chromium as it is found at SS 10.

Among the major metals present in the Aliakmon River, nickel, copper, zinc, and titanium are present mostly in the water soluble forms and iron, manganese, chromium and strontium in particulate-associated forms. Strontium is not detectable in particulate-associated forms while titanium is not detectable in water soluble forms. The ratios of water soluble to particulate-associated forms for each element and at each sampling site are shown in Table 18.

The ratio between particulate-associated concentrations of iron over that for manganese at the different sampling sites is presented in Table 19. This ratio is close to 50 at all the stations on the Aliakmon River while at SS 1 it is equal to 59

Table 18 Ratios of the concentrations of soluble to particulate-associated forms of metallic elements at the different sampling sites

SS	*Fe*	*Mn*	*Cr*	*Ni*	*Cu*	*Zn*
1	0.08	2.29	0.42	1.55	6.0	6.4
2	0.34	0.44	0.50	3.50	3.7	7.2
3	—[a]	—	—	—	—	—
4	0.07	1.63	1.63	2.00	5.1	6.9
5	1.15	2.62	8.20	—	18.8	11.2
6	0.04	0.53	0.37	0.85	5.0	4.3
7	0.08	1.55	0.48	1.60	4.3	5.2
8	0.02	0.28	0.58	0.47	1.9	2.9
9	0.03	0.19	0.51	0.35	1.3	11.1
10	0.04	0.22	0.12	0.48	1.8	3.3
11	0.12	0.79	0.56	1.17	6.5	7.3
12	0.10	0.40	0.73	1.13	3.5	16.6
13	0.21	0.42	1.00	1.67	8.8	22.6
14	0.05	0.79	0.49	0.50	7.9	19.8
15	0.12	0.54	1.15	1.83	2.3	20.9

[a]— Denotes not calculated.

Table 19 Ratios of the concentrations of the particulate-associated forms of iron to the respective concentrations of manganese at the different sampling sites

SS	*Fe/Mn*	*SS*	*Fe/Mn*	*SS*	*Fe/Mn*
1	59	6	45	11	58
2	15	7	53	12	60
3	53	8	52	13	36
4	46	9	60	14	38
5	7	10	58	15	34

and SS 2 15, thus differentiating the two streams which give rise to the Aliakmon River. However, a ratio of iron/manganese close to 50 is maintained at stations 3, 4 and up to SS 12, while at the subsequent stations it is gradually decreased to 34 (SS 15). At SS 5 the ratio is equal to 7, distinguishing the waters of the Orestias lake from the waters of the Aliakmon River. It is thought that ferrogmanganese concretions originating from SS 1 move down the Aliakmon River and that the composition of the river waters is altered as the river traverses the Thessaloniki plain. The iron content of these concretions rises to 97–98%.

River sediment core samples were collected from SS 10, 11, 12 and 15. These core samples were sectioned at two to three depths and each section, after being separated into two fractions, a silt (particle size 2–60 μm) and a clay (particle size <2 μm) fraction, by particle size analysis and were analyzed by the PIXE method. The results are presented in Tables 20 and 21. Table 20 shows the metal

Table 20 Elemental analysis[a] of Aliakmon River silt sediment core samples

	10a	*10b*	*11a*	*11b*	*11c*	*12*	*15a*	*15b*
K	562	665	716	742	665	435	691	460
Ca	1670	2070	2170	2395	2270	1000	1670	1470
Ti	56	50	57	63	52	56	69	61
V	3.9	3.9	3.9	2	2	5.9	2	2
Cr	33	37	25	27	31	244	12	13
Mn	24	22	24	22	22	27	24	16
Fe	931	859	913	877	824	842	931	842
Ni	10.9	11.9	10.2	8.7	10.5	14.2	8.1	8.2
Cu	0.57	0.74	1.13	0.82	0.72	1.59	0.93	1.02
Zn	2.25	2.31	1.88	1.64	1.39	3.35	2.95	3.12
Ga	0.16	0.20	0.27	0.24	0.26	0.23	0.27	0.32
As	0.23	0.16	0.08	0.16	0.08	0.21	0.15	0.09
Rb	1.03	0.97	1.16	0.96	0.96	0.92	1.16	1.10
Sr	1.45	1.48	1.71	1.68	1.46	1.03	1.65	1.65
Y	0.24	0.27	0.18	0.27	0.25	0.27	0.37	0.27
Zr	0.75	0.70	0.80	0.92	0.49	0.68	1.81	0.77
Ba	3.75	2.73	4.65	4.65	5.04	5.17	3.88	1.57
Pb	0.09	0.16	0.18	0.15	0.68	0.36	0.23	0.22

[a] Results are expressed in m moles per kg of silt sediment. The 10a (0–5 cm) and 10b (5–10 cm) are the two layers of the sediment core sample taken from site 10. The 11a (0–5 cm), 11b (5–10 cm) and 11c (10–15 cm) are the three layers of the sediment core sample taken from site 11. The SS 12 is the top (0–5 cm) layer of the sediment at site 12. The 15a (0–5 cm) and 15b (5–10 cm) are the two layers of the sediment core sample taken from site 15.

Table 21 Elemental analysis[a] of Aliakmon River clay sediment core samples

	10a	*10b*	*11a*	*11b*	*11c*	*12*	*15a*	*15b*
K	615	486	639	665	615	332	615	460
Ca	1600	1500	1750	2000	1720	870	1250	975
Ti	69	50	65	65	56	48	75	59
V	3.9	3.9	3.9	3.9	3.9	3.9	2	—
Cr	27	23	17	13	29	56	12	10
Mn	27	25	27	29	22	33	27	25
Fe	1092	1003	1110	1092	1003	985	1218	1164
Ni	13.3	13.9	13.2	12.6	12.5	19.5	12.9	9.4
Cu	1.05	1.11	1.02	1.2	1.05	1.95	2.09	2.01
Zn	2.97	3.36	2.02	2.14	2.13	8.01	5.05	4.18
Ga	0.33	0.30	0.26	0.34	0.23	0.11	0.39	0.27
As	0.13	0.16	0.23	0.16	0.08	0.25	0.15	0.15
Rb	1.03	0.96	1.20	1.16	0.97	0.71	1.43	1.25
Sr	1.18	1.22	1.47	1.51	1.34	0.90	1.21	1.08
Y	0.28	0.18	0.22	0.25	0.34	0.19	0.45	0.39
Zr	0.54	0.83	0.86	0.86	0.56	0.39	0.80	1.09
Ba	3.52	4.52	2.74	3.52	3.89	5.08	5.13	4.70
Pb	0.73	0.28	0.26	0.41	0.68	0.38	1.02	0.35

[a] See footnote in Table 20.

content profile of the silt fractions while Table 21 shows the analysis of the clay fractions. For each element, the concentration means and standard deviations in the top layer (0–5 cm) for silt and clay fractions are shown (Table 22). Also, the ratio between the mean concentrations of each element in the silt and clay fraction has been calculated and is shown in the Table 22.

The elements potassium, calcium, chromium and strontium are found mostly in the coarse silt fractions, while the rest of the elements determined (titanium, vanadium, manganese, iron, nickel, copper, zinc, arsenic and lead) are found mostly in the finer-grained clay fractions. The sediment enrichment factors (SEF), calculated as previously reported (Katsanos *et al.*, 1987), for the silt and clay fractions are shown in Tables 23 and 24.

Table 22 Concentration mean and standard deviation values of different metallic elements in the silt and clay fractions of the Aliakmon River sediments samples

	Silt	*Clay*	*Silt/Clay*
K	617 ± 117	553 ± 115	1.12
Ca	1839 ± 471	1458 ± 394	1.26
Ti	58 ± 6	60 ± 9	0.97
V	3.2 ± 1.4	3.4 ± 0.9	0.94
Mn	22 ± 3	27 ± 3	0.84
Fe	877 ± 43	1083 ± 83	0.81
Cr	29 ± 14	23 ± 15	1.25
Ni	10.3 ± 2.1	13.4 ± 2.8	0.77
Cu	0.94 ± 0.32	1.4 ± 0.5	0.67
Zn	2.4 ± 0.7	3.7 ± 2.0	0.63
As	0.15 ± 0.06	0.29 ± 0.37	0.52
Sr	1.51 ± 0.22	1.24 ± 0.20	1.22
Pb	0.26 ± 0.19	0.51 ± 0.27	0.51

Table 23 Sediment enrichment factors (SEF) of Aliakmon River silt sediment core samples

	10	*11*	*15*	*C*[a]
Ti	0.00	0.00[b]	0.00	0.00
K	−0.25	0.00	0.35	0.90
Ca	−0.30	0.00	0.00	1.00
V	0.00	1.15	0.00	0.25
Cr	−0.20	0.00	−0.20	2.75
Mn	0.00	0.00	0.35	0.87
Fe	0.00	0.00	0.00	0.71
Ni	−0.20	0.30	0.00	0.21
Cu	−0.30	0.50	0.00	0.00
Zn	−0.00	0.25	0.00	0.22
Ga	0.30	0.25	−0.25	0.56
As	0.30	−0.45	0.50	0:88
Rb	0.00	0.35	0.00	0.57
Sr	0.00	0.00	0.00	0.94
Y	−0.20	−0.25	0.20	0.74
Zr	0.00	0.00	1.10	1.30
Ba	0.25	0.00	1.20	0.87
Pb	−0.50	0.30	0.00	0.00

[a]—SEF values for Axios (Vardar) River core sediment (silt clay combined) sample.
[b] Values between −0.15 to 0.15 are considered as zero enrichment.

Table 24 Sediment enrichment factors of Aliakmon River clay sediment core samples

	10	*11*	*15*
Ti	0.00[a]	0.00	0.00
K	0.00	0.00	0.00
Ca	−0.20	0.00	0.00
V	−0.25	0.00	—
Cr	0.00	0.30	0.00
Mn	−0.20	0.00	0.00
Fe	−0.20	0.00	0.00
Ni	−0.30	0.00	0.00
Cu	−0.30	0.00	−0.20
Zn	−0.45	0.00	0.00
Ga	−0.20	−0.25	0.00
As	−0.40	0.45	−0.20
Rb	−0.20	0.00	0.00
Sr	−0.30	0.00	0.00
Y	0.00	0.00	0.00
Zr	−0.55	0.00	0.00
Ba	−0.45	−0.20	0.00
Pb	0.90	−0.25	1.30

[a] See footnote b of Table 23.

In the sediment of SS 10, there is a general depletion of all elements especially those bound to the clay fractions (Table 24), with the exception of lead which is enriched in the clay fractions (SEF = 0.25), arsenic (SEF = 0.30), and barium (SEF = 0.25) which are enriched in the silt fractions. These changes in the concentration of metals in the sediments at SS 10 are apparently the result of both natural weathering processes and the activities of a chromium mine located in the area upstream of SS 10.

At SS 11, the elements, vanadium, nickel, copper, zinc, gallium, rubidium and lead are enriched in the silt fractions (Table 23), while in the clay fractions only chromium and arsenic are enriched. At SS 12 only the top (0–5 cm) sediment layer was sampled and analyzed. The concentrations of the different metallic elements showed a slightly irregular distribution in both the silt and clay fractions at SS 12 compared to the top-sediment layers from other sampling sites (Tables 20 and 21).

In both the sediment fractions at SS 12 a strong depletion is observed in the concentrations of calcium and potassium while nickel, copper and zinc, lead and chromium are enriched. The concentration of chromium has been increased by almost 8 times in the silt fraction at SS 12 compared to the top core fractions at other sampling sites.

At SS 15, the concentrations of the different metallic elements are either increased or remain unchanged. The concentration of zinc is increased in both layers of the sediment core sample and in both silt and clay fractions, while copper and lead concentrations are increased only in the clay fractions and manganese in the silt fractions. The SEF values at SS 15 (Table 23) show that the elements potassium, manganese, arsenic, yttrium, zinc, and barium are enriched in the silt fraction while in the clay fractions only lead is enriched and copper and arsenic are depleted. The high enrichment of lead in the clay fraction at SS 15 is probably due to the heavy road traffic in the area where the SS 15 is located.

For comparison, the SEF values in the sediment of the Axios, another river of Greece discharging to Thermaikos Bay, are included in the Table 23. The Axios (Vardar) River is a relatively highly polluted river (Papadopoulou-Mourkidou *et al.*, 1986) and its sediment is highly enriched in most of the metallic elements except titanium, copper and lead. In contrast to the Axios River, the sediment of the Aliakmon River in the corresponding area, close to its discharge, is slightly enriched in only a few elements (K, Mn, As, Y, Zr, Ba and Pb).

CONCLUSIONS

At present the Aliakmon River can be considered as an unpolluted river. This river receives elements from natural geological sources, from slightly polluted small community waste discharges, from a chromium mine, and from agricultural activities mainly in the lowland. The different metallic elements are transported by the river waters as ferromanganese concretions to which chromium, nickel, copper and zinc are also bound. The ratio of the concentrations of the particulate-associated forms of iron to the respective concentrations of manganese is in the range of 50 to 60 (55 ± 4) for most of the river and through the final stretch preceding its discharge to Thermaikos Bay this ratio is decreased to 36 ± 2.

The clay fractions of the river sediments are more enriched in metallic elements than the respective silt fractions.

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