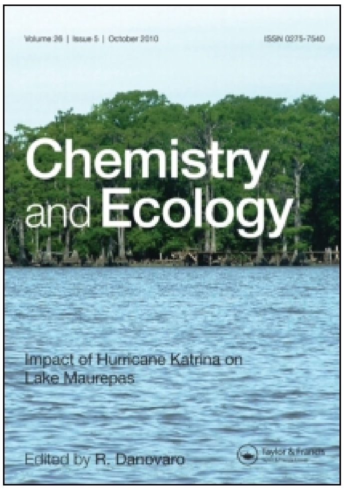

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Elemental Analysis of Water and Sediments by External Beam Pixe Part 3: Axios (Vardar) River, Greece

E. Papadopoulou-mourkidou[a]; G. A. Mourkides[a]; A. A. Katsanos[b]; P. K. Kakanis[b]
[a] Agricultural Chemistry Laboratory, Aristotelian University, Thessaloniki, Greece [b] Tandem Accelerator Laboratory, NRC Democritos, Attiki, Greece

To cite this Article Papadopoulou-mourkidou, E. , Mourkides, G. A. , Katsanos, A. A. and Kakanis, P. K.(1986) 'Elemental Analysis of Water and Sediments by External Beam Pixe Part 3: Axios (Vardar) River, Greece', Chemistry and Ecology, 2: 4, 335 — 350
To link to this Article: DOI: 10.1080/02757548608080738
URL: http://dx.doi.org/10.1080/02757548608080738

Chemistry in Ecology, 1986, Vol. 2, pp. 335–350
0275-7540/86/0204-0335 $18.50/0

Printed in the United Kingdom

Elemental Analysis of Water and Sediments by External Beam Pixe

Part 3: Axios (Vardar) River, Greece†

E. PAPADOPOULOU-MOURKIDOU and G. A. MOURKIDES
Agricultural Chemistry Laboratory, Aristotelian University, Thessaloniki, Greece
and
A. A. KATSANOS and P. K. KAKANIS
Tandem Accelerator Laboratory, NRC Democritos, Aghia Paraskevi, Attiki, Greece

(Received December 19, 1985)

The Axios (Vardar) River originates from the south west part of Yugoslavia, transverses Greece, and discharges into the Thermaikos bay in the north Aegean Sea.

The proton induced X-ray emission (PIXE) method with external beam was used for the elemental analysis of water and sediment samples, while measurements of water temperature, dissolved oxygen content, conductivity, pH, and the water flow were made *in situ*. Water samples were also analysed for total phosphates, nitrates, chlorophyll, and BOD. The data collected for a 16-month period indicate that the Axios River is polluted as far as the metal content is concerned; its primary productivity is low and it is slightly enriched during its course into the Greek territory.

KEY WORDS Proton induced X-ray emission; trace elements; water pollution; Axios River, Greece

---

† This work was partially supported by a grant from the Environmental Protection and Agricultural Research Section, Department of Agriculture, Greece.

INTRODUCTION

The Axios River, shown in Figure 1, originates from the south west part of Yugoslavia (San Planina and Sura Gora) where it is called the Vardar River; transverses the cities of Skopje and Titov Veles which are located on Yugoslavian soil and discharges into the Thermaikos bay in the north Aegean Sea. Its length is about 470 km and only the last 80 km are located in the Greek territory. The Vardar basin includes woody, agricultural, municipal, and industrial activities while the Axios basin is a rural area with only agricultural activities. The water quality of the Axios (Vardar) River and the composition of its sediment are affected by urban and rural non-point as well as municipal and industrial point-pollution sources.

The pollution of the natural water bodies of northern Greece has been studied and monitored for the last 10 years (Mourkides *et al.*, 1978, 1983 and 1984). The study of the Axios River started in 1982 and is continued till today; however, research on the metal content in the waters and sediments of the Axios River has been conducted only for a 16-month period starting August, 1982. This study is of major importance for Greece since the water flow rate and the water quality of the Axios River are affected primarily by Yugoslavian natural and human activities, then it transverses Greek territory to discharge into the Thermaikos bay affecting the fauna and flora of the north Aegean Sea. In addition, the quality of the river water has to be evaluated before Greece makes any plans for major uses of it. Today the Axios water is used only as irrigation water for farming in the surrounding lowland area.

EXPERIMENTAL

1 Site description

The Axios River basin has cold winters and hot summers with monthly mean air temperature 6.7°C in January and 26°C in July, while the Vardar basin has a much colder climate. The annual precipitation in Thessaloniki, the major city located in the Axios River basin, averages 486 mm. The Vardar River has five tributaries

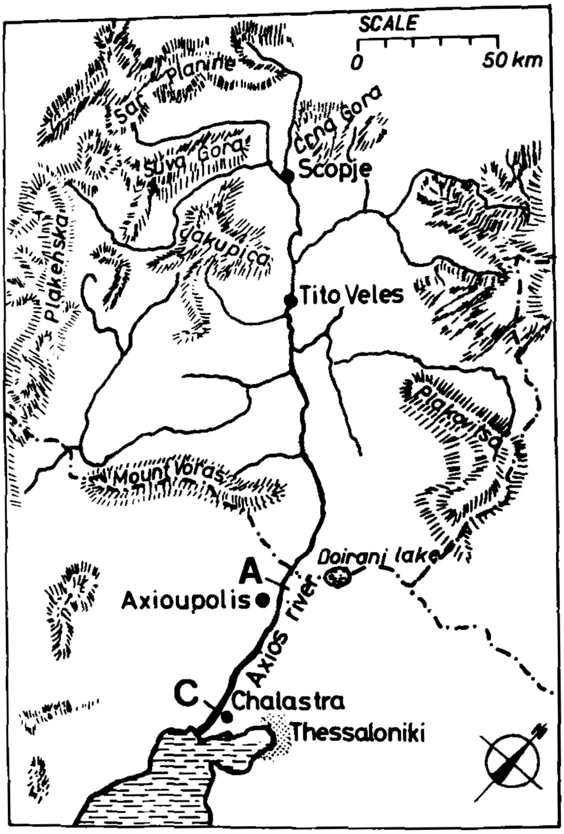

FIGURE 1 Geographical area transversed by Axios (Vardar) River.

(Treska, Lepenac, Pcinja, Bregalnica, and Crna Reca) and some streams, while the Axios River has only one tributary originating from a muddy area.

Two sampling sites have been selected. One site, A, is located close to the village of Axioupolis where the Vardar River transverses into the Greek territory and the other site, C, is close to the village of Chalastra a couple of kilometers from its discharge point into the Thermaikos bay (Figure 1). At site A the load of the river due to Yugoslavian natural and anthropogenic pollution sources is monitored, while at site C the load enrichment caused by non-point pollution sources of the Greek territory is monitored.

2 Materials and methods

Water and sediment samples were collected about once per month for the period August, 1982 to March, 1984.

Water samples collected from the middle of the river bed were transported to the laboratory in an insulated ice chest filled with crushed ice and were analyzed for nitrates, total phosphates, chlorophyll, BOD, and for metallic elements.

The water temperature, dissolved oxygen, pH, and conductivity were measured *in situ* using the Horiba water quality control electrode, Model U-7. The chlorophyll content was determined according to the method of Strickland–Parsons (1982) and the total phosphates according to the method of Murphy–Riley (1962). The Technicon autoanalyzer was used for determination of the nitrate-nitrogen. The water flow rates were measured on each sampling date by personnel from the Department of Agriculture, Greece.

The water samples used for the elemental analysis were filtered under suction through 0.45 μm cellulose acetate filters (Millipore), the filtrates were acidified with nitric acid to a final concentration of 0.5% and both the filtrates and the filtration cakes were prepared for the PIXE analysis (Mourkides *et al.*, 1983). Elements in the filtrate are referred to as water soluble elements and in the filtration cake as particulate-associated elements.

The sediment core samples were taken with the Phleger corer (Kahlsico International), sectioned and analyzed by the PIXE method. In addition, the core layers were subjected to particle-size analysis using the pipette method, and the phosphorus content was determined according to the methods of Olsen–Sommers (1982) and Golterman (1976 and 1982). Finally the pH and the content of calcium carbonate of each layer were also measured.

The minimum detection limit (MDL) for all the metallic elements was 0.3 ppb for the water samples (soluble materials), 0.1 ppb (related to the water volume) for the filtration cakes (particulates), and 1–5 ppm for the sediments. The relative standard deviations were 10% for those elements present at least 10 times above the

MDL value, and 20–50% for those with concentrations close to the MDL values.

RESULTS AND DISCUSSION

The mean and the respective standard deviation values of water temperature, pH, dissolved oxygen, BOD, conductivity, chlorophyll, nitrate-nitrogen, and total phosphates derived from monthly measurements obtained during a 16-month period are presented in Table I.

TABLE I
General parameters[a] of Axios River water

	Sampling sites A	Sampling sites C
Total phosphates (ppm)	0.54 ± 0.33	0.50 ± 0.28
Nitrate–nitrogen (ppm)	0.95 ± 0.36	1.42 ± 0.22
Chlorophyll-*a* (ppm)	0.85 ± 0.69	1.48 ± 2.33
BOD (ppm)	1.84 ± 1.28	2.01 ± 1.59
Dissolved oxygen (ppm)	10.2 ± 1.6	10.1 ± 1.7
% Saturation	96.8 ± 15.6	98.1 ± 6.2
Conductivity (μmho/cm)	380.0 ± 88.3	384.6 ± 155.5
pH	7.5 ± 0.5	7.6 ± 0.7
Temperature (°C)	14.1 ± 6.8	16.2 ± 6.7

[a] Mean values and standard deviations are given for a 16-month period.

The dissolved oxygen gave values ranging from 85 to 100% saturation. Supersaturation in oxygen was recorded in early summer. Most of the BOD values are low (1 to 2 ppm), however values of 3 to 4 ppm were also measured. The pH values ranged from 6.8 to 8.4 and the conductivity from 300 to 550 μmho/cm.

The concentrations of chlorophyll-*a* were usually very low (<1.70 ppm) indicating a low primary productivity in the river. In one case (June, 1983) a concentration of 6.7 ppm of chlorophyll-*a* was measured. The nitrate-nitrogen concentrations were rather high ranging from 0.87 to 1.77 ppm with an annual average value of 0.95 at site A and 1.42 ppm at site C. In a yearly basis the total nitrate-nitrogen which is passing through site A amounted to 6850 tons. The total phosphate concentrations were also relatively high for river waters and ranged from 0.08 to 1.04 ppm at site A, and from 0.10 to 1.00 ppm at site C. As the river transverses the Greek cropland its phosphate load is sometimes increased, while at other times it is decreased. On a yearly basis the total phosphates arriving at site A amounted to 2500 tons of phosphorus. Phosphate concentrations were higher during the warm summer months than during the cold winter months. Apparently phosphates are released from the river sediment into the running water during the summer. The concentrations of total phosphates are not influenced greatly by the river flow rate.

The concentrations of nitrate-nitrogen and chlorophyll-*a* were usually higher at site C than at site A, as is indicated also from their concentration mean values for site A and site C, respectively. The standard deviation values of almost all of the parameters shown in Table I are relatively high indicating a very high annual variation in the quality of the Axios River water.

From the data presented in Table I it can be concluded that the Axios River has high dissolved oxygen, nitrate-nitrogen and total phosphate content while its primary productivity is low. The concentrations of nitrate-nitrogen, chlorophyll-*a*, and BOD being higher at site C than at site A indicate an increase in water pollution due to the agricultural activities in the low-land of the Greek territory.

The concentrations of the different metallic elements in the Axios River water are presented in the Tables II and III; the concentrations of the elements in their water soluble forms are given in Table II and the respective concentrations of the particulate-associated forms in Table III. At site A the most abundant water soluble element is calcium and its concentration varied from 35 to 64 ppm with a mean value of 50 ± 9 ppm; calcium in its particulate-associated form ranged from 0.005 to 6.92 ppm with a mean value 1.06 ± 1.70 ppm. Both the water soluble and particulate-associated loads of calcium were about the same at both sampling sites. This is also true for all the other elements except for the water soluble forms of manganese, iron and zinc. These three elements had higher concentrations at site C than at site A. It is worth mentioning here that at both sampling sites the concentrations of the

TABLE II
Concentrations[a] of soluble elements in the water of Axios River

Date	SS	TDS	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Rb	Sr	Y	Zr	Mo	Pb
30.08.82	A	304	54	nd	19	10	2	41	3	3	13	nd	nd	nd	—	nd	nd	nd	—
	C	347	60	nd	nd	4	8	35	2	3	44	nd	nd	nd	—	nd	nd	nd	—
12.09.82	A	358	58	nd	14	6	4	35	4	3	21	nd	nd	nd	—	nd	nd	nd	—
	C	394	61	nd	15	4	5	41	6	5	67	nd	nd	nd	—	nd	nd	nd	—
12.10.82	A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	C	356	56	nd	13	10	99	1930	12	4	24	nd	nd	nd	185	nd	nd	nd	—
14.12.82	A	365	60	nd	11	3	2	155	10	8	108	nd	nd	nd	190	nd	nd	nd	3
	C	368	55	nd	8	3	9	299	14	11	71	nd	nd	nd	195	nd	nd	nd	4
16.03.83	A	333	64	nd	nd	7	nd	10	3	3	77	3	nd	nd	283	nd	nd	nd	2
	C	347	67	nd	nd	nd	nd	10	1	2	48	5	nd	nd	220	nd	nd	nd	2
14.04.83	A	320	45	nd	6	5	5	45	2	3	39	3	nd	3	127	nd	nd	n d	2
	C	316	44	nd	6	6	11	34	3	5	785	3	nd	2	134	nd	nd	nd	2
18.05.83	A	316	46	nd	10	9	4	39	2	4	33	3	nd	2	142	nd	nd	nd	5
	C	320	48	nd	12	4	9	73	2	4	33	3	nd	2	142	nd	nd	nd	5
15.06.83	A	300	41	nd	5	7	3	29	2	4	25	5	nd	1	152	nd	nd	nd	2
	C	352	44	nd	15	4	6	23	3	4	29	5	nd	2	155	nd	nd	nd	2
13.07.83	A	232	35	nd	6	4	4	29	2	4	13	2	nd	2	112	nd	nd	nd	2
	C	236	34	nd	6	2	2	29	2	4	13	2	nd	3	121	nd	nd	nd	1
14.09.83	A	296	47	nd	8	nd	6	31	3	3	203	5	nd	4	141	nd	nd	nd	4
	C	343	48	nd	11	3	3	27	3	5	34	4	nd	4	178	nd	nd	nd	4
12.10.83	A	390	52	4	15	3	3	13	2	3	25	3	nd	4	172	nd	nd	nd	2
	C	362	52	8	26	7	12	14	3	2	23	4	nd	1	168	nd	nd	nd	4
16.11.83	A	310	56	nd	10	8	4	46	4	3	30	3	nd	3	249	nd	nd	nd	4
	C	383	66	12	3	5	36	445	3	3	22	5	nd	3	297	nd	nd	hd	3
14.12.83	A	346	58	nd	10	9	7	44	3	4	35	4	nd	3	274	nd	nd	nd	8
	C	345	49	3	7	6	16	57	2	3	24	6	1	2	304	nd	nd	nd	3
18.01.84	A	320	44	4	12	9	6	109	3	8	33	5	nd	nd	176	nd	nd	nd	3
	C	330	44	3	16	4	11	141	3	8	20	4	nd	nd	185	nd	nd	nd	4
08.02.84	A	292	43	4	10	5	8	70	2	2	20	2	nd	2	159	nd	nd	nd	2
	C	286	39	6	22	15	7	32	2	3	27	3	nd	2	155	nd	nd	nd	3
19.03.84	A	281	41	nd	4	5	11	42	2	4	18	1	nd	2	159	nd	nd	7	6
	C	282	50	nd	7	4	8	45	2	3	18	3	1	nd	171	nd	nd	nd	3

[a] Concentrations are expressed in ppb apart from Ca and TDS which are in ppm; nd, SS, and TDS denote values below 0.4 ppb, sampling station, and total dissolved solids, respectively.

TABLE III

Concentrations[a] of the particulate-associated elements in the water of Axios River

Date	SS	FR	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Rb	Sr	Y	Zr	Mo	Pb
30.08.82	A	63	6920	420	12	70	224	6710	15	10	56	nd	nd	nd	nd	nd	nd	nd	nd
	C		2400	170	4	20	82	2610	5	4	21	nd	nd	nd	nd	nd	nd	nd	nd
12.09.82	A	127.67	440	28	2	14	19	463	3	1	8	2	nd	nd	nd	nd	nd	nd	2
	C		2412	177	8	26	95	3104	9	3	18	nd	nd	nd	nd	nd	nd	nd	15
12.10.82	A	—	710	48	3	12	25	757	2	1	9	nd	nd	2	3	nd	nd	nd	7
	C	102.97	1002	68	2	8	33	1037	2	1	7	nd	nd	3	4	nd	nd	nd	4
14.12.82	A	125.97	91	11	1	2	9	194	1	1	5	1	nd	nd	nd	nd	nd	nd	1
	C		187	19	2	3	14	387	1	1	5	1	nd	nd	nd	nd	nd	nd	1
16.03.83	A	93.48	5	3	nd	1	2	60	nd	nd	2	nd	nd	nd	nd	nd	nd	nd	1
	C		35	2	nd	1	2	49	nd	nd	2	nd	nd	nd	nd	nd	nd	nd	1
14.04.83	A	128.96	515	37	5	17	25	690	2	1	11	nd	nd	2	1	nd	nd	nd	7
	C		1620	125	10	56	78	2138	5	4	22	nd	1	2	2	nd	5	nd	11
18.05.83	A	69.81	138	7	2	3	7	116	nd	nd	5	nd	nd	nd	nd	nd	nd	nd	8
	C		185	15	2	4	14	214	1	1	7	nd	nd	nd	nd	nd	nd	nd	nd
15.06.83	A	84.46	2933	281	36	66	148	5518	16	8	20	2	1	10	14	nd	9	nd	8
	C		3305	328	50	82	170	6585	38	8	19	nd	nd	15	20	nd	9	nd	9
13.07.83	A	277.46	608	123	13	20	73	2404	4	2	14	nd	nd	4	4	nd	2	nd	10
	C		1322	197	31	40	121	3543	8	5	14	1	nd	8	7	nd	4	nd	8
14.09.83	A	124.48	1110	81	1	16	46	1327	3	2	17	nd	nd	4	5	nd	nd	nd	12
	C		747	63	3	8	31	1034	3	2	12	nd	nd	2	4	nd	nd	nd	7
12.10.83	A	61.42	177	7	1	3	5	138	1	1	7	nd	nd	nd	nd	nd	nd	nd	2
	C		237	25	nd	3	15	424	1	1	7	nd	nd	nd	nd	nd	nd	nd	3
16.11.83	A	82.89	240	10	nd	17	9	295	1	1	8	nd	nd	nd	2	nd	nd	nd	7
	C		860	79	1	15	39	1433	2	2	11	nd	nd	3	4	nd	nd	nd	9
14.12.83	A	112.93	252	16	1	9	20	384	1	1	8	1	nd	nd	2	1	nd	nd	9
	C		1277	114	1	25	71	2002	4	2	18	1	nd	nd	9	5	5	nd	14
18.01.84	A	269.09	1315	107	4	21	60	1784	4	2	20	nd	nd	3	6	nd	nd	nd	20
	C		599	47	2	8	31	834	2	2	13	nd	nd	1	nd	nd	nd	nd	15
08.02.84	A	385.55	825	87	4	13	60	1686	4	2	18	nd	nd	1	3	nd	nd	nd	10
	C		1109	137	3	16	80	2524	4	4	20	nd	nd	6	4	nd	nd	nd	18
19.03.84	A	279.49	725	60	nd	10	37	1144	1	1	9	nd	1	3	3	nd	2	nd	12
	C		828	74	3	12	44	1369	1	1	10	nd	nd	3	4	2	3	nd	10

[a] Concentrations are expressed in ppb; nd and SS denote values below 0.4 ppb and sampling station, respectively. The flow rate (FR) is expressed in m^3 per second.

particulate-associated iron, 1479 ± 1948 (site A) and 1830 ± 1650 ppb (site C), exceed the acceptable levels issued by WHO (Tebbutt, 1977) for the quality of drinking water.

The mean concentration of manganese in particulate form was found to be 48 ± 60 ppb at site A and 58 ± 46 ppb at site C, however, values of 120 to 220 ppb were also recorded making the water of the Axios River unsuitable for drinking purposes (Tebbutt, 1977 and US, NRC 1977). At both sites, the concentrations of the particulate forms of chromium and the soluble forms of strontium were also high.

The concentrations of vanadium, nickel, and copper both in the soluble and the particulate-associated forms were low. Arsenic was present only in its soluble form and its concentrations ranged from <0.4 to 6 ppb.

At both sites yttrium, zirconium, and molybdenum were not found in detectable quantities while rubidium was found only in its soluble form and in concentrations ranging from 1 to 4 ppb.

The mean concentration values of TDS (318 ± 38 ppm at site A and 335 ± 40 ppm at site C) show that the water of the Axios is slightly loaded relative to the water of unpolluted rivers and this load is increased by 5.6% at site C. There is a negative correlation between the water flow rates and the TDS contents with correlation coefficients −0.54 and −0.73 for sites A and C, respectively. The river flow rates recorded during the experimental period are given in Table III and the monthly mean values of water flow rates for a ten-year period are given in Table IV.

The correlation matrices for the particulate-associated forms of the elements presented in the Tables V and VI show that there are strong positive correlations among titanium, iron, manganese, copper, calcium, chronium, nickel, vanadium, and zinc. It may be that these elements exist in the particulates of the Axios River as ferromanganese nodules with the elements having the ratios of Fe/Mn = 28, Ti/Mn = 1.6, Cu/Mn = 0.053, and Ni/Mn = 0.78. Strontium is correlated only with iron, chromium, nickel, and vanadium with correlation coefficients over 0.50. Lead was correlated only with strontium ($r = 0.51$) at site A and with zinc ($r = 0.60$) at site C. Thus it may be considered that lead has originated mainly from anthropogenic pollution sources and likely to be derived from automobile exhaust emissions.

TABLE IV
Yearly variation of Axios River flow rate for a ten-year period

Month	Flow rate[a]
Jan.	167 ± 68
Feb.	184 ± 78
March	220 ± 166
April	224 ± 81
May	277 ± 195
June	181 ± 86
July	108 ± 74
Aug.	64 ± 31
Sept.	82 ± 28
Oct.	83 ± 18
Nov.	166 ± 119
Dec.	169 ± 101

[a] Flow rates are expressed in m^3/sec and have been calculated for each month by taking into account the flow rate of each month in the period of 1974–1983.

The abundance of soluble calcium in the water of the Axios River indicates that the river originates in and/or transverses calcaceous soils and minerals. The correlation matrix for the water soluble elements (data are not shown in Table) shows that there is positive correlation between calcium and TDS and negative between calcium and the water flow rate. At site A, iron showed strong positive

TABLE V
Correlation matrix for the particulate-associated elements at site A

	Ti	Fe	Mn	Cu	Ca	Cr	Ni	V	Zn	Sr	Pb
Ti	1.00										
Fe	0.99	1.00									
Mn	1.00	0.99	1.00								
Cu	0.98	0.98	0.97	1.00							
Ca	0.96	0.92	0.96	0.94	1.00						
Cr	0.95	0.97	0.95	0.97	0.90	1.00					
Ni	0.95	0.98	0.95	0.98	0.88	0.98	1.00				
V	0.71	0.78	0.70	0.75	0.52	0.80	0.85	1.00			
Zn	0.92	0.88	0.93	0.88	0.97	0.83	0.80	0.41	1.00		
Sr	0.43	0.52	0.42	0.46	0.22	0.55	0.58	0.79	0.16	1.00	
Pb	−0.05	−0.02	−0.03	−0.15	−0.05	−0.05	−0.08	0.03	−0.03	0.51	1.00

TABLE VI
Correlation matrix for the particulate-associated elements at site C

	Ti	Fe	Mn	Cu	Ca	Cr	Ni	V	Zn	Sr	Pb
Ti	1.00										
Fe	0.99	1.00									
Mn	0.99	0.98	1.00								
Cu	0.95	0.95	0.95	1.00							
Ca	0.94	0.91	0.90	0.85	1.00						
Cr	0.88	0.90	0.90	0.90	0.81	1.00					
Ni	0.86	0.90	0.83	0.85	0.79	0.85	1.00				
V	0.84	0.88	0.85	0.87	0.68	0.86	0.85	1.00			
Zn	0.75	0.64	0.76	0.75	0.79	0.68	0.45	0.38	1.00		
Sr	0.75	0.80	0.74	0.71	0.60	0.76	0.85	0.81	0.36	1.00	
Pb	0.32	0.38	0.42	0.34	0.32	0.32	0.18	0.12	0.60	0.27	1.00

correlation with nickel ($r = 0.75$) and zinc a negative correlation with chromium ($r = -0.61$). However, at site C iron showed strong positive correlation with manganese ($r = 0.98$), nickel ($r = 0.66$), and copper ($r = 0.65$). Nickel was also correlated with copper ($r = 0.65$) and manganese ($r = 0.55$). For both sampling sites the correlation coefficients between pairs of other elements were less than 0.50 and more than −0.50.

Equations for least square linear regression lines derived by regressing pairs of elements are presented in Table VII. For the water soluble elements, the regression equation of nickel vs iron has higher y-intercept and regression coefficient (slope) for site C than for site A, while in the respective equation describing the relationship between zinc vs chromium the y-intercept and the regression coefficient are higher for site A than for site C. For the particulate-associated elements the regression coefficients are approximately the same for both sampling sites except for the equations of calcium vs titanium where the regression coefficient is higher for site A than for site C.

The particle-size analysis of the Axios River sediment core samples as well as their content in phosphorus, calcium carbonate and their pH values are presented in Table VIII. The core sample from each site has been divided into layers indicated as A_1 (0 to 5 cm) and A_2 (5 to 10 cm) for site A and C_1 (0 to 5 cm) and C_2 (5 to 10 cm) for site C, respectively; the analyses were conducted for each layer separately. The total phosphate content was not determined since the fractionation of phosphorus into the phosphorus available to higher plants (Olsen) and into the phosphorus available

TABLE VII
Regression equations

Water Soluble Elements		
$y = 154.77 + 3.281x$	$y = \text{TDS}$,	$x = \text{Ca}$
$y = 5.75(-130.00) + 13.87(84.36)x$	$y = \text{Ni}$,	$x = \text{Fe}$
$y = 111.74(66.97) - 10.91(2.59)x$	$y = \text{Zn}$,	$x = \text{Cr}$
Particulate-Associated Elements		
$y = 3.14(7.89) + 0.30(0.27)x$	$y = \text{Mn}$,	$x = \text{Fe}$
$y = -3.04(8.35) + 0.58(0.51)x$	$y = \text{Ti}$,	$x = \text{Fe}$
$y = 4.21(-2.92) + 0.17(0.22)x$	$y = \text{Cr}$,	$x = \text{Ti}$
$y = -135.66(98.44) + 14.46(10.09)x$	$y = \text{Ca}$,	$x = \text{Ti}$
$y = 5.08(7.26) + 0.10(0.55)x$	$y = \text{Zn}$,	$x = \text{Ti}$

Numbers in parentheses are the respective y-intercept and slope values for site C.

to algae (Golterman) was preferred. As it is indicated in Table VIII the surface layers of both sites have higher contents in both forms of phosphorus, and the phosphorus available to algae is two times less than the amount available to higher plants. While the calcium carbonate content is low the sediments are alkaline as indicated by their alkaline pH values.

The concentrations of the different metallic elements in the layers of the sediment core samples are presented in Table IX and the sediment enrichment factors (SEF) of the respective elements in Table X. The SEF values have been calculated on the basis of an

TABLE VIII
Physical and chemical analyses of Axios River sediment core samples

	A_1	A_2	C_1	C_2
Silt (%)	9.2	13.5	2.7	2.7
Clay (%)	9.5	37.8	1.7	1.6
Sand (%)	81.3	48.7	95.6	95.7
P (Olsen) (ppb)	51	12	36	9
P (Golterman) (ppb)	27	4	18	4
PH	8.8	8.5	8.7	8.9
$CaCO_3$ (ppm)	3.1	6.2	2.2	2.2

A_1 (0–5 cm) and A_2 (5–10 cm) are the two layers of the sediment core sample taken from site A. C_1 (0–5 cm) and C_2 (5–10 cm) are the two layers from the sediment core sample taken from site C.

TABLE IX
Elemental analysis[a] of Axios River sediment core samples

	Site A		Site C		
	A_1	A_2	C_1	C_2	C_3
K	8000	13000	8000	8000	6000
Ca	11000	37000	14000	13000	9000
Ti	2200	2600	800	1500	500
V	90	70	40	60	70
Cr	270	1300	40	20	20
Mn	600	800	300	300	200
Fe	22000	28000	10000	11000	9000
Ni	39	64	20	31	17
Cu	20	30	17	29	19
Zn	101	149	39	66	43
Ga	13	16	10	12	8
As	17	19	11	11	4
Br	—	—	6	4	—
Rb	70	55	56	67	50
Sr	203	140	184	190	231
Y	16	32	11	11	15
Zr	124	197	59	48	9
Ba	719	442	588	981	514
Pb	79	88	33	54	33

[a] Concentrations are expressed in ppm. A_1 (0–5 cm) and A_2 (5–10 cm) are the two layers of the sediment core sample taken from site A. C_1 (0–5 cm), C_2 (5–10 cm), and C_3 (10–20 cm) are the layers from the sediment core sample taken from site C.

equation proposed by Kemp *et al.* (1976) as modified by Katsanos *et al.* (1985). This equation is:

$$\mathrm{SEF} = (E_s/\mathrm{Ti}_s) - (E_n/\mathrm{Ti}_n)/(E_n/\mathrm{Ti}_n),$$

where E_s is the concentration of a certain element E in the sediment core layer S and Ti_s is the respective concentration of Ti; E_n and Ti_n are the concentrations of the elements E and Ti, respectively, in the baseline layer. Titanium was taken as the conservative element.

For site A, the SEF values indicate that elimination of potassium, calcium, chromium, nickel, copper, zinc, yttrium, and zirconium and enrichment of vanadium, rubidium, strontium, and barium have occurred. The zero SEF values for iron and manganese indicate that

TABLE X
Sediment enrichment factors of River Axios sediment core samples

	A_1/A_2	C_1/C_2	C_1/C_3
Ti	0.00	0.00	0.00
K	−0.30	0.90	−0.20
Ca	−0.60	1.00	0.00
V	0.50	0.25	−0.64
Cr	−0.99	2.75	0.25
Mn	0.00	0.87	0.00
Fe	0.00	0.71	−0.31
Ni	−0.30	0.21	−0.26
Cu	−0.30	0.00	−0.44
Zn	−0.20	0.22	−0.44
As	0.00	0.88	0.72
Rb	0.50	0.57	−0.30
Sr	0.70	0.94	−0.50
Y	−0.40	0.74	−0.54
Zr	−0.24	1.30	3.10
Ba	0.92	0.87	−0.29
Pb	0.00	0.00	−0.37
Ga	0.00	0.56	−0.22

A_1 (0–5 cm) and A_2 (5–10 cm) are the two layers of the sediment core sample taken from site A; C_1 (0–5 cm), C_2 (5–10 cm), and C_3 (10–15 cm) are the three layers of the sediment core sample taken from site C. Values between −0.15 to +0.15 were considered as zero enrichment.

these elements behave the same way in the sediment core along with titanium, demonstrating again that they move as ferromanganese nodules associated with titanium, chromium, nickel, and other elements.

At site C, with exception of lead and copper an enrichment of all the elements under study has occurred at the top layer. It is more likely that elements are removed from the upland and are deposited on the lowland. The enrichment of arsenic in the surface sediment core layer of site C is an indication of agricultural pollution. However, SEF values calculated for C_1/C_3 (C_3 is the sediment core layer with depth 10 to 15 cm) show depletion of all the elements except for chromium, arsenic, and zinc which are enriched. The data indicate that arsenic pollution has been going on for a long time.

CONCLUSIONS

The content of the Axios River water in nitrate-nitrogen and total phosphates is high. The phosphorus content of the sediment core samples determined both by the method of Olsen and Golterman are also high. However, the primary productivity of the Axios River as indicated by its chlorophyll content is low.

The most abundant water soluble element is calcium. Calcium has a strong and positive correlation with TDS while both calcium and TDS have a negative correlation with the Axios River water flow rate.

In the particulate-associated forms of the different metallic elements it appears that ferromanganese nodules associated with chromium, nickel, and other elements move down the river and/or are deposited on the river sediment.

The concentrations of iron and manganese in the particulate-associated forms are high, and therefore the water of the Axios River cannot be used for drinking without proper treatment.

When the Axios River enters Greece it is slightly polluted due to municipal, industrial, and agricultural activities, and its pollution load is slightly increased during its course in Greek territory primarily due to agricultural activities of the lowland.

References

Golterman, H. L. (1976). Sediments as a source of phosphate for algal growth. *In Interactions between sediments and fresh water.* H. L. Golterman (ed) pp. 286–293. Dr. Junk and B.V. Publishers, The Hague.

Golterman, H. L. (1982). Sediments, modifying and equilibrating factors in chemistry of freshwater. *In Sediment/Freshwater Interaction.* P. G. Sly (ed) pp. 2–35. Dr. Junk and B.V. Publishers, The Hague.

Katsanos, A. A., Panayotakis, N., Tzoumezi, M., Papadopoulou-Mourkidou, E. and Mourkides, G. A. (1985). Elemental analysis of waters and sediments by external beam PIXE Part 2. Industrial zone of Ptolemais, Greece. ***Chemistry in Ecology.*** In Press.

Kemp, A. L. W., Thomas, R. L., Dell, C. I. and Jacket, J. M. (1976). Cultural impact on the geochemistry of sediments in Lake Erie. *Journal Fisheries Research Board Canada,* **33**(3), 440–462.

Mourkides, G. A., Tsikritsis, G. E., Tziouris, S. E. and Mengisoglou, U. (1978). The Lakes of Northern Greece. I. Trophic status. 1979. *Scientific Annals, School of Agriculture, Aristotelian University,* **21,** 93–131, Thessaloniki, Greece.

Mourkides, G. A., Katsanos, A. A. and Tzoumezi, M. (1983). Elemental analysis of waters and sediments by external Beam PIXE. Part 1. Vegoritis Lake, Greece. *Chemistry in Ecology,* **1,** 245–259.

Mourkides, G. A. and Tziouris, S. E. (1984). The Lakes of Northern Greece. II. The trophic status of Koronia and Kastoria. *Agricultural Research,* **8,** 75–86. Publis. Ministry of Agriculture, Greece.

Olsen, P. J. and Sommers, L. E. (1982). *Phosphorus. In methods of Soil Analysis.* C. A. Black (ed.) American Society of Agronomy, Madison, Wisconsin, USA pp. 403–430.

Strickland, J. D. H., and Parsons, T. R. (1977). *A practical handbook of seawater analysis,* pp. 185–192. Fisheries Research Board of Canada, Ottawa, 1972.

Tebbutt, T. H. Y. (1977). *Principles of water quality control.* pp. 14. Pergamon Press, Oxford. 2nd ed.

US, National Research Council. (1977). Drinking water and health. *National Academy of Sciences.* Washington, D.C.