

This article was downloaded by:

On: 15 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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 2. Industrial Zone of Ptolemais, Greece

A. A. Katsanos<sup>a</sup>; N. Panayotakis<sup>a</sup>; M. Tzoumezi<sup>a</sup>; E. Papadopoulou-mourkidou<sup>b</sup>; G. A. Mourkides<sup>b</sup>

<sup>a</sup> Tandem Accelerator Laboratory, NRC Demokritos, Attiki, Greece <sup>b</sup> Agricultural Chemistry Laboratory, Aristotelian University, Thessaloniki, Greece

**To cite this Article** Katsanos, A. A. , Panayotakis, N. , Tzoumezi, M. , Papadopoulou-mourkidou, E. and Mourkides, G. A.(1987) 'Elemental Analysis of Water and Sediments by External Beam PIXE Part 2. Industrial Zone of Ptolemais, Greece', *Chemistry and Ecology*, 3: 1, 75 – 100

**To link to this Article: DOI:** 10.1080/02757548708070835

**URL:** <http://dx.doi.org/10.1080/02757548708070835>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Elemental Analysis of Water and Sediments by External Beam PIXE Part 2. Industrial Zone of Ptolemais, Greece\*

A. A. KATSANOS, N. PANAYOTAKIS and M. TZOUMEZI  
*Tandem Accelerator Laboratory, NRC Demokritos, Aghia Paraskevi, Attiki, Greece*

and

E. PAPADOPOULOU-MOURKIDOU and G. A. MOURKIDES  
*Agricultural Chemistry Laboratory, Aristotelian University, Thessaloniki, Greece*

*(Received June 5, 1986)*

In the industrial zone of Ptolemais, Greece there are two coal-fired power plants, one nitrogen-fertilizer producing plant and a factory making coal-bricks. The industrial and the municipal waste effluents of this area are discharged into the lake Vegoritis via a small stream named Solou. Water and core or grab sediment samples taken from the Solou stream and Vegoritis Lake were analyzed for metallic elements by the proton induced X-ray emission (PIXE) method and the different pollution sources of the area under study, as far as metal pollution is concerned, were tentatively identified. The communities contribute to the pollution with loads of Pb and Ni; Ca, Cr, and Mo are contributed mainly by industries, while Fe, Zn, Mn, Sr, and Br have their origin to both sources. Also the sediment enrichment factors (SEF) are calculated and discussed.

**KEY WORDS** Greece; PIXE; Beam; Industry

---

\* This work has been partially supported by a grant from the Environmental Protection Section, Department of Agriculture, Greece.

This paper was accepted by the previous editor, Dr. E. J. Perkins.

## INTRODUCTION

In Greece, in addition to other energy sources, coal has also been utilized for power generation for the last twenty five years. However, coal-mining operations and the construction of coal-fired power plants have been proceeded without any concern about the impact of such activities on the surrounding environment. Some years ago, various monitoring programs were initiated to assess the effect of coal-fired power plants and coal-mining operations on the environment of northern Greece.

The utilization of coal for power generation besides mobilizing energy also mobilizes a number of potentially hazardous components including a variety of trace metallic elements and radio-nuclides. Although the amount of heavy elements in coal is generally low, the annual emission of trace elements into the environment from a given plant may reach significant levels considering the fact that the consumption of coal by a given plant may reach the order of  $20 \times 10^6$  tons of coal per year.

Coal-mining operations and use of coal for power production can cause water quality problems either by enriching water bodies with heavy loads of suspended solids, metals, and various water soluble substances, or by deoxygenating water bodies. The pollution of surface or underground water bodies may lead eventually to land pollution and contamination of the produced food (Klein and Russell, 1975; Dressen, *et al.*, 1977). Specific physiological disorders associated with excessive intake of one or more of the potentially harmful elements by plants, animals or man are well documented (Bertine and Goldberg, 1971; Klein and Russell, 1973; Lee, *et al.*, 1975; Cook, 1977; Valkovic, 1983).

In the industrial zone of Ptolemais in northern Greece, a stream some 50 km in length named Solou receives the waste effluents from two coal-fired power plants and other industries located on its banks, as well as the municipal and sewage effluents from the city of Ptolemais. The ultimate recipient of the Solou stream effluent is Vegoritis Lake (Ostrovou Lake) (Mourkides, *et al.*, 1983); a lake 60 km<sup>2</sup> with a maximum depth of 50 m.

This study has been undertaken to pinpoint the different pollution sources of the Solou stream, as far as metal contamination is concerned, so that control measures can be taken and further

disruption of the aquatic environment avoided. The proton induced X-ray emission (PIXE) method was used for the elemental analysis of sediment and water samples (Mourkides *et al.*, 1983; Katsanos, 1980; Cahill, 1980). This method detects automatically and simultaneously all heavy elements and, therefore, it is not necessary to predetermine which elements to look for. It is a powerful technique suitable for multi-elemental analysis of a wide variety of samples with good sensitivity (Valkonic, 1983).

## EXPERIMENTAL

### Pollution sources

*Coal-fired power plants.* There are two coal-fired power plants in the area. The Kardias plant, Plant-K, which consists of four 300 MW units and the Ptolemais plant, Plant-P, which consists of three units producing a total of 650 MW. These plants consume  $14 \times 10^6$  and  $6 \times 10^6$  tons of lignite per year, respectively.

*Coal-bricks factory, Plant-B.* This factory uses  $0.8 \times 10^6$  tons of lignite per year.

*Nitrogen-fertilizer producing factory, Plant-F.* It produces daily 440 tons of ammonium nitrate, 476 tons of ammonium sulfate, and 579 tons of ammonium dolomite nitrate ( $\text{NH}_4\text{NO}_3 + \text{CaCO}_3$ ). The maximum yearly consumption of lignite is  $1.6 \times 10^6$  tons.

*Municipal waste and sewage effluents of the city of Ptolemais.* The city has a population of 30,000 people and its municipal waste and sewage effluents are discharged directly into a small tributary which subsequently joins the Solou stream.

*Slaughtering house, Plant-SH.* This is a small unit where 30 to 40 cows are slaughtered per week.

### Site description

Nineteen sampling stations located on/or close to the Solou stream were selected and their locations are illustrated in Figure 1.

*Site 1.* This site is located close to the origin of the Solou stream. The area used to be a small lake which has lately been drained.

*Sites 2 and 3.* These sites located downstream of the coal-fired power plant, Plant-K, which utilizes well water and its waste

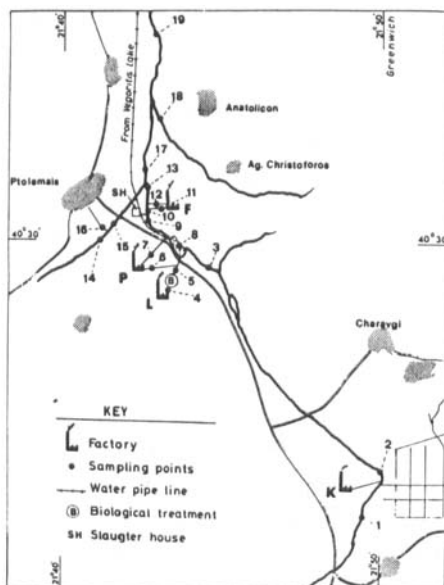


FIGURE 1 Map of the industrial zone of Ptolemais, Greece.

effluents are subjected to primary treatment before being discharged into the Solou stream.

**Sites 4 and 5.** The waste effluents of Plant-B are subjected to biological treatment before being discharged into the Solou stream. Sites 4 and 5 are located before and after the biological waste treatment facilities of Plant-B.

**Sites 6, 7 and 8.** These sites are located in the area of the coal-fired power plant, Plant-P. Plant-P recycles water from the lake Vegoritis; lake water is transferred through a pipeline into a pond at a rate of  $48,000 \text{ m}^3$  per day, and pond water is pumped out by Plant-P. The overflow water of the pond is discharged into the Solou stream. A fraction from the waste effluents of Plant-P after being treated (primary treatment) is returned to the pond; whereas the rest of the waste effluents including some of the water borne ash is discharged directly into the Solou stream. In addition the domestic wastes from the small factory community after being given primary treatment are discharged directly into the stream. Site 6 is located at the exit of the treated waste effluents of Plant-P and site 7

at the exit where the untreated waste effluents of Plant-P and the treated domestic effluents are discharged. Site 8 is in the pond.

*Sites 9 and 10.* In the area between sites 9 and 10 the waste effluents of Plant-SH are discharged.

*Sites 11, 12 and 13.* Plant-F utilizes well and rain water and its waste effluents are discharged directly into the Solou stream. Site 11 is located at the chemical waste effluents exit, site 12 at the waste water exit, and site 13 downstream of these points.

*Sites 14, 15, 16, and 17.* The municipal and sewage effluents of Ptolemais (site 16) are discharged into a small tributary of the Solou stream. Sites 14 and 15 are located in the tributary and upstream and downstream, respectively, from the discharge point of the municipal and sewage effluents of the city of Ptolemais, Site 17 is located downstream from the tributary.

*Site 18.* This site is located in a by-stream of the Solou stream named St. Christophoros. This by-stream is surrounded by an agricultural area.

*Site 19.* This is located in the Solou stream and close to its discharge point into Vegoritis Lake.

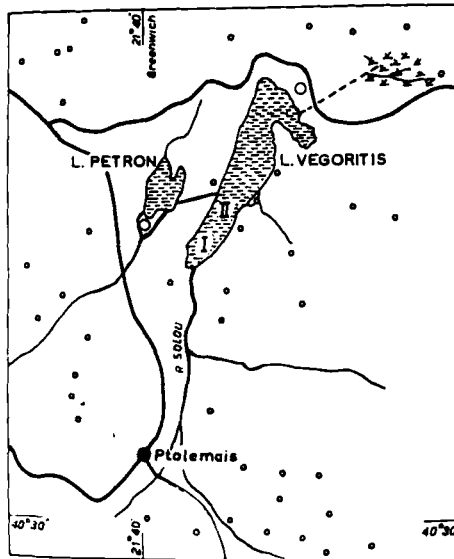


FIGURE 2 Map of the area around Vegoritis Lake, Greece.

In addition water and sediment grab samples were collected from two stations (I and II) located in the northeast site of Vegoritis Lake (Figure 2).

### **Sample collection**

Water samples were collected in June and August of 1982 and in March, May, September, and October of 1983. Temperature, pH, dissolved oxygen, conductivity, and turbidity were recorded *in situ* using a portable water quality monitor, Model U-7 (Horiba). One litre polyethylene bottles were used for the collection and the transportation of samples to the laboratory. Each water sample was filtered through a 0.45  $\mu\text{m}$  acetate cellulose filter (Millipore); the filtrate was acidified with  $\text{HNO}_3$  to a final concentration of 0.5%  $\text{HNO}_3$ ; both the filtrate and the filtration cake were prepared for the PIXE analysis. The filtrate is referred as solution (S) and the filtration cake as particulate (P). The water flow of the Solou stream was measured at different points using a propeller stream current velocity meter (Pygmy current meter, Kahlsico International Corporation).

Sediment core samples were taken with a Phleger corer (K.I.C) from the sampling sites 1, 9, 13, and 18 and sediment grab samples with an Ekamgrab (K.I.C) from stations I and II in Lake Vegoritis. In addition a surface sediment sample was taken at site 18 only. The core samples were divided into fractions of 2 cm depth and each fraction was dried and analyzed by the PIXE method (Mourkides, *et al.*, 1983). Samples of different coal types produced in the Ptolemais area were also collected and analyzed by the same method.

### **Sample preparation and PIXE analysis**

The proton induced X-ray emission (PIXE) method with external beam was used for the elemental analysis of all samples. This method has been previously described (Mourkides, *et al.*, 1983). The sediment samples were dried at 120°C and the filters were freeze-dried before both were analyzed by the PIXE method. The water samples were treated with ammonium oxalate solution to neutralize the excess of nitric ions and evaporated to dryness by an infra-red lamp and a pellet of the dry residue was prepared.

The neutralization of the excess of nitric acid was found necessary to avoid a hygroscopic residue.

The minimum detection limit (MDL) for all elements was 0.3 ppb for the water samples (soluble materials), 0.1 ppb (referred to the water column) for the filtration cakes (particulates) and 1–5 ppm for the sediments. In certain cases the MDL was due to interferences by the major elements of the samples. The relative standard deviations were 10% for those elements present in concentrations of 10 times or more above the MDL, and 20–50% for those with concentrations close to the MDL values.

## RESULTS AND DISCUSSION

The water temperature, pH, dissolved oxygen, conductivity, and turbidity recorded *in situ* at the different sampling sites are presented in Table I. The mean temperature of the Solou stream water is about 10°C apart from higher values recorded at sampling

TABLE I  
Water characteristics of the different sampling sites measured on March, 1983

| Site | Temperature<br>°C | pH       | Dissolved<br>oxygen mg l <sup>-1</sup> | Conductivity<br>(ms/cm) | Turbidity<br>(ppm) |
|------|-------------------|----------|--|-------------------------|--------------------|
| 1    | 10.9              | 8.3      | 11.8                                   | 0.34                    | 39                 |
| 2    | 15.9              | 9.4      | 11.4                                   | 1.04                    | 70                 |
| 3    | 10.5              | 8.7      | 12.0                                   | 0.72                    | 44                 |
| 4    | 9.5               | 8.8      | 9.0                                    | 0.46                    | 50                 |
| 5    | 14.3              | 8.5      | 9.0                                    | 0.70                    | 70                 |
| 6    | 11.7              | 9.1      | 10.4                                   | 0.71                    | 105                |
| 7    | 18.1              | 9.0      | 8.2                                    | 1.16                    | 70–600             |
| 8    | 18.1              | 8.4      | 12.5                                   | 0.76                    | 2                  |
| 9    | 11.0              | 8.8      | 11.1                                   | 0.69                    | 48                 |
| 10   | 11.8              | 9.3      | 11.8                                   | 0.65                    | 60                 |
| 11   | 21.0              | 8.5–10.0 | 4.6–8.0                                | 0.64–6.96               | 24–600             |
| 12   | 21.5              | 7.8–9.3  | 5.8–7.3                                | 1.23–2.37               | 22–130             |
| 13   | 13.4              | 8.7–9.7  | 7.0–9.0                                | 0.98–2.07               | 26–126             |
| 14   | 8.0               | 8.3      | 12.2                                   | 0.28                    | 47                 |
| 15   | 8.6               | 8.2      | 7.4                                    | 0.35                    | 54                 |
| 16   | 10.8              | 7.9      | 5.0                                    | 0.62                    | 127                |
| 17   | 11.2              | 8.3–9.5  | 5.3–8.5                                | 0.71–1.55               | 21–125             |
| 18   | 6.6               | 8.8      | 11.9                                   | 0.29                    | 14–48              |
| 19   | 9.8               | 9.4      | 5.0–8.1                                | 0.59–1.42               | 23–127             |



sites located close to the effluent discharges of the different industrial plants.

All sampling sites have alkaline pH values ranging from 7.9 to 9.7. There is a difference of about one pH unit between the origin (pH 8.3) and the end (pH 9.4) of the Solou stream. Higher pH values were recorded at one of the waste exits of the fertilizer producing plant, Plant-F. The generally alkaline waters of the Solou stream are likely to cause metal precipitation. However, they can also be harmful for the development of some fish species (Alabaster and Lloyd, 1980; McKee and Wolf, 1963).

There is a substantial drop in dissolved oxygen content in the waters of the Solou stream along its course to the lake Vegoritis. Low dissolved oxygen values were also recorded in the waste effluents of Plant-F, in the municipal and sewage effluents of the city of Ptolemais, and in the waters of the Solou stream at the sampling sites located downstream from the waste discharge points of Plant-F and the city of Ptolemais. However, all recorded values of dissolved oxygen are above the critical levels (Alabaster and Lloyd, 1980). The water bodies are also enriched (data are not shown on Table) in phosphates derived from the municipal effluents of Ptolemais, while Plant-F enriches the waters with ammonia, nitrates, and salts.

*Composition of lignite samples.* Knowledge of the chemical composition is the first step in assessing the impact of coal use on the surrounding area. The results from the analyses of different coal

TABLE II  
Metal contents<sup>a</sup> in Ptolemais-type lignite samples

| Lignite type <sup>b</sup> | Ca      | Ti  | V  | Cr  | Mn  | Fe     | Ni | Cu | Zn | Pb | Br | As | Mo |
|---------------------------|---------|-----|----|-----|-----|--------|----|----|----|----|----|----|----|
| A                         | 31,000  | 380 | 40 | 30  | 50  | 9,400  | 30 | 20 | 8  | 20 | 13 | ND | ND |
| B                         | 24,000  | 380 | 40 | 40  | 50  | 6,100  | 20 | 22 | 21 | 28 | 13 | ND | ND |
| C                         | 133,000 | 510 | 60 | 30  | 170 | 7,300  | 40 | 40 | 9  | 18 | 8  | ND | ND |
| D                         | 29,000  | 870 | 70 | 130 | 120 | 11,500 | 50 | ND | ND | ND | ND | ND | ND |
| E                         | 51,000  | 770 | 80 | 80  | 150 | 9,300  | 50 | 41 | 34 | 18 | 12 | ND | ND |
| F                         | 5,400   | 800 | 20 | 15  | 100 | 16,000 | 15 | 19 | 39 | 16 | —  | 15 | 3  |
| G                         | 10,000  | 500 | 25 | 10  | 50  | 10,000 | 15 | 15 | 50 | 25 | —  | 5  | 5  |

<sup>a</sup> Concentrations are expressed in mg kg<sup>-1</sup>.

<sup>b</sup> Type A is used by the coal-bricks making factory; types B and C are used by the coal-fired power plants; types D and E are used by the nitrogen-fertilizer producing plant. F and G denote the USA and worldwide lignite metal content averages, respectively (After Valkonic, 1983).

ND denotes not detectable by PIXE.

TABLE III  
Metal contents<sup>a</sup> in the Solou stream water upstream and downstream from the waste discharge point of Plant-K

| Date | August, 1982 |     |        |     |        |       | March, 1983 |     |        |     |        |     |
|------|--------------|-----|--------|-----|--------|-------|-------------|-----|--------|-----|--------|-----|
|      | 1            |     | 2      |     | 3      |       | 1           |     | 2      |     | 3      |     |
| Site | S            | P   | S      | P   | S      | P     | S           | P   | S      | P   | S      | P   |
| TDS  | 862          | —   | 716    | —   | 530    | —     | 328         | —   | 874    | —   | 720    | —   |
| Ca   | 53,400       | 580 | 60,300 | 475 | 91,100 | 1,985 | 84,741      | 41  | 41,513 | 408 | 74,338 | 168 |
| Ti   | ND           | 5   | ND     | 4   | 15     | 60    | ND          | 0.6 | ND     | 4.8 | ND     | 4   |
| V    | ND           | ND  | ND     | ND  | 9      | 4     | ND          | 0.3 | ND     | 0.6 | 18     | 0.3 |
| Cr   | 9            | 2   | ND     | 1   | 2      | 8     | 7           | 0.4 | 17     | 1.1 | 9      | 0.7 |
| Mn   | 4            | 2   | ND     | 3   | 29     | 30    | 10          | 0.7 | 5      | 1.6 | 43     | 2.1 |
| Fe   | 22           | 65  | 8.4    | 77  | 22     | 1,160 | 30          | 16  | 11     | 77  | 12     | 75  |
| Ni   | 3            | 1   | 2      | 1   | 3      | 4     | 1           | 0.1 | 4      | 0.4 | 3      | 0.4 |
| Cu   | 5.2          | 1   | 2.9    | 1   | 2.2    | 2     | 2           | 0.1 | 7      | 0.5 | 4      | 0.1 |
| Zn   | 22           | 4   | 15     | 2   | 22     | 6     | 25          | 1.2 | 26     | 1.5 | 24     | 1.1 |
| As   | 1            | ND  | 1      | ND  | 1      | 0.3   | ND          | ND  | ND     | ND  | 1.4    | ND  |
| Se   | ND           | ND  | ND     | ND  | ND     | ND    | 0.1         | ND  | 0.3    | ND  | 0.7    | ND  |
| Br   | 31           | ND  | 15     | ND  | 11     | ND    | 2           | ND  | 34     | ND  | 32     | ND  |
| Rb   | 5            | ND  | ND     | ND  | ND     | ND    | ND          | ND  | 10     | ND  | 6      | ND  |
| Sr   | 153          | ND  | 188    | ND  | 187    | ND    | 94          | ND  | 190    | 0.4 | 202    | ND  |
| Mo   | 26           | ND  | ND     | ND  | ND     | ND    | ND          | ND  | 20     | ND  | 11     | ND  |
| Pb   | 8            | ND  | 6      | ND  | 5      | 1     | 2           | ND  | 7      | 0.5 | 3      | 0.3 |

<sup>a</sup> Concentrations are in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .  
S, P, TDS, and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

type samples taken from the area of Ptolemais and utilized by the industrial plants of the area are given in Table II.

Comparing the metal contents of the Ptolemais-type lignite samples (A, B, C, D, E) (Table II) with reported metal contents of USA-type lignites (F) and worldwide lignite averages (G) (Valkovic, 1983), it is concluded that in general the Ptolemais-type lignite samples have higher concentrations of Ca, V, Cr, and Ni, the concentration of Zn is low, while As and Mo are not detectable. In detail the lignite type C has high levels of Ca, Mn, Ni, and Cu, while the lignite types D and E are rich in Mn, Cr, Ni, and Cu.

*Plant-K.* The metal contents in the water samples collected from the Solou stream upstream (site 1) and downstream (sites 2 and 3), respectively, from the waste discharge point of the coal-fired power plant, Plant-K, are presented in Table III. There is a progressive decrease in total dissolved solids (TDS) from site 1 to site 3 in the August 1982 sampling, whereas the situation is reversed in the March 1983 sampling (Table III). In the August 1982 sampling, there is also an increase in Ca, Ti, V, Mn, and Fe and a decrease in Br, Mo, and Pb along the course of the Solou stream from site 1 to site 3, while in the sampling of March 1983 Ti, V, Cr, Mn, Fe, Ni, Cu, Br, Rb, Sr, Mo, and Pb are increased and Ca is decreased (Table III).

*Plant-B.* The metal contents in the raw waste effluent (site 4) and the treated waste effluent (site 5) samples of the coal-bricks factory, Plant-B are given in Table IV. There is a substantial decrease in the metal contents of the treated waste effluents of Plant-B. Both the water soluble and the particulate forms of Ca, Mn, Fe, and As and the particulate forms of Ti, V, Ni, Cu, Sr, and Pb are decreased, while the water soluble forms of Zn, Br, and Sr and the particulate form of Zn are not changed.

*Plant-P.* The metal contents in the waste effluents of the coal-fired power plant, Plant-P (sites 6 and 7) and the pond (site 8) are given in Table V. These effluents are enriched mainly in Ca, Fe, Sr, and Mn. At site 7, where the municipal wastes from the factory workers community are discharged, there is also a slight increase in the Pb content.

The ultimate effect on the water quality of the Solou stream brought about by the industries operated in the areas of Kardias and Ptolemais, as far as metal pollution is concerned, is indicated by

TABLE IV  
Metal contents<sup>a</sup> in waste effluent samples of Plant-B

| Date  | August, 1982 |        |        |       | March, 1983 |     |
|-------|--------------|--------|--------|-------|-------------|-----|
| Sites | 4            |        | 5      |       | 5           |     |
|       | S            | P      | S      | P     | S           | P   |
| TDS   | 585          | —      | 515    | —     | 688         | —   |
| Ca    | 103,700      | 12,914 | 80,300 | 1,030 | 86,718      | 720 |
| Ti    | ND           | 107    | ND     | 5     | ND          | 2.6 |
| V     | ND           | 7      | ND     | ND    | 26          | ND  |
| Cr    | ND           | 11     | ND     | ND    | ND          | ND  |
| Mn    | 19           | 36     | ND     | 5     | 13          | 1.3 |
| Fe    | 71           | 2,300  | 28     | 182   | 19          | 75  |
| Ni    | ND           | 4      | ND     | 0.4   | 3           | 0.2 |
| Cu    | ND           | 6      | 2.4    | 0.5   | 3           | 0.4 |
| Zn    | 17           | 3      | 17     | 3     | 27          | 1.0 |
| As    | 1            | 1      | ND     | ND    | ND          | ND  |
| Br    | 12           | ND     | 10     | ND    | 26          | ND  |
| Rb    | ND           | ND     | ND     | ND    | 4           | ND  |
| Sr    | 200          | 18     | 195    | ND    | 227         | 0.4 |
| Mo    | ND           | ND     | ND     | ND    | ND          | ND  |
| Pb    | ND           | 4      | ND     | ND    | 2           | ND  |

<sup>a</sup> Concentrations are in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .

S, P, TDS, and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

the analyses of water samples taken from site 9 (Table VI). By comparing site 1 (Table III) with site 9 it is indicated that an enrichment takes place at site 9 in Ca, Fe, Mn, and Sr.

In Table VI are also given the results from the analyses of water samples taken from site 10 which is located on the Solou stream and downstream from the discharge point of Plant-SH. This unit during its working days enriches the stream mainly in Fe and secondarily in Mn and/or Ca. The iron content in the waste effluents of Plant-SH is estimated to be 1,500 ppm (data are not shown on Table).

*Plant-F.* The results from the analyses of the waste effluents of the nitrogen-fertilizer producing plant, Plant-F, are presented in Table VII. The effluents collected from site 12 (waste water) appear to be more concentrated in various elements than the respective effluents from site 11 (chemical wastes). The enrichment at site 12 is especially notable for the elements Ca, Fe, Mn, Sr, Mo, Ni, Br,

TABLE V  
Metal contents\* in waste effluent samples of Plant-P

| Date  | August, 1982 |         |        | March, 1983 |       |       | October, 1983 |     |     |
|-------|--------------|---------|--------|-------------|-------|-------|---------------|-----|-----|
|       | S            | P       | S      | S           | P     | S     | P             | S   | P   |
| Sites | 6            | 7       | 6      | 7           | 6     | 7     | 8             | 8   | 8   |
| TDS   | 524          | 833     | 777    | 978         | —     | —     | 544           | —   | —   |
| Ca    | 49,200       | 102,600 | 73,930 | 72,062      | 2,079 | 3,085 | 32,556        | 249 | 249 |
| Ti    | ND           | ND      | ND     | ND          | 10    | 34    | ND            | ND  | 4   |
| V     | 30           | ND      | ND     | 33          | 0.9   | 2.2   | 10            | ND  | ND  |
| Cr    | ND           | 12      | ND     | 5           | 1.3   | 4.4   | 5             | ND  | ND  |
| Mn    | 15           | 9       | 16     | 89          | 6.0   | 19.5  | 5             | 5   | 3   |
| Fe    | 87           | 45      | 26     | 15          | 215   | 955   | 25            | 57  | 57  |
| Ni    | 3            | 4       | 2      | 6           | 0.9   | 3.2   | 2             | ND  | ND  |
| Cu    | 3            | 8       | 4      | 2           | 0.8   | 33    | 7             | 1   | 1   |
| Zn    | 10           | 16      | 16     | 22          | 1.9   | 51    | 87            | 5   | 5   |
| As    | 3            | 2       | 2      | 6           | ND    | 1     | 3             | ND  | ND  |
| Se    | ND           | ND      | ND     | 1           | ND    | ND    | ND            | ND  | ND  |
| Br    | 11           | 36      | 51     | 48          | ND    | 1     | 7             | ND  | ND  |
| Rb    | 5            | 8       | 6      | 9           | ND    | 1     | 6             | ND  | ND  |
| Sr    | 160          | 327     | 264    | 294         | 1.9   | 5.1   | 122           | 1   | 1   |
| Y     | ND           | ND      | ND     | ND          | ND    | ND    | ND            | ND  | ND  |
| Zr    | ND           | ND      | ND     | ND          | ND    | ND    | ND            | ND  | ND  |
| Mo    | 11           | ND      | 12     | 22          | ND    | ND    | 8             | ND  | ND  |
| Pb    | ND           | 12      | ND     | 1           | ND    | 9     | 5             | ND  | 1   |

\* Concentrations are in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .  
S, P, TDS, and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

TABLE VI  
Metal contents\* in the Solou stream water in the area of Plant-SH

| Date | June, 1982 |     |        | August, 1982 |        |     | March, 1983 |     |        | October, 1983 |        |     |        |       |       |       |
|------|------------|-----|--------|--------------|--------|-----|-------------|-----|--------|---------------|--------|-----|--------|-------|-------|-------|
|      | S          | P   | S      | S            | P      | S   | S           | P   | S      | P             | S      | P   |        |       |       |       |
| TDS  | 1,007      | --- | 979    | ---          | 662    | --- | 619         | --- | 791    | ---           | 846    | --- | 588    | ---   | 760   | ---   |
| Ca   | 86,000     | 161 | 93,000 | 140          | 73,000 | 344 | 73,800      | 734 | 54,498 | 71            | 71,191 | 337 | 43,605 | 1,048 | 9,102 | 2,452 |
| Ti   | ND         | ND  | ND     | ND           | ND     | 21  | ND          | 18  | ND     | 1.0           | ND     | 6.0 | 2      | 18    | ND    | 5     |
| V    | ND         | ND  | 16     | ND           | 11     | ND  | 25          | ND  | ND     | 0.1           | ND     | 0.3 | 12     | 1     | 11    | ND    |
| Cr   | ND         | ND  | 60     | ND           | ND     | 7   | ND          | 5   | 5      | 0.4           | ND     | 0.4 | 8      | 3     | 12    | 20    |
| Mn   | 78         | 72  | 23     | ND           | 10     | 8   | 13          | 9   | 16     | 0.9           | 27     | 3.5 | 4      | 5     | 3     | 3     |
| Fe   | 78         | 72  | 222    | 53           | 26     | 328 | 135         | 229 | 20     | 27            | 61     | 92  | 28     | 465   | 97    | 188   |
| Ni   | 3          | ND  | ND     | ND           | ND     | 1   | ND          | 1   | 4      | 0.1           | 2      | ND  | 1      | 5     | 15    | 1     |
| Cu   | 10         | 1   | 7      | 2            | 5      | 2   | 6           | 1   | 5      | 0.4           | 3      | 2   | 2      | 2     | 2     | 2     |
| Zn   | 27         | 8   | 15     | 9            | 13     | 6   | 19          | 7   | 32     | 1.3           | 32     | 3.8 | 10     | 6     | 17    | 13    |
| As   | 2          | ND  | 5      | ND           | 1      | ND  | ND          | ND  | 0.7    | ND            | 3      | ND  | 1      | ND    | 2     | ND    |
| Se   | ND         | ND  | ND     | ND           | ND     | ND  | ND          | ND  | 2.0    | ND            | 0.8    | ND  | ND     | ND    | 1     | ND    |
| Br   | 36         | 1   | 34     | ND           | 37     | ND  | 19          | ND  | 40     | ND            | 40     | ND  | 20     | ND    | 8     | ND    |
| Rb   | 13         | ND  | 9      | ND           | 4      | ND  | 8           | ND  | 5      | ND            | 0.8    | ND  | 4      | ND    | 2     | ND    |
| Y    | ND         | ND  | ND     | ND           | ND     | ND  | ND          | ND  | ND     | ND            | ND     | ND  | ND     | ND    | ND    | ND    |
| Zr   | ND         | ND  | ND     | ND           | ND     | ND  | ND          | ND  | ND     | ND            | ND     | ND  | ND     | ND    | ND    | ND    |
| Sr   | 250        | ND  | 290    | ND           | 195    | ND  | 200         | 4   | 156    | ND            | 222    | ND  | 117    | ND    | 91    | 5     |
| Mo   | 15         | ND  | 15     | ND           | 13     | ND  | 10          | ND  | 13     | ND            | 10     | ND  | 14     | ND    | ND    | ND    |
| Pb   | 7          | 6   | ND     | 4            | 3      | ND  | 10          | ND  | 4      | 0.4           | 2      | ND  | 2      | ND    | 4     | ND    |

\* Concentrations are in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .

S, P, TDS, and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

TABLE VII  
Metal contents\* in the liquid waste effluents of Plant-F

| Date  | August, 1982 |       |        | March, 1983 |        |      | April, 1983 |        |         | October, 1983 |        |       |        |
|-------|--------------|-------|--------|-------------|--------|------|-------------|--------|---------|---------------|--------|-------|--------|
|       | S            | P     | S      | P           | S      | P    | S           | P      | S       | P             | S      | P     |        |
| Sites | 11           | 12    | 11     | 12          | 11     | 12   | 11          | 12     | 11      | 12            | 11     | 12    |        |
| TDS   | 871          | —     | 503    | 740         | —      | 512  | —           | 1,192  | —       | 632           | —      | 956   |        |
| Ca    | 20,300       | 3,200 | 11,118 | 2,800       | 17,171 | 859  | 90,560      | 15,000 | 147,000 | 4,600         | 38,000 | 1,600 | 94,972 |
| Ti    | ND           | ND    | ND     | 34          | ND     | 1.3  | ND          | 30     | ND      | 78            | 5      | 12    | 2      |
| V     | ND           | ND    | ND     | 6           | ND     | 0.1  | 21          | 3      | ND      | 7             | 12     | 1     | 16     |
| Cr    | 9            | 18    | 60     | 28          | 35     | 18.5 | 15          | 34     | 10      | 14            | 4      | 6     | 9      |
| Mn    | ND           | 3     | 130    | 22          | 8      | 2    | 40          | 14     | 30      | 3             | 6      | 9     | 23     |
| Fe    | 71           | 233   | 1,000  | 2,480       | 77     | 130  | 260         | 1,422  | 1,088   | 1,529         | 38     | 264   | 125    |
| Ni    | 4            | ND    | 40     | 2           | 5      | 0.1  | 13          | 5      | 41      | 3             | 2      | 2     | 7      |
| Cu    | 2.7          | 3     | ND     | 9           | 1      | 0.7  | 10          | 7      | 8       | 6             | 4      | 2     | 12     |
| Zn    | 22           | 9     | 70     | 58          | 35     | 2.4  | 30          | 24     | 25      | 18            | 9      | 7     | 41     |
| As    | ND           | ND    | ND     | 2           | 0.5    | ND   | 7           | ND     | 24      | 3             | 1      | ND    | 2      |
| Se    | ND           | ND    | ND     | ND          | ND     | ND   | 6           | ND     | 14      | ND            | ND     | ND    | 1      |
| Br    | 9            | ND    | ND     | ND          | 2      | ND   | 32          | ND     | 31      | ND            | 19     | ND    | 11     |
| Rb    | ND           | ND    | ND     | ND          | 3      | ND   | 21          | ND     | 105     | ND            | ND     | ND    | 3      |
| Sr    | 120          | 5     | 250    | ND          | 96     | 1.7  | 292         | 30     | 376     | 8             | 136    | ND    | 287    |
| Mb    | ND           | ND    | ND     | ND          | ND     | ND   | 30          | ND     | 43      | ND            | 5      | ND    | 15     |
| Pb    | ND           | ND    | ND     | 95          | 3      | ND   | 3           | ND     | 6       | 4             | 3      | 1     | 5      |

\* Concentrations are in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .

S, P, TDS, and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

and As. The waste effluents at site 11 are mainly rich in Cr. The elements present at site 11 are probably coming from the utilized coal types, types D and E, (Table II). The source of the elements at site 12 is the waste water from the factory utility units. The waste effluents of this plant do not receive any treatment before being discharged into the Solou stream and therefore, Plant-F can be considered as a serious pollution point for the area under study. In addition, the temperature in the waste effluents of Plant-F is about 10°C higher than the average temperature of the Solou stream water. These effluents have also the highest pH, conductivity, and turbidity values and the lowest dissolved oxygen values recorded in the area.

In Table VIII are shown the metal contents in the water of site 13 which is located downstream from the waste discharge points of Plant-F.

*City of Ptolemais.* The metal contents in the municipal and

TABLE VIII  
Metal contents<sup>a</sup> at sampling site 13

| Date | August, 1982   |     | March, 1983 |      | May, 1983 |       | October, 1983 |      |
|------|----------------|-----|-------------|------|-----------|-------|---------------|------|
|      | S <sup>b</sup> | P   | S           | P    | S         | P     | S             | P    |
| TDS  | —              | —   | 628         | —    | 724       | —     | 624           | —    |
| Ca   | —              | 921 | 37,156      | 1446 | 19,000    | 4,573 | 44,705        | 1215 |
| Ti   | —              | ND  | ND          | 0.9  | ND        | 15    | ND            | 11   |
| V    | —              | ND  | 29          | 0.3  | 4         | 2     | 14            | 1    |
| Cr   | —              | 13  | 11          | 1.5  | ND        | 8     | ND            | 4    |
| Mn   | —              | 5   | 9           | 1.9  | 7         | 4     | 13            | 7    |
| Fe   | —              | 585 | 107         | 38   | 374       | 526   | 106           | 237  |
| Ni   | —              | ND  | 4           | 0.4  | 20        | 2     | 5             | 2    |
| Cu   | —              | 3   | 3           | 0.7  | 4         | 2     | 4             | 3    |
| Zn   | —              | 12  | 19          | 1.4  | 20        | 8     | 12            | 7    |
| As   | —              | ND  | 1.3         | ND   | 4         | ND    | ND            | ND   |
| Se   | —              | ND  | ND          | 2.2  | 4         | ND    | 1             | ND   |
| Br   | —              | ND  | 25          | ND   | 25        | ND    | 8             | ND   |
| Rb   | —              | ND  | 4           | ND   | 34        | ND    | 6             | 1    |
| Sr   | —              | ND  | 147         | ND   | 106       | 11    | 140           | 3    |
| Mo   | —              | ND  | 7           | ND   | 13        | ND    | 6             | ND   |
| Pb   | —              | 4   | 2           | ND   | 5         | 5     | 5             | 3    |

<sup>a</sup> Concentrations are expressed in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .

<sup>b</sup> This sample has been destroyed.

S, P, TDS, and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.



sewage waste effluents of the city of Ptolemais and in the water samples taken from a small by-stream of the Solou stream upstream and downstream from the point where the municipal and sewage waste effluents of Ptolemais City are discharged are shown in Table IX. The municipal and sewage wastes (site 16) are rich mainly in Fe, Zn, Mn, Sr, Pb, and Br. However, the concentrations of the respective elements in the water of the receiving by-stream are not significantly affected (site 15). It is more likely that some of the elements are precipitated by phosphate and/or other ion loads which are present in the municipal and sewage waste effluents (data are not shown). At site 14 the concentrations of Fe, Zn, and Mn are relatively high also due to the waste effluents discharging from a dairy farm located in the area.

By comparing the concentrations of trace elements in the municipal wastewaters of U.S. (Gallow and Jacobs, 1977; Dowdy, *et al.*, 1977) and the municipal wastewaters of the city of Ptolemais (Table IX) it can be concluded that the city of Ptolemais is not yet a serious pollution source for the Solou Stream and/or the Vegoritis Lake.

*Solou Stream.* The profile of the concentrations of the different metallic elements in the water of the Solou stream along its way to the Lake Vegoritis is illustrated by the analyses samples taken from sites 1, 2, 3, 9, 10, 13, 17, and 19 (Tables III, VI, VIII, and X). These sites have been selected in such a way so that the impact on the water quality of the Solou stream by a certain industrial activity can be assessed. A comparison between Tables VIII and X shows that TDS and the concentrations of some elements are higher in August (dry season) than in March. The equilibrium between soluble and particulate metal loads is also changed. In August, the profile of metal concentrations is affected mainly by the industrial activities of the surrounding area, while in March this profile is influenced primarily by rain precipitation and soil erosion.

The status of the Solou stream after receiving the waste effluents of Plant-F is shown in Table VIII and after receiving the municipal and sewage wastes from Ptolemais City in Table X (site 17). The whole picture indicates that Plant-F causes only a slight enrichment in Fe and Cr. Apparently, different reactions which take place in the water of the stream precipitate most of the elements which are discharged from the two point pollution sources. Table X shows

TABLE IX  
Metal contents<sup>a</sup> in the municipal wastes of the city of Ptolemais and the small by-stream where they are discharged

| Date  | August, 1982 |       |        |       | March, 1983 |     |        |     | October, 1983 |       |  |  |
|-------|--------------|-------|--------|-------|-------------|-----|--------|-----|---------------|-------|--|--|
| Sites | 14           |       | 15     |       | 14          |     | 15     |     | 16            |       |  |  |
|       | S            | P     | S      | P     | S           | P   | S      | P   | S             | P     |  |  |
| TDS   | 227          | —     | 341    | —     | 264         | —   | 353    | —   | 530           | —     |  |  |
| Ca    | 44,600       | 721   | 39,100 | 955   | 51,269      | 26  | 53,241 | 99  | 25,333        | 4,450 |  |  |
| Ti    | ND           | 275   | ND     | 71    | ND          | 1.8 | ND     | 2.1 | 2             | 124   |  |  |
| V     | ND           | 14    | 10     | 2     | ND          | ND  | 8      | 0.2 | 13            | 7     |  |  |
| Cr    | ND           | 8     | ND     | 7     | 1           | 0.3 | 1      | 0.2 | ND            | 4     |  |  |
| Mn    | 25           | 78    | 110    | 15    | 29          | 1.4 | 53     | 1.2 | 47            | 23    |  |  |
| Fe    | 44           | 4,130 | 70     | 1,130 | 33          | 47  | 49     | 49  | 97            | 1,126 |  |  |
| Ni    | 2            | 5     | 3      | 1     | 2           | 0.2 | 1      | 0.1 | 6             | 5     |  |  |
| Cu    | 4            | 5     | 4      | 3     | 3           | 0.1 | 1      | 0.5 | 5             | 8     |  |  |
| Zn    | 36           | 13    | 28     | 14    | 27          | 0.8 | 38     | 3.2 | 50            | 69    |  |  |
| As    | ND           | ND    | 3      | ND    | 0.5         | ND  | 0.2    | ND  | 3             | 3     |  |  |
| Se    | ND           | ND    | ND     | ND    | ND          | ND  | 0.3    | ND  | ND            | ND    |  |  |
| Br    | 2            | ND    | 12     | ND    | 4           | ND  | 11     | ND  | 44            | ND    |  |  |
| Rb    | ND           | ND    | ND     | ND    | 1           | ND  | 2      | ND  | 14            | ND    |  |  |
| Sr    | 88           | ND    | 135    | ND    | 86          | ND  | 115    | ND  | 149           | 7     |  |  |
| Y     | ND           | ND    | ND     | ND    | ND          | ND  | ND     | ND  | ND            | ND    |  |  |
| Zr    | ND           | ND    | ND     | ND    | ND          | ND  | ND     | ND  | ND            | ND    |  |  |
| Mo    | ND           | ND    | ND     | ND    | ND          | ND  | 2      | ND  | ND            | ND    |  |  |
| Pb    | ND           | ND    | 4      | 4     | 1           | ND  | 2      | ND  | 5             | 10    |  |  |

<sup>a</sup> Concentrations are in  $\mu\text{g l}^{-1}$  except for TDS which is in  $\text{mg l}^{-1}$ .

S, P, TDS and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

also the results from water samples taken from the by-stream St. Christophoros (site 18). The water of this stream is not polluted and hence it might serve as a dilutant for the water of the Solou stream. However, the presence of As in the water of St. Christophoros during the summer might be an indication of pollution by arsenical pesticides which are used in the surrounding agricultural area.

In conclusion, the Solou stream enriches Vegoritis Lake in metals at levels not considered likely to create serious pollution problems at the present time. This is in agreement with our previous work (Mourkides *et al.*, 1983). However, the continuous enrichment of the lake with metallic elements, regardless of how low this enhancement is, will eventually accumulate high levels of metals creating a

TABLE X  
Metal contents\* at the sampling sites 17, 18, and 19

| Date | August, 1982 |     |         |     |        |       | March, 1983 |     |        |     |        |     | May, 1983 |       |       |       |    |    |
|------|--------------|-----|---------|-----|--------|-------|-------------|-----|--------|-----|--------|-----|-----------|-------|-------|-------|----|----|
|      | Site         | 17  | 18      | 18  | 19     | 19    | 17          | 17  | 18     | 18  | 19     | 19  | 17        | 17    | 17    | 17    | 19 | 19 |
| TDS  | 733          | —   | 449     | —   | 734    | —     | 552         | —   | 358    | —   | 632    | —   | 584       | —     | 496   | —     | —  | —  |
| Ca   | 67,900       | 900 | 116,700 | 414 | 74,800 | 1,875 | 51,066      | 583 | 75,227 | 128 | 59,286 | —   | 28,000    | 4,265 | 4,200 | 6,171 | —  | —  |
| Ti   | ND           | 18  | ND      | 6   | ND     | 38    | ND          | 2.0 | ND     | 1.5 | ND     | 1.5 | ND        | 20    | ND    | 15    | —  | —  |
| V    | ND           | ND  | ND      | ND  | ND     | 5     | 40          | 0.7 | 6      | 0.3 | ND     | 0.3 | ND        | 5     | ND    | 2     | —  | —  |
| Cr   | ND           | 15  | ND      | 1   | 5      | 10    | 8           | 1.2 | 3      | 0.5 | 7      | 0.7 | 4         | 13    | 5     | 12    | —  | —  |
| Mn   | 77           | 7   | 2       | 1   | 50     | 9     | 41          | 1.6 | 5      | 0.6 | 46     | 2.0 | 29        | 16    | 20    | 16    | —  | —  |
| Fe   | 400          | 450 | 25      | 63  | 412    | 505   | 57          | 53  | 20     | 26  | 51     | 40  | 239       | 528   | 137   | 463   | —  | —  |
| Ni   | 7            | 1   | ND      | 1   | 5      | 2     | 6           | 0.6 | 2      | 0.3 | 2      | 0.1 | 11        | 1     | 8     | 2     | —  | —  |
| Cu   | 9            | 3   | 0.4     | 0.4 | 5      | 3     | 3           | 0.6 | 1      | 0.1 | 3      | 0.3 | 4         | 2     | 3     | 2     | —  | —  |
| Zn   | 21           | 14  | 16      | 2   | 16     | 13    | 24          | 2   | 29     | 1   | 31     | 2   | 21        | 11    | 18    | 12    | —  | —  |
| As   | 3            | ND  | ND      | ND  | 2      | ND    | ND          | ND  | 0.3    | ND  | 2      | ND  | 3         | ND    | 1     | ND    | —  | —  |
| Se   | ND           | ND  | ND      | ND  | ND     | ND    | ND          | 0.4 | ND     | ND  | ND     | 0.7 | 2         | ND    | 1     | ND    | —  | —  |
| Br   | 9            | ND  | 4       | ND  | 13     | ND    | 17          | ND  | 1      | ND  | 46     | ND  | 12        | ND    | 9     | ND    | —  | —  |
| Rb   | 18           | ND  | ND      | ND  | 18     | ND    | 7           | ND  | 2      | ND  | 4      | ND  | 22        | ND    | 16    | ND    | —  | —  |
| Sr   | 217          | ND  | 141     | ND  | 225    | 2     | 186         | ND  | 98     | ND  | 175    | ND  | 125       | 11    | 147   | 8     | —  | —  |
| Mo   | ND           | ND  | ND      | ND  | ND     | ND    | 8           | ND  | ND     | ND  | 6      | ND  | 14        | ND    | 11    | ND    | —  | —  |
| Pb   | 5            | ND  | 2       | ND  | 10     | 3     | 1           | ND  | 1      | ND  | 3      | 0.2 | 4         | 5     | 4     | 3     | —  | —  |

\* Concentrations are in  $\mu\text{g l}^{-1}$ , except for TDS which is in  $\text{mg l}^{-1}$ .  
S, P, TDS and ND denote soluble, particulate, total dissolved solid, and not detectable, respectively.

toxic environment for the development of the fauna and flora. For instance, if an element is present in the water of the Solou stream at a concentration of 10 ppb and considering a flow rate for the Solou stream of  $0.3 \text{ m}^3 \text{ sec}^{-1}$  it will give Vegoritis Lake a load of 94.6 kg/year. In order to check the effect of this level of enrichment on the water quality of Vegoritis Lake, water and sediment grab samples were also taken from two stations (I and II) located at the northeast end of the Lake (Figure 2). The results of these analyses are presented in Tables XI and XII. Comparisons of these data with previously reported data (Mourkides, *et al.*, 1983) indicate that the concentrations of As, Br, and Sr have been decreased while the concentrations of all other elements studied have been increased. The concentrations of Fe, V, Cu, Mn, and Cr have been increased

TABLE XI  
Metal contents<sup>a</sup> in water samples<sup>b</sup> from Vegoritis Lake

| Sites <sup>c</sup> | IA     |     | IB     |     | IIA    |     | IIB    |     |
|--------------------|--------|-----|--------|-----|--------|-----|--------|-----|
|                    | S      | P   | S      | P   | S      | P   | S      | P   |
| TDS                | 344    | —   | 336    | —   | 332    | —   | 339    | —   |
| Ca                 | 22,375 | 96  | 21,885 | 98  | 23,826 | 66  | 21,512 | 89  |
| Ti                 | ND     | 3   | 2      | 3   | ND     | 2   | 3      | 2   |
| V                  | 8      | ND  | 5      | ND  | 4      | ND  | 6      | ND  |
| Cr                 | 1      | ND  | 2      | 1   | ND     | ND  | 2      | 1   |
| Mn                 | 2      | 1   | 3      | 1   | 3      | 1   | 4      | 1   |
| Fe                 | 21     | 35  | 17     | 45  | 20     | 31  | 16     | 24  |
| Ni                 | 2      | 1   | 3      | 0.5 | 2      | 0.5 | 1      | 0.5 |
| Cu                 | 2      | 0.5 | 3      | 0.5 | 3      | 0.5 | 3      | 0.5 |
| Zn                 | 8      | 4   | 16     | 6   | 15     | 4   | 22     | 4   |
| As                 | 1      | ND  | 1      | ND  | 1      | ND  | 1      | ND  |
| Se                 | ND     | ND  | ND     | ND  | ND     | ND  | ND     | ND  |
| Br                 | 5      | ND  | 3      | ND  | 5      | ND  | 4      | ND  |
| Rd                 | 2      | ND  | 3      | ND  | 1      | ND  | 2      | ND  |
| Sr                 | 96     | ND  | 90     | ND  | 101    | ND  | 91     | ND  |
| Y                  | ND     | ND  | ND     | ND  | ND     | ND  | ND     | ND  |
| Zr                 | ND     | ND  | ND     | ND  | ND     | ND  | ND     | ND  |
| Mo                 | 2      | ND  | 3      | ND  | ND     | ND  | 2      | ND  |
| Pb                 | 2      | ND  | 3      | ND  | 2      | ND  | 3      | ND  |

<sup>a</sup> Concentrations of TDS and Ca are in  $\text{mg l}^{-1}$  and of all other elements in  $\mu\text{g l}^{-1}$ .

<sup>b</sup> Sampling was made in September, 1983.

<sup>c</sup> I and II are sampling stations located at the northeast site of Vegoritis Lake. "A" denotes surface water and "B" bottom water.

TDS, S, P, and ND denote total dissolved solid, soluble, particulate, and not detectable, respectively.

TABLE XII  
Metal contents<sup>a</sup> in Vegoritis Lake  
sediment samples<sup>b</sup>

| Site | I    | II   |
|------|------|------|
| Ca   | 87.0 | 88.0 |
| Ti   | 4.3  | 5.0  |
| Mn   | 0.8  | 0.9  |
| Fe   | 55.0 | 55.0 |
| V    | 136  | 245  |
| Cr   | 455  | 439  |
| Ni   | 157  | 243  |
| Cu   | 41   | 38   |
| Zn   | 82   | 93   |
| As   | 7    | ND   |
| Se   | ND   | ND   |
| Br   | 4    | ND   |
| Rb   | 95   | 92   |
| Sr   | 137  | 147  |
| Y    | 28   | 32   |
| Zr   | 122  | 120  |
| Pb   | 51   | 56   |

<sup>a</sup> Concentrations of Ca, Ti, Mn, and Fe are in  $\text{g kg}^{-1}$  while for all other elements are in  $\text{mg kg}^{-1}$ .

<sup>b</sup> Sampling was made in September, 1983.

ND denotes not detectable.

by 1180%, 433%, 400%, 337% and 328%, respectively. The concentrations of the other elements have been increased at a lesser rate. The level of the enrichment is lower at station II than at station I indicating that the loads of some elements are diluted as they enter the lake and for other elements these loads are decreased via precipitation processes occurring on the way from station I to station II. However, Mn and Cu were found to be present in higher concentrations at station II than station I. It is suspected that this metal enrichment in the northeast site of Lake Vegoritis is caused by the overflow waters from Lake Petron. This lake is in the vicinity of Vegoritis Lake to which it is connected by a canal (Figure 2). Analyses of sediment samples taken from station II indicate mainly a decrease in the concentrations of Ca and Pb and an increase in Cr and As. With the estimated rate of metal pollution in the Lake Vegoritis it is expected that the northeast site of the lake will be

unproductive in a few decades. Therefore, the treatment of the industrial waste effluents discharged into the Solou stream should be mandatory for all the industries of the area.

*Sediment Enrichment.* Kemp *et al.*, (1974) introduced a ratio, the Sediment Enrichment Factor (SEF), to quantify the element enrichment in recent sediment core samples from Lake Erie and to compare them internally. The SEF parameter was not applied strictly to our data, however, since the PIXE method does not determine Al, and Al has been replaced by Ti to normalize the data. Kemp was studying the anthropogenic effects on Lake Erie and used as reference depth the concentrations of metals in the sediment layers below the Ambrosia horizon. Since our interest is limited to the effects of industry over the last 25 years the lower sections of the core sediment samples were used as reference. The formula used for calculation of the SEF values is the formula proposed by (Kemp, *et al.*, (1976)) is

$$SEF = [E_S/Ti_S] - (E_A/Ti_A)/(E_A/Ti_A)$$

where,  $E_S$  is the concentration of an element E in a particular fraction S and  $Ti_S$  is the concentration of Ti in the same fraction;  $E_A$  is the concentration of an element E in fraction A which is at the horizon upon which this calculation is based and  $Ti_A$  is the concentration of Ti in fraction A.

The SEF value is an estimate of the degree of normalcy of the most recent sediment. Zero SEF values represent elements with constant concentrations in the layers of a core sediment; positive values indicate increase of element concentrations and negative values indicate loss/dilution of the elements from the sediment matrix. It was not possible to date the cores. The SEF values were calculated based upon the elemental composition of the 28–30 cm horizon of site 1, the 6–8 cm layer of site 9, and the 10–12 cm horizon of site 13. The profile of metal contents in the Solou stream sediment is shown in Table XIII and Table XIV presents the sediment enrichment factors calculated according to the proposed modification. The concentrations of the elements Ti, V, Cr, Mn, Fe, Ni, Rb, Pb, Y, and Zr are lower in the sediment fractions 5 and 6 and they are progressively increased toward the surface of the sediment core. In contrary the concentrations of Ca, Cu, Sr are maximum in the sediment fractions 5 and 6 and they are lowered

TABLE XIII  
Metal contents<sup>a</sup> in the Solou stream sediment profile at origin (Site 1)

|    | Sediment fractions <sup>b</sup> |        |        |        |         |         |        |        |        |        |        |        |        |        |
|----|---------------------------------|--------|--------|--------|---------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
|    | 1                               | 2      | 3      | 4      | 5       | 6       | 7      | 8      | 9      | 10     | 11     | 12     | 13     | 14     |
| Ca | 64,979                          | 57,879 | 52,688 | 62,932 | 112,902 | 105,510 | 88,043 | 45,777 | 50,829 | 54,102 | 44,136 | 24,907 | 19,474 | 22,523 |
| Ti | 658                             | 725    | 575    | 661    | 157     | 266     | 519    | 1,207  | 1,155  | 1,131  | 1,256  | 1,522  | 1,487  | 1,571  |
| V  | 53                              | 44     | 72     | 31     | 33      | 33      | 55     | 89     | 68     | 108    | 101    | 92     | 56     | 135    |
| Cr | 111                             | 175    | 161    | 127    | 47      | 43      | 100    | 136    | 130    | 194    | 197    | 157    | 122    | 175    |
| Mn | 264                             | 268    | 253    | 282    | 132     | 124     | 222    | 107    | 111    | 327    | 339    | 298    | 386    | 332    |
| Fe | 10,904                          | 11,482 | 9,847  | 11,242 | 5,550   | 7,239   | 8,117  | 12,536 | 12,374 | 11,572 | 14,314 | 17,511 | 16,995 | 17,559 |
| Ni | 54                              | 80     | 81     | 80     | 19      | 25      | 52     | 58     | 74     | 79     | 90     | 67     | 105    | 85     |
| Cu | 23                              | 15     | 21     | 23     | 33      | 36      | 28     | 22     | 4      | 10     | 11     | 21     | 11     | 9      |
| Zn | 23                              | 21     | 29     | 22     | 26      | 26      | 28     | 25     | 24     | 20     | 28     | 30     | 28     | 34     |
| As | 6                               | ND     | 3      | 6      | 4       | 3       | 2      | 8      | 8      | 3      | 7      | ND     | 8      | 6      |
| Se | 3                               | ND     | ND     | ND     | ND      | ND      | ND     | ND     | ND     | ND     | ND     | ND     | ND     | ND     |
| Br | 2                               | 1      | 2      | ND     | ND      | ND      | ND     | ND     | ND     | 4      | ND     | ND     | ND     | ND     |
| Rb | 17                              | 19     | 15     | 18     | 6       | 6       | 14     | 26     | 22     | 20     | 24     | —      | 33     | 34     |
| Sr | 53                              | 50     | 63     | 53     | 84      | 85      | 64     | 28     | 30     | 30     | 26     | —      | 22     | 24     |
| Y  | ND                              | 7      | 11     | ND     | ND      | ND      | 6      | 11     | 7      | 9      | 7      | —      | —      | 14     |
| Zr | 19                              | 29     | 25     | 19     | ND      | ND      | 20     | 43     | 44     | 37     | 43     | —      | 62     | 62     |
| Pb | 3                               | 11     | 12     | ND     | ND      | ND      | 6      | ND     | ND     | 9      | 3      | —      | 4      | 9      |

<sup>a</sup> Concentrations are in mg kg<sup>-1</sup>.

<sup>b</sup> The sediment core sample was taken from the origin of the Solou stream, sampling site No 1. Each fraction is of 2-cm depth; No 1 fraction is the surface fraction and No 14 is the last fraction.

ND denotes not detectable.

! Due to technical problems these elements were not analysed.

TABLE XIV  
Sediment Enrichment Factors (SEF) in the Solou stream deposits profile at origin (Site 1)

|    | Fractions <sup>a</sup> |     |     |      |      |      |      |      |      |      |      |      |      |     |
|----|------------------------|-----|-----|------|------|------|------|------|------|------|------|------|------|-----|
|    | 1                      | 2   | 3   | 4    | 5    | 6    | 7    | 8    | 9    | 10   | 11   | 12   | 13   | 14  |
| Ti | 0.0 <sup>b</sup>       | 0.0 | 0.0 | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0 |
| Ca | 4.9                    | 4.6 | 5.4 | 5.7  | 49.3 | 26.7 | 10.9 | 1.7  | 2.1  | 2.3  | 1.5  | 0.0  | 0.0  | 0.0 |
| V  | 0.0                    | 0.0 | 0.5 | -0.5 | 1.4  | 0.4  | 0.0  | 0.0  | -0.3 | 0.0  | 0.0  | -0.3 | 0.0  | 0.0 |
| Cr | 0.5                    | 1.2 | 1.5 | 0.7  | 1.7  | 0.5  | 0.7  | 0.0  | 0.0  | 0.5  | 0.4  | 0.0  | -0.3 | 0.0 |
| Mn | 0.9                    | 0.8 | 1.1 | 1.1  | 3.0  | 1.2  | 1.0  | -0.6 | -0.5 | 0.4  | 0.3  | 0.0  | 0.0  | 0.0 |
| Fe | 0.5                    | 0.4 | 0.5 | 0.5  | 2.2  | 1.4  | 0.4  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0 |
| Ni | 0.5                    | 1.0 | 1.6 | 1.2  | 1.2  | 0.7  | 0.9  | 0.0  | 0.0  | 0.3  | 0.3  | 0.0  | 0.3  | 0.0 |
| Cu | 4.8                    | 2.5 | 5.0 | 4.8  | 34.0 | 21.5 | 15.7 | 2.5  | 0.0  | 0.5  | 0.5  | 1.3  | 0.0  | 0.0 |
| Zn | 0.6                    | 0.3 | 1.3 | 0.5  | 6.5  | 3.5  | 1.5  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0 |
| As | 1.4                    | ND  | 0.4 | 1.4  | 5.7  | 2.0  | 0.0  | 0.7  | 0.8  | -0.3 | -0.5 | —    | -0.6 | 0.0 |
| Rb | 0.0                    | 0.0 | 0.0 | 0.0  | 0.7  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | —    | 0.0  | 0.0 |
| Sr | 4.3                    | 3.6 | 6.2 | 4.2  | 34.0 | 19.9 | 7.1  | 0.5  | 0.7  | 0.7  | 0.3  | —    | 0.0  | 0.0 |
| Pb | 0.0                    | 0.0 | 2.4 | ND   | ND   | ND   | 1.0  | ND   | ND   | 0.4  | -0.6 | —    | -0.5 | 0.0 |

<sup>a</sup> The sediment core sample was taken from the origin of the Solou stream, sampling site No 1. Each fraction is of 2-cm depth; fraction No 1 is the surface fraction and No 14 is the last fraction.

<sup>b</sup> SEF values between -0.2 and +0.2 are designated as zero values.  
ND denotes not detectable.



TABLE XV  
Metal contents<sup>a</sup> in the Solou stream sediments<sup>b</sup> at power plant sites

| Sites | 9      |        |        | 13     |         |         | 18      |         |         |         |        |        |
|-------|--------|--------|--------|--------|---------|---------|---------|---------|---------|---------|--------|--------|
|       | 1      | 2      | 3      | 4      | 1       | 2       | 3       | 4       | 5       | 6       | 1A     | 1B     |
| Ca    | 94,000 | 87,000 | 44,000 | 35,000 | 360,000 | 330,000 | 310,000 | 300,000 | 200,000 | 250,000 | 24,000 | 21,000 |
| Ti    | 4,353  | 5,123  | 4,689  | 4,797  | 1,163   | 1,254   | 1,066   | 1,039   | 1,852   | 1,541   | 1,399  | 1,638  |
| V     | 139    | 246    | 200    | 159    | 105     | 119     | 98      | 94      | 117     | 53      | 111    | 148    |
| Cr    | 541    | 396    | 464    | 825    | 167     | 222     | 272     | 266     | 271     | 316     | 306    | 357    |
| Mn    | 913    | 669    | 1,120  | 1,078  | 758     | 763     | 548     | 567     | 661     | 641     | 436    | 589    |
| Fe    | 45,000 | 46,000 | 50,000 | 47,000 | 20,000  | 19,000  | 16,000  | 18,000  | 28,000  | 24,000  | 2,300  | 2,800  |
| Ni    | 244    | 205    | 245    | 210    | 44      | 51      | 28      | 57      | 101     | 88      | 217    | 261    |
| Cu    | 32     | 43     | 17     | 29     | 74      | 58      | 56      | 107     | 351     | 246     | 59     | 47     |
| Zn    | 71     | 78     | 70     | 120    | 292     | 188     | 165     | 172     | 351     | 394     | 71     | 197    |
| As    | 14     | 11     | ND     | ND     | 16      | 13      | 7       | 18      | 9       | 3       | 8      | 8      |
| Se    | ND     | ND     | ND     | ND     | ND      | ND      | ND      | 12      | ND      | 8       | ND     | ND     |
| Br    | 7      | 13     | 8      | 9      | 7       | 9       | 8       | 12      | 13      | 10      | 15     | ND     |
| Rb    | 72     | 79     | 90     | 101    | 36      | 26      | 14      | 27      | 34      | 37      | 49     | 57     |
| Sr    | 121    | 95     | 91     | 79     | 381     | 363     | 411     | 386     | 269     | 338     | 126    | 118    |
| Y     | 27     | 24     | 22     | 14     | 11      | 12      | ND      | 9       | 24      | 27      | ND     | ND     |
| Zr    | 118    | 158    | 152    | 166    | 45      | 29      | 30      | 28      | 45      | 60      | 93     | 48     |
| Pb    | 38     | 41     | 45     | 43     | 38      | 30      | 48      | 63      | 54      | 56      | ND     | 24     |

<sup>a</sup> Concentrations are in mg kg<sup>-1</sup>.

<sup>b</sup> Sediment core samples were obtained from the sampling sites No 9, 13, and 18. Each fraction is of 2-cm depth and fraction No 1 is the surface fraction. 1A and 1B denote fractions with particle size below 0.5 mm and 0.5–1.0 mm, respectively. ND denotes not detectable.

towards the surface of the sediment. The concentrations of the elements Zn and As are constant throughout the sediment profile.

The SEF values are higher at fraction 5 (Table XIV) indicating a high degree of enrichment in this fraction. In fraction 4 the respective SEF values are decreased sharply and remain constant almost throughout fraction 1.

The influence on the composition of the Solou stream sediment caused by the waste effluents of the coal-fired power plants and the nitrogen-fertilizer producing unit are shown in Tables XV and XVI (sites 9 and 13). At both sites the concentration of Ca and its SEF value are increased relative to their respective values at site 1. There is a trend of Ca enrichment towards the surface layers of the sediment core sample indicating that precipitation of Ca is occurring

TABLE XVI  
Sediment Enrichment Factors<sup>a</sup> (SEF) in the Solou stream deposits at power plant sites

| Sites | 9                |     |     |      | 13                     |      |      |      |     |      |
|-------|------------------|-----|-----|------|------------------------|------|------|------|-----|------|
|       | 1                | 2   | 3   | 4    | Fractions <sup>b</sup> |      | 3    | 4    | 5   | 6    |
| Ti    | 0.0 <sup>c</sup> | 0.0 | 0.0 | 0.0  | 0.0                    | 0.0  | 0.0  | 0.0  | 0.0 | 0.0  |
| Ca    | 1.3              | 0.8 | 0.0 | 0.0  | 1.9                    | 1.4  | 1.7  | 1.7  | 0.0 | 0.5  |
| V     | -0.3             | 0.0 | 0.0 | 0.0  | 0.4                    | 0.5  | 0.5  | 0.4  | 0.0 | 0.5  |
| Cr    | 0.3              | 0.0 | 0.0 | 0.7  | 0.0                    | 0.0  | 0.7  | 0.7  | 0.0 | 0.0  |
| Mn    | 0.0              | 0.5 | 0.0 | 0.0  | 0.8                    | 0.7  | 0.4  | 0.5  | 0.0 | 0.0  |
| Fe    | 0.0              | 0.0 | 0.0 | 0.0  | 0.0                    | 0.0  | 0.0  | 0.0  | 0.0 | 0.0  |
| Ni    | 0.0              | 0.0 | 0.0 | 0.0  | -0.3                   | -0.3 | -0.5 | 0.0  | 0.0 | 0.0  |
| Cu    | 1.0              | 1.3 | 0.0 | 0.7  | -0.7                   | -0.8 | -0.7 | -0.5 | 0.0 | 0.0  |
| Zn    | 0.9              | 0.8 | 0.0 | 0.0  | 0.3                    | 0.0  | 0.0  | 0.0  | 0.0 | 0.3  |
| As    | XX               | XX  | 0.0 | 0.0  | 1.8                    | 1.1  | 0.3  | 2.6  | 0.0 | -0.6 |
| Se    | 0.0              | 0.0 | 0.0 | 0.0  | —                      | —    | —    | XX   | 0.0 | XX   |
| Br    | 0.0              | 0.5 | 0.0 | 0.0  | 0.0                    | 0.0  | 0.0  | 0.6  | 0.0 | 0.0  |
| Rb    | 0.0              | 0.0 | 0.0 | 0.0  | 0.7                    | 0.0  | -0.3 | 0.4  | 0.0 | 0.3  |
| Sr    | 0.4              | 0.0 | 0.0 | 0.0  | 1.3                    | 1.0  | 1.7  | 1.6  | 0.0 | 0.5  |
| Y     | 0.0              | 0.0 | 0.0 | -0.4 | -0.9                   | -0.9 | XX   | -0.3 | 0.0 | -0.3 |
| Zr    | 0.0              | 0.0 | 0.0 | 0.0  | 0.6                    | 0.0  | 0.0  | 0.0  | 0.0 | 0.6  |
| Pb    | 0.0              | 0.0 | 0.0 | 0.0  | 0.0                    | 0.0  | 0.5  | 1.1  | 0.0 | 0.0  |

<sup>a</sup> SEF values were calculated on the basis of the fractions No 3 and No 5 for the core samples from sites 9 and 13, respectively.

<sup>b</sup> Each fraction is of 2-cm depth; fraction No 1 is the surface fraction.

<sup>c</sup> SEF values between -0.2 and +0.2 are designated as zero values.

XX denotes statistically significant high enrichment.

on the bed of the Solou stream. This enrichment is higher (SEF value 2.0) at site 9 than at site 13 (SEF value 0.9). This precipitation of Ca might be expected as the effluents of the power plants are highly concentrated in soluble and particulate Ca.

The data presented in Table XVI indicate that the sediment of the Solou stream is enriched in Ca, Mn, As, V, and Sr, while Ni, Cu, and Y are leached from the sediment matrix.

## References

- Alabaster, J. S. and Lloyd, R. L. (1980). *Water Quality Criteria for Freshwater Fish*, pp 297. Butterworths, London.
- Bertine, K. K. and Goldberg, E. D. (1971). Fossil fuel combustion and the major sedimentary cycle. *Science*, **178**, 233–235.
- Cahill, T. A. (1980). Microprobes and particle induced X-ray analytical systems. *Annual Review of Nuclear Particle and Science*, **30**, 211–252.
- Cook, J. (1977). Environmental pollution by heavy metals. *Journal of Environmental Studies* **9**, 253–266.
- Dowdy, R. H. Larson, R. E. and Epstein, E. (1977) Sewage sludge and effluent use in agriculture. In *Land Application of Waste Materials*. Soil Conservation Society of America, pp 138–153. Ankeny, Iowa.
- Dreesen, D. R. Gladney, E. S. Owens, J. W. Perkins, B. L., Wienke, C. L. and Wangen, L. E. (1977). Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from coal fired power plant. *Envir. Sci. Technol.* **11**, 1017–1019.
- Galloway, H. M. and Jacobs, L. W. (1971). Sewage sludge characteristics and management. In *Utilizing Municipal Sewage Wastewaters and Sludges on Land for Agricultural Production*. North Central Regional Extension Publication No 52, pp 3–17. Michigan State University, East Lansing, Michigan.
- Katsanos, A. A. (1980). Elemental analysis of biological materials. *IAEA Technical Report Series* No 197, 231–251.
- Kemp, A. L. W., Thomas, R. L., Dell, C. F. and Jaquet, J. M. (1976). Cultural impact on the geochemistry of sediments in Lake Erie. *Journal of the Fisheries Research Board of Canada*, **33**, 440–462.
- Klein, D. H. and Russell, P. (1973). Heavy metals: Fallout around a power plant. *Environmental Science and Technology*, **7**, 357–358.
- Lee, R. E. Jr., Crist, H. L., Riley, A. E. and Macleod, K. E. (1975). Concentration and size of trace metal emissions from a power plant, a steel plant and a cotton gin. *Environmental Science and Technology*, **9**, 643–647.
- 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.
- Valkonic, V. (1983). *Trace Elements in Coal*, Vol. I pp 57–67 and Vol. II pp 27–28, 74–75. CRC Press Inc., Boca Raton, Florida.