Δελτίο της Ελληνικής Γεωλογικής Εταιρίας τομ. XXXVI, 2004
Πρακτικά 10ου Διεθνούς Συνεδρίου, Θεσ/νίκη Απρίλιος 2004

Bulletin of the Geological Society of Greece vol. XXXVI, 2004
Proceedings of the 10th International Congress, Thessaloniki, April 2004

HEAVY METALS AND TOXIC TRACE ELEMENTS CONTENTS IN SOILS OF SELECTED AREAS OF THE KAVALA PREFECTURE, NORTHERN GREECE

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ABSTRACT

In the present study a total of sixteen samples (3 surrounding rocks and 13 uncultivated topsoils) from the industrial zone east of the city of Kavala, Northern Greece, was collected and analyzed for their content in 41 elements. The extraction of the elements was based on the digestion of 0.1 g of each sample with 2 ml HNO_3 and the soil fraction used was the < 200μm. The analytical methods used were ICP-OES for the elements Ca, Mg, K, B, Sr, Fe, Na, Si, S, P, and Al and ICP-MS for the elements Mn, Zn, Cu, Ti, V, Cr, Rb, Ba, Th, La, Ce, As, Sn, Co, Se, Y, Zr, Mo, Cd, Cs, W, Sb, Li, U, Ag, Ni, Hg, Ga, Ge and Pb. The mean element concentrations of the thirteen topsoil samples were compared with the mean values for soil types Fluvisols and Leptosols. The results showed that they are enriched for the elements Ag, As and Pb by 21, 15 and 3 times, respectively. Moreover, the topsoils were compared with the three surrounding rock samples. The results showed that the concentrations of Ca, Mg, K, Fe, Si, S, Al, P Na, B, Ce, Co, Cs, Ga, Ge, Hg, La, Li, Mo, Ni, Rb, Se, Sn, Sr, Th, U and W in the topsoils are mainly influenced by their concentrations in the surrounding rocks. The elements Ag, As, Ba, Cd, Cr, Cu, Mn, Pb, Sb, Ti, Y, V, Zn, and Zr are enriched in the topsoils. The enrichment of Ag, As, Cd, Cr, Cu, Mn, Pb, Sb, and Zn is mainly due to the widespread presence of PBG sulphides, Mn, Cd, and As in the surrounding mineralizations. The enrichment took place, quite possibly, during the formation of Drama and Nestos basins, during Tertiary, and is possibly being continued until today. However, the human activities that take place in the area are also, at least partially, responsible for this enrichment.

1 INTRODUCTION

Man's impact on the geosphere has been very broad and complex, and often has led to irreversible changes. Natural geological and biological alterations of the earth's surface are generally very slow. On the other hand, man-made or stimulated changes have accumulated extremely quickly in the last decades. These changes disturb the natural balance of the geosphere, which has been formed evolutionarily during a long period of time. These changes most often lead to a degradation of the natural human environment. Although man's impact on the biosphere has been dated from the Neolithic Period, the deterioration of ecosystems due to pollution has become increasingly acute during the latter decades of the 20th century (Kabata-Pendias & Pendias 1992, UN 2002).

Such a case is studied in the present work. The study area is the industrial area of the city of Kavala. It is located at the northeastern part of Greece, approximately 180 km to the east of Thessaloniki and 680 km from Athens and has approximately 150.000 inhabitants. Important geographical features of the wider area are the mountains Pangeo, Lekani, Phalakro and Menikio, as well as the Drama basin and Nestos River. The climate shows central European features with cold winters and warm summers. The annual average precipitation ranges from 500 to 700 mm. The mean temperature is 4.0°C in January and 24.5 °C in July and the prevailing wind is from the SE (H.N.M.S. 1978, Georgakopoulos et al. 2001)

The Kavala area has a long history; such demonstrate the findings in several important archaeological sites. The visit of Apostle Paul at 49-50 A.C. is one of the most historical events and, in general, the human occupation is notable, through ancient, Roman, Byzantine and contemporary times. Land in the area is mainly used for agricultural, industrial and residential purposes. Several recreational and tourist activities take place along the coastline. Kavala was a major warehousing and export centre for the tobacco-growing districts of northern Greece. East of the town, the Philippi peatland supports among others, maize cultivation. Bee keeping is also important, and local vineyards produce table grapes and table wines (Prefecture of Kavala 2004).

The industrial zone of Kavala city is situated about 10 km to the east of the city. The main industrial activities are the Phosphoric Fertilizers Industry (P.F.I.), the Kavala Oil plant, the "Xifias" Fishery and some medium-size enterprises that exploit and commerce industrial rocks (marbles) (Georgakopoulos et al. 2002). The top quality marble of the area has been traveling all over the world since antiquity. Other activities that take place in the area are the new national highway (Egnatia odos) and the construction of a new port (Philippos B). These activities, although accompanied by some reclamation plans to minimise their environmental impacts, generate significant volumes of solid wastes and air emissions. The environmental importance of these features is consequence mainly of the magnitude of the involved products.

1.1 Geological setting

The study area (Fig. 1) is a part of the Rhodope massif, which mainly consists of: a) gneisses, schists and amphibolites (Permian-Eocene), b) marbles (Permian-Eocene), c) granitic and granodioritic rocks (Cretaceous-Oligocene), d) lacustrine, continental and marine deposits (Mio-Pliocene), e) lacustrine and continental deposits (Pleistocene), and f) alluvial deposits and talus cones (upper Pleistocene-Holocene) (IGME 1973, 1999, Kilias & Mountrakis 1998, Georgakopoulos et al. 2001, Christofides et al. 2001).

2 METHODOLOGY

The methodology used included the following steps: a) careful sampling of the study area, b) preparation of all collected samples for analytical purposes, and c) chemical determination of major and trace elements, by ICP- OES and ICP- MS.

2.1 Sampling

Uncultivated surface soil, very sensible to anthropogenic influences, has been selected for the purposes of the present study. This kind of samples is well suited for gaining information on the long-term impact of trace metals accumulation (Kabata-Pendias & Pendias 1992, Llorens 1996, Ramsey 1997, Fernández-Turiel et al. 2001, Gallego et al. 2002, Self & Soltanpour 2002). A total of thirteen surface soil samples and three surrounding rocks were collected (Fig. 1).

2.2 Sample preparation

The samples were dried in an oven at 40°C (USEPA 1996, Fernández-Turiel et al. 2001, Gallego et al. 2002, Navas & Machín 2002). All the samples were sieved and splitted into three fractions: a) > 1cm, b) 0.2mm – 1cm, and c) < 0.2mm (200μm).), from which the third split was selected for further treatment and analysis. The < 200 μm fraction is usually used due to the fact that the environmental available trace elements mainly remain in this fraction (Tobías et al. 1997, Fernández-Turiel et al. 2001). The > 200 μm fraction is usually made up of rock fragments not related to anthropogenic activities. It is likely that larger particles and rocks would contain, on a weight basis, considerably less contaminant than the smaller ones and, also it is well known that the bioavailability of particles decreases with grain size (Gallego et al. 2002).

The elements of interest were extracted by a leaching procedure using analytical quality nitric acid (HNO_3). The HNO_3 extraction procedure is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available” (Pickering 1986, USEPA 1996, 1998a, Llorens 1996, Walsh et al. 1997, Quevauviller 1998a, 1998b, 2002, Chen & Ma 2001). Analytical

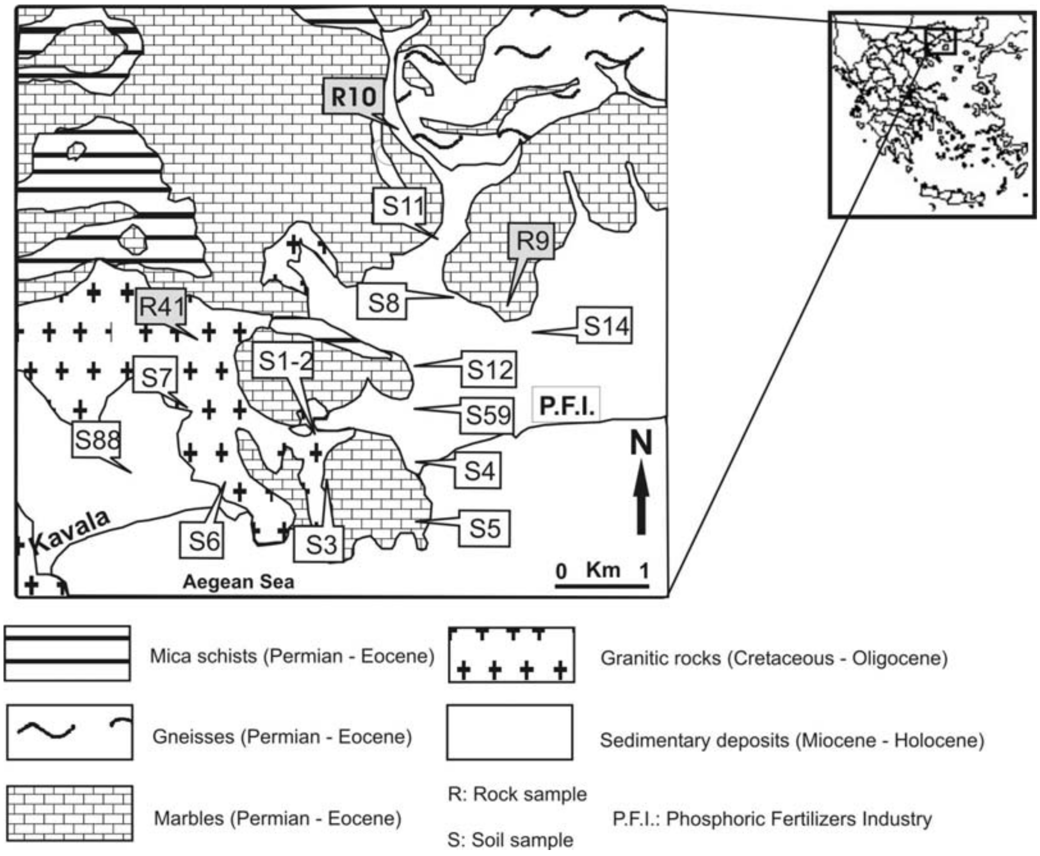

Figure 1. Geology, sampling sites of the study area and location of the Phosphoric Fertilizers Industry.

grade HNO_3 has been selected in order to work with extreme conditions, and maintain, at the same time, the compatibility of the leachate with the input solution in ICP-MS and ICP-OES (direct determination after dilution).

In this study, a split of 0.1g of each sample was placed into 14mm diameter polyethylene tubes. Then, 2ml of HNO_3 were added. All samples were placed in a rotary shaker for 24 h. After the extraction procedure, the solution was filtered (Schleicher & Schmell 5892 white ribbon, ash-less, filter paper circles of 125mm diameter) in 100 ml volume flasks. The volume flasks were made up volume with Milli-Q type purified water of 18.2 $M\Omega$/cm. The final solution was placed in HDPE (high-density polyethylene) bottles, labelled, and stored in dark at 4^oC until analysis (such solutions can sustain their trace elements content for several months).

2.3 Analytical methods

In the present case, the geochemical determination has been carried out by means of the combination of a) Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and b) Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The analyses were performed at the Faculty of Geology of the University of Barcelona, the SCT – UB (Scientific Technical Services of the University of Barcelona), and IJA – CSIC (Institute of Earth sciences "Jaume Almera" – Spanish Council for Scientific Research), Barcelona (Spain). A PERKIN ELMER OPTIMA 3200RL with a PERKIN ELMER Autosampler AS-90plus was used for the ICP-OES analyses, while a PERKIN ELMER SCIEX ELAN 6000 with a PERKIN ELMER AS-91 automatic sampler was used for the ICP-MS analyses.

2.4 Quality control

In order to check the quality of the results, the same procedure as the samples of the present study was followed by six standards (CANMET SO-1, SO-2, SO-3, SO-4, CANMET NRCC-MESS-2, and NIST SRM 2704), as well as by four duplicates of a randomly selected soil sample. Then, the analytical repeatability, the extraction procedure repeatability, and the extraction procedure recovery were calculated. All three factors gave values that were very satisfying for the majority of the elements. Moreover, to compare the extraction procedure recovery using HNO_3 with other extraction methods, the standard reference material NIST SRM 2704 was used. The recoveries obtained with HNO_3 are similar to those using the method 3051a and the extraction with aqua regia (Chen & Ma 1998, 2001). It can be concluded that the HNO_3 leaching procedure is an excellent alternative for soil environmental studies. It is a fast, simple, and low cost extraction procedure, directly compatible with the most powerful techniques of inorganic analysis (ICP-OES and ICP-MS).

3 RESULTS AND DISCUSSION

From the major elements (Ca, Mg, K, Fe, Na, Si, S, Al, P) the most abundant is Ca with an average concentration of 46.7 g kg^{-1} and the highest being 131.36 g kg^{-1} in sample S88. This was expected since limestone is the dominant type of rock in the study area. The average concentration values for the rest of the major elements are between 0.1 g kg^{-1} (for Na) and 7.31 g kg^{-1} (for Fe). Sulphur has an average concentration of 0.28 g kg^{-1}, Si of 0.31 g kg^{-1}, P of 1.02 g kg^{-1}, K of 2.06 g kg^{-1} Mg of 4.1 g kg^{-1}, and Al of 6.81 g kg^{-1}. The overuse of fertilizers can be responsible for the accumulation of Ca, Mg, Fe, and Al in the topsoils of an area (Wilden et al. 2001). However, this accumulation can only happen temporarily, since these elements can migrate to deeper soil horizons. Caution is needed when the concentrations of Fe and Al are relatively high, because Fe can lead to the release of other elements (e.g. As) and Al could become toxic for plants (Kabata-Pendias & Pendias 1992, Chen et al. 2000). Nevertheless, this is not valid in the present study because Fe is negatively correlated to As (Fig. 2).

The most abundant trace element is Mn with an average concentration of 693.99 mg kg^{-1}. Other trace elements with average concentrations higher than 100 mg kg^{-1} are As, Ba, Mn, and Ti. Boron, Ce, Cr, Cu, La, Ni, Pb, Rb, Sr, V, Y, and Zn have average concentrations between 10 and 100 mg kg^{-1}, while the rest of the elements (Ag, Cd, Co, Cs, Ga, Ge, Hg, Li, Mo, Sb, Se, Sn, Th, U, W, and Zr) have average concentrations lower than 10 mg kg^{-1} (Tab. 1).

Arsenic shows the highest value with 1634.46 mg kg^{-1} for sample S7. It also has a high average concentration (168.24 mg kg^{-1}). Arsenic is considered to be a class A human carcinogen element in the USA (USEPA 1998b, Chen et al. 2000) and its tolerance concentration limits in topsoils vary from 0,8 – 20 mg kg^{-1} for some states in the USA to 25 – 50 mg kg^{-1} in Canada (Chen, 2001). Lead is another element with a high average value (74.63 mg kg^{-1}) and single observations (e.g. 481.51 mg kg^{-1}). Lead is considered as Hazardous Air Pollutant (HAP) and as the number one element on the “National Priority List” of the USEPA (Cappuyns et al. 2002, USEPA 2003). It is also considered to be toxic to the plants in concentrations exceeding 100 – 500 mg kg^{-1} (Kabata-Pendias & Pendias, 1992). The higher concentrations of Pb and As always occur in the same samples (Fig. 3). Other elements with relatively high average concentration values are Cu (35.19 mg kg^{-1}), and Cr (12.37 mg kg^{-1}). Soils normally contain around 34 mg kg^{-1} Cu (Manta et al. 2002). Non-polluted soils contain less than 0.1 mg kg^{-1} Cr (Abrahim & Parker 2002).

The mean trace element concentrations of the topsoils of the present study were compared with the world average value for soil types Fluvisols and Leptosols (FAO, 1974, Kabata-Pendias & Pendias, 1992). These two types of soils were selected due to the fact that they are the most abundant types of soils in the study area. The enrichment of an element was described by an enrichment factor, which was defined as the ratio of an element concentration in a sample to the world average given by Kabata-Pendias and Pendias (1992). The results showed that the elements Ag, As and Pb are enriched by 21, 15, and 3 times, respectively (Tab. 2).

Moreover, the topsoils were compared with the three surrounding rock samples. According to the enrichment factors calculated, the concentrations of Ca, Mg, K, Fe, Si, S, Al, P Na, B, Ce, Co, Cs, Ga, Ge, Hg, La, Li, Mo, Ni, Rb, Se, Sn, Sr, Th, U, and W in the topsoils are mainly influenced

Table 1. Concentration values for the thirteen soil samples and the three surrounding rock samples of the present study. Major elements (Ca, Mg, K, Fe, Na, Si, S, Al, P) in g kg^{-1} and trace elements in mg kg^{-1}. LOD, Limit of detection.

	Soil samples								
Element	S1	S2	S3	S4	S5	S6	S7	S8	S11
Ca	5,8	28,2	32,1	62,6	128,8	2,8	16,4	131,4	86,1
Mg	3,6	5,9	5,3	6,2	2,2	1,0	2,5	1,8	1,7
K	1,4	2,1	1,0	2,0	1,3	1,2	0,8	1,5	1,2
Fe	6,6	9,8	4,9	9,3	3,2	2,7	5,3	4,7	3,9
Na	0,3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Si	0,3	0,3	0,4	0,3	0,2	0,4	0,3	0,3	0,5
S	0,2	0,2	0,4	0,3	0,3	0,2	0,2	0,5	0,4
Al	6,0	7,9	6,7	8,6	4,4	2,8	3,3	5,7	6,3
P	0,6	0,8	0,8	1,0	1,0	0,5	0,6	1,1	0,7
Ag	8,3	0,3	0,3	9,3	0,2	0,1	2,0	1,9	0,6
As	9,3	1,6	48,4	7,3	28,6	6,9	1634,5	126,7	30,8
B	21,0	17,3	16,1	14,3	10,9	8,3	26,6	13,9	23,4
Ba	79,0	122,8	170,3	165,1	101,7	75,8	77,8	99,1	166,3
Cd	0,6	0,3	1,3	0,3	0,9	0,2	1,0	1,2	1,2
Ce	10,9	6,1	34,0	5,5	31,7	15,2	16,8	23,3	33,8
Co	4,8	10,0	11,0	9,6	9,7	4,4	5,8	5,3	7,2
Cr	5,0	15,0	11,6	13,2	11,2	2,2	11,3	9,2	10,9
Cs	1,9	2,3	0,6	2,6	0,5	1,2	0,5	0,3	0,4
Cu	10,1	9,3	97,7	13,2	17,5	11,7	112,4	22,1	22,0
Ga	3,3	4,4	1,7	4,6	1,3	1,2	1,3	1,2	1,4
Ge	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1
Hg	0,1	0,1	0,5	0,1	0,1	0,1	0,3	0,1	0,1
La	5,4	2,4	18,4	2,7	17,0	7,3	8,3	12,8	17,5
Li	8,0	11,2	3,6	11,9	2,2	2,0	2,7	1,8	2,3
Mn	396,5	732,7	1391,6	591,4	549,1	278,1	669,6	481,4	636,4
Mo	0,4	0,2	0,2	0,2	0,2	0,2	0,2	0,1	0,1
Ni	3,3	8,6	15,2	9,6	26,8	2,9	14,9	13,1	14,9
Pb	15,2	4,8	73,2	12,0	33,8	14,8	481,5	68,1	38,8
Rb	19,0	29,2	6,3	17,6	8,7	17,3	6,2	6,5	6,1
Sb	0,7	0,2	1,0	0,3	0,2	0,2	1,9	0,5	0,3
Se	<LOD	<LOD	<LOD	<LOD	1,6	<LOD	<LOD	2,1	1,7
Sn	0,4	0,5	0,4	0,3	0,5	0,5	1,4	0,5	0,4
Sr	5,7	8,1	16,7	19,1	36,6	16,6	19,5	43,9	24,0
Th	4,3	2,9	3,8	1,2	1,9	11,1	5,9	1,8	3,3
Ti	224,7	335,4	21,2	382,8	18,6	44,7	21,6	27,1	15,2
U	0,4	0,3	0,4	0,7	0,3	1,2	1,5	0,4	0,3
V	25,1	39,2	22,5	37,1	19,4	14,8	18,5	14,9	21,6
W	0,7	0,4	8,7	0,5	0,5	0,3	1,2	0,4	0,5
Y	7,9	6,3	25,3	5,7	10,1	6,4	8,7	16,7	19,2
Zn	97,3	62,2	34,1	54,5	30,1	16,8	91,7	35,5	25,0
Zr	0,8	0,2	2,7	0,4	1,9	0,3	3,2	3,1	3,6

Table 1. (continued).

	Soil samples				Surounding rocks		
Element	S12	S14	S59	S88	Limestone	Gneiss	Granite
Ca	32,7	43,4	30,1	6,4	372,2	12,0	2,6
Mg	2,4	2,0	5,6	13,1	3,8	1,9	1,8
K	1,3	0,8	3,1	9,0	<LOD	2,0	1,4
Fe	6,9	5,1	8,1	24,5	0,3	6,5	5,1
Na	0,1	0,6	0,3	<LOD	0,3	<LOD	0,0
Si	0,2	0,2	0,4	0,3	0,1	0,4	0,3
S	0,6	0,2	0,1	0,0	0,7	0,0	0,1
Al	8,4	6,3	6,2	16,0	0,0	3,7	3,2
P	3,5	0,6	0,8	1,4	0,5	1,3	0,6
Ag	0,3	0,6	0,5	<LOD	0,1	0,1	0,3
As	42,5	40,6	207,7	2,3	5,2	0,9	2,3
B	10,2	7,6	2,0	7,4	11,1	20,1	1,1
Ba	165,4	323,8	126,9	260,4	19,5	57,8	41,5
Cd	1,3	0,8	0,8	0,2	0,4	0,1	0,2
Ce	28,9	31,2	11,5	7,3	0,4	2,9	17,8
Co	9,8	7,1	9,5	13,0	4,5	2,8	3,5
Cr	22,2	9,8	31,9	7,0	0,6	5,8	7,8
Cs	1,0	0,8	1,8	11,6	0,0	0,9	1,5
Cu	52,0	19,6	43,2	26,6	2,3	11,1	5,9
Ga	2,6	1,8	2,9	7,4	0,0	2,4	1,7
Ge	0,0	0,0	0,0	0,1	0,0	0,0	0,0
Hg	0,1	0,2	0,0	0,0	0,2	0,0	0,0
La	15,9	16,4	5,6	3,2	1,0	1,4	8,4
Li	3,7	3,2	7,9	38,3	0,1	5,4	6,0
Mn	1041,4	847,5	686,0	720,3	24,9	230,3	207,7
Mo	0,2	0,8	<LOD	0,1	0,1	0,4	0,0
Ni	19,8	12,9	28,8	7,8	17,2	2,6	7,4
Pb	60,6	37,1	119,9	10,1	3,1	2,5	13,7
Rb	16,6	9,2	26,8	133,8	0,1	20,9	17,5
Sb	0,4	0,2	0,4	0,0	0,1	0,1	0,1
Se	1,9	<LOD	<LOD	<LOD	2,6	<LOD	<LOD
Sn	0,9	0,4	0,2	0,2	0,4	1,0	0,2
Sr	32,3	19,8	15,0	32,7	151,9	11,1	6,1
Th	2,8	4,5	2,6	8,2	0,1	1,2	5,4
Ti	80,5	12,6	96,4	1114,7	0,7	150,2	108,9
U	0,4	0,3	0,2	0,9	0,0	0,5	1,3
V	20,3	22,8	26,1	82,6	0,5	14,8	12,8
W	0,9	1,4	0,3	0,2	3,6	0,1	0,1
Y	15,3	18,6	6,2	5,1	4,0	4,3	6,9
Zn	72,4	25,5	56,7	66,0	8,9	26,3	30,4
Zr	3,4	3,1	0,9	0,4	0,2	0,3	1,1

Table 2. Comparison between the mean elemental concentrations of the thirteen topsoils and the mean values for soil types Fluvisols and Leptosols (Kabata-Pendias & Pendias 1992). (Concentrations in mg kg^{-1}).

	Present study		Kabata-Pendias & Pendias (1992)		Present study	Kabata-Pendias & Pendias (1992)	
Element	min	max	min	max	mean	mean (Fluvisols and Leptosols)	Enrichment factor
Ag	0.09	9.30	0.03	3.2	1.9	0.09	21.0
As	1.56	1634.46	0.7	197	168.2	11.4	14.7
B	2.04	26.62	1	467	13.8	38.8	0.4
Ba	75.83	323.81	10	2368	148.8	622.0	0.2
Cd	0.16	1.29	0.01	2.7	0.8	0.49	1.6
Ce	5.47	33.99	<5	225	19.7	50.2	0.4
Co	4.36	13.05	0.1	70	8.2	12.6	0.7
Cr	2.20	31.87	1.4	1500	12.4	70.9	0.2
Cs	0.34	11.57	0.3	26	2.0	13.00	0.2
Cu	9.33	112.44	1	323	35.2	28.2	1.2
Ga	1.19	7.44	1	70	2.7	28.0	0.1
Ge	0.02	0.06	<0.1	2.1	0.0	1.25	0.0
Hg	0.02	0.54	0.004	5.8	0.1	0.12	1.2
La	2.40	18.37	<2	231	10.2	33.4	0.3
Li	1.82	38.34	0.01	175	7.6	36.0	0.2
Mn	278.13	1391.63	7	9200	694.0	571.8	1.2
Mo	0.08	0.83	0.01	17.8	0.2	2.00	0.1
Ni	2.90	28.78	0.2	660	13.7	17.8	0.8
Pb	4.85	481.51	1.5	286	74.6	28.4	2.6
Rb	6.11	133.77	<20	210	23.3	62.5	0.4
Sb	0.04	1.87	0.05	2.32	0.5	0.98	0.5
Se	0.58	2.13	0.01	3.5	1.0	0.48	2.0
Sn	0.17	1.41	<0.1	7.7	0.5	1.13	0.4
Sr	5.74	43.94	5	1000	22.3	172.1	0.1
Th	1.19	11.06	0.4	76	4.2	6.35	0.7
Ti	12.62	1114.71	200	24000	184.3	3600	0.1
U	0.24	1.47	0.1	45	0.6	1.98	0.3
V	14.78	82.59	0.7	530	28.1	68.2	0.4
W	0.25	8.67	na	na	1.2	1.50	0.8
Y	5.13	25.34	<10	150	11.7	26.3	0.4
Zn	16.77	97.30	3	770	51.4	67.8	0.8
Zr	0.22	3.62	70	550	1.8	140.0	0.0

by their concentrations in the surrounding rocks. On the other hand, the elements Ag, As, Ba, Cd, Cr, Cu, Mn, Pb, Sb, Ti, Y, V, Zn, and Zr are enriched in the topsoils. The enrichment of Ag, As, Cd, Cr, Cu, Mn, Pb, Sb and Zn is mainly due to the widespread presence of PBG sulphides, Mn, Cd, and As in the surrounding mineralizations (Psilovikos 1990, Filippidis et al. 1996, Christanis et al. 1998). The enrichment took place, quite possibly, during the genesis of the Drama and Nestos basins, in Tertiary, and is possibly being continued until today. As and Pb show the highest enrichment factors, a fact that is mainly attributed to the extreme values of these elements in sample S7 (As: 1634.5 mg kg^{-1}, Pb: 481.5 mg kg^{-1}).

The enrichment of Ba and V is probably a consequence of the human activities in the area. Both elements are correlated with the production and usage of fertilisers. The high concentration values of Mg, K, and Fe in one sample (S88) are quite possibly due to the usage of fertilisers. These elements are among the main constituents in the chemical composition of the P.F.I. products (P.F.I., 2004). Sample S88 also shows high values for Al, Co, Cs, Li, and Rb. These high values could be related to the presence of clay minerals in elevated concentrations in this sample. All four elements tend to be adsorbed in clay minerals and Co can also be "hidden" in Fe-Mn-oxides (Kabata-Pendias & Pendias 1992). The high value of P in sample S12 is probably also due to the use of phosphoric fertilisers. Arsenic, Cd, Cr, Cu, Mn, Pb, and Zn are found with high concentration values in almost all topsoil samples of the study area. There is information that connects the former elements with the production and usage of fertilisers and pesticides, as well as with combustion of petrol and diesel (for Pb) (Kabata-Pendias & Pendias 1992). Furthermore, As, Cd, Cu, Mn and Zn are found enriched in the products (phosphoric fertilizers and pesticides) produced in Kavala area (P.F.I., 2004). Moreover, the national highway connecting Kavala and Xanthi, passes through the study area. Hence, the leaching of the above elements from their potential sources and their enrichment in the local soils is another possible way of how the topsoils are being affected by the human activities.

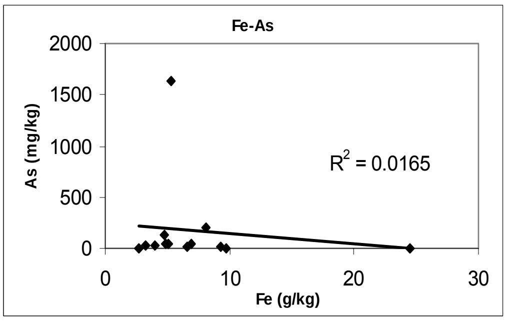

Figure 2. Iron *vs*. Arsenic in Kavala soils.

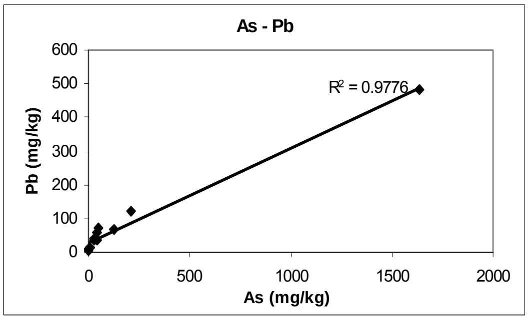

Figure 3. Arsenic *vs*. Lead in Kavala soils.

4 CONCLUSIONS

The concentrations of Ca, Mg, K, Fe, Si, S, Al, P Na, B, Ce, Co, Cs, Ga, Ge, Hg, La, Li, Mo, Ni, Rb, Se, Sn, Sr, Th, U, and W in the topsoils of the study area are mainly influenced by their concentrations in the surrounding rocks. The enrichment of Ag, As, Cd, Cr, Cu, Mn, Pb, Sb, and Zn is mainly due to the widespread presence of PBG sulphides, Mn, Cd, and As in the surrounding mineralizations. Arsenic and Pb show the highest enrichment factors. The high concentration values of Ba and V, as well as those of Mg, K, Fe, Al, and P in some samples, are probably a consequence of the human activities in the area.

Arsenic, Cd, Cr, Cu, Mn, Pb, and Zn show high concentration values in almost all topsoil samples of the study area. Because information exists that connects these elements with the production and usage of fertilisers and pesticides, as well as with combustion of petrol, these human activities in the area could be, at least partially, responsible for their elevated concentrations. Leaching processes of the elements from their potential sources is the main reason for their enrichment in the local soils.

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