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TRACE ELEMENT CONTENTS IN UNCULTIVATED SURFACE SOILS IN THE KAVALA AREA, NORTHERN GREECE

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Abstract

A total of 65 uncultivated surface soils samples from the area surrounding the city of Kavala, Northern Greece, was collected and analyzed for their abundance in 22 trace elements. The extraction of the elements from the < 200μm soil fraction was based on the digestion of 0.1 g of each sample with 2 ml HNO_3. The analytical methods used were ICP-OES and ICP-MS and the elements analyzed were Ag, As, B, Ba, Cd, Co, Cr, Cs, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, W, and Zn. The chemistry of the surrounding rocks and mineralizations has mainly affected the trace elements contents of the surface soils samples. The average elemental concentrations of the 65 uncultivated surface soil samples were compared with the average values for normal soils of the USA. Arsenic, Pb, and Zn were found to be enriched in the surface soils of the present study by a factor of 7.6, 3.3, and 2.7, respectively, indicating that human activities have contributed to their enrichment, since these elements are strongly connected to the industrial and agricultural activities in the area.

Key words: *surface soil, trace elements, environmental research.*

Περίληψη

Στην παρούσα εργασία λήφθηκαν 65 δείγματα ακαλλιέργητων επιφανειακών εδαφών από την περιοχή της Καβάλας και αναλύθηκαν για την περιεκτικότητά τους σε 22 ιχνοστοιχεία. Η διαλυτοποίηση των δειγμάτων έγινε με τη χρήση 2 ml HNO_3 και το κλάσμα που χρησιμοποιήθηκε ήταν το < 200μm. Οι αναλυτικές μέθοδοι που χρησιμοποιήθηκαν ήταν η ICP-OES και η ICP-MS και τα στοιχεία που αναλύθηκαν τα Ag, As, B, Ba, Cd, Co, Cr, Cs, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, W, και Zn. Τα περιβάλλοντα πετρώματα και οι μεταλλευτικές εμφανίσεις της περιοχής φαίνεται πως είχαν τον κυρίαρχο ρόλο στη διαμόρφωση της περιεκτικότητας σε ιχνοστοιχεία των αναλυθέντων εδαφών. Οι μέσες περιεκτικότητες των 65 αναλυθέντων δειγμάτων συγκρίθηκαν με τις μέσες περιεκτικότητες των εδαφών των ΗΠΑ. Το As, ο Pb και ο Zn βρέθηκαν εμπλουτισμένα στα επιφανειακά εδάφη της περιοχής μελέτης κατά 7,6, *3,3 και 2,7 φορές, αντίστοιχα, υποδεικνύοντας ότι οι ανθρώπινες δραστηριότητες που λαμβάνουν χώρα στην περιοχή συνέβαλαν στον εμπλουτισμό τους.*

Λέξεις κλειδιά: *επιφανειακά εδάφη, ιχνοστοιχεία, περιβαλλοντική έρευνα.*

1. Introduction

Trace elements, especially trace metals, are considered to be one of the main sources of pollution in the environment because they lead to changes and to a degradation of the natural environment. Human activities mobilize and redistribute elements in the environment, often causing adverse effects. Both industry and agriculture have contributed significantly to the elevated concentrations of environmentally important trace elements through waste disposal, atmospheric deposition, fertilizer and pesticide use, and other means (Georgakopoulos *et al.* 1996, 2001, 2002, Hesterberg 1998, Kabata-Pendias and Pendias 2001, Grigoriadou *et al.* 2004, Cui *et al.* 2005).

Sediments and soils are the principal sinks for trace metals. The study of the distribution of metals in sediments and soils is very important from an environmental point of view, because they concentrate metals and represent an appropriate medium to monitor contamination (Georgakopoulos *et al.* 1996, 2001, 2002, Kabata-Pendias and Pendias 2001, Sarkar *et al.* 2004, Kelepertsis *et al.* 2006). Trace metals environmental importance is closely related to their accumulation and potential toxicity. High levels of trace metals in sediments and soils may result in an increased metal uptake by crops and vegetables which, in turn, may have a negative effect on animals and human health (Kabata-Pendias and Pendias 2001, Cui *et al.* 2005).

The scope of this study was to conduct a first assessment on the geochemical fingerprint of the surface soils of Kavala area.

1.1. Study area

The study area (Fig. 1) is located around the city of Kavala and its industrial zone, and lies between latitudes 40°48′ and 41°06′ and longitudes 24°15′ and 24°40′. The land-uses in the area of interest are mainly agricultural, industrial and residential. The main industrial activities are the Phosphoric Fertilizers Industry (P.F.I.), the Kavala Oil Land Facilities (K.O.L.F.) and some medium-size enterprises that exploit and commerce industrial rocks (marbles). 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; Petalas et al., 2004).

1.2. Geological setting

The study area is a part of the Rhodope massif and it consists of metamorphic and plutonic-eruptive rocks (Fig. 1) with an extent of about 24km from east to west. The main rock types in the area are: a) gneisses, schists and amphibolites (Permian-Eocene), b) marbles (Permian-Eocene), c) granitic and granodioritic rocks (Cretaceous-Oligocene), and d) sedimentary deposits (Miocene-Holocene). The intense plutonism of the Rhodope is represented by granites, granodiorites, monzonites, quartz monzonites and diorites of Eocene, Oligocene, and Miocene age (Kilias and Mountrakis 1998, Christofides *et al.* 2001, Rondoyanni *et al.* 2004). Additionally, the Pyrite-Blende-Galena (PBG), Au, Cu, Mn, and Fe mineralizations and ore deposits are widespread in the study area (Maratos and Andronopoulos 1966, Filippidis *et al.* 1996, Vavelidis *et al.* 1996, 1997).

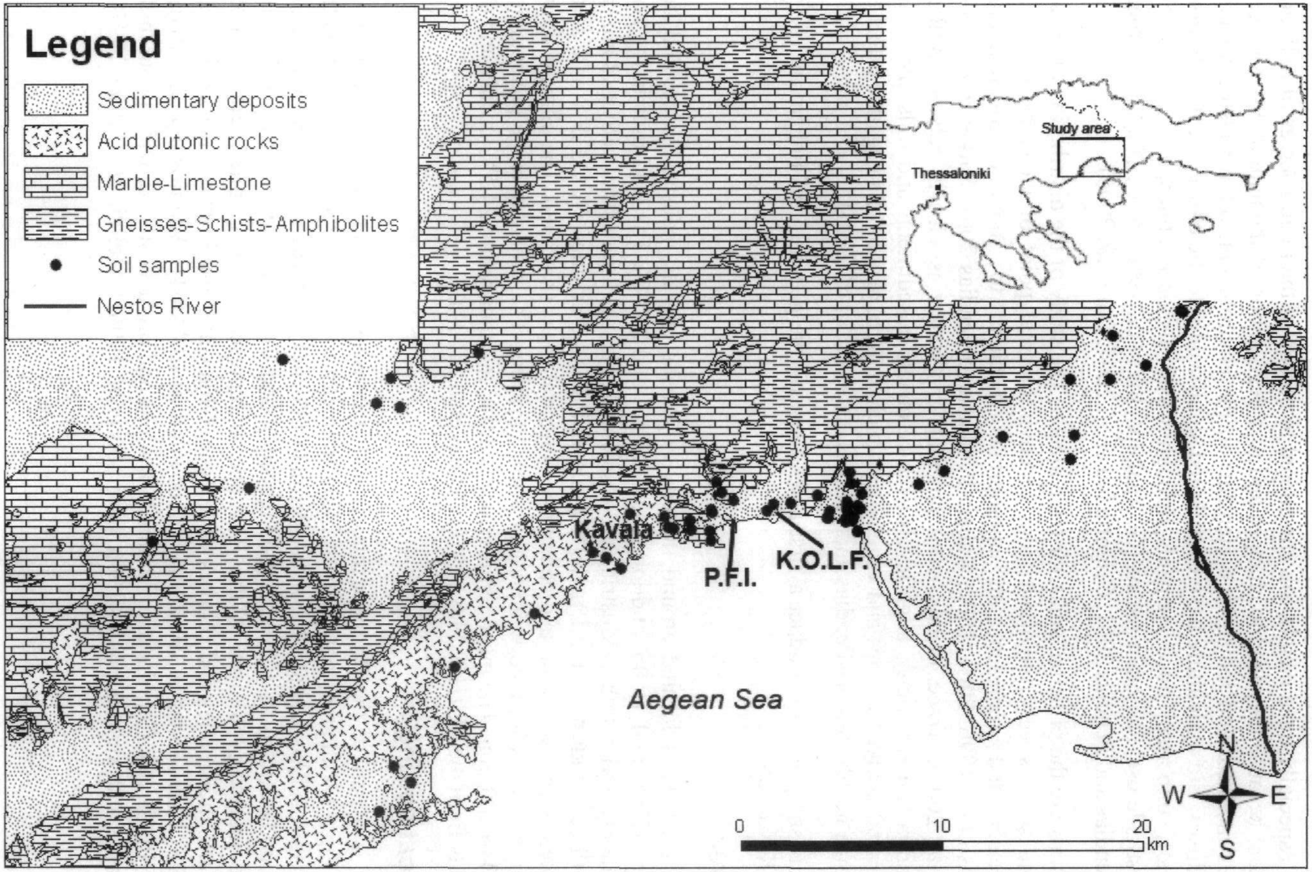

Figure 1 - Simplified geological map of the study area and location sites of the samples (modified, after IGME 1983)

2. Methodology

2.1. Sampling

In total, 65 uncultivated surface soil (0-20 cm) samples were collected between 2-11-2002 and 17-1-2003 (Fig. 1). Uncultivated surface soil was selected because it is very sensible to anthropogenic influences. This kind of samples is well suited for gaining information on the long-term impact of trace metals accumulation (Ramsey 1997, Fernández-Turiel *et al.* 2001, Chen 2001, Kabata-Pendias and Pendias 2001).

2.2. Sample preparation

All samples were dried in an oven at 40°C. After sieving all samples, the < 200 μm fraction was used since the environmentally available trace elements mainly remain in this fraction (Fernández-Turiel *et al.* 2001, Kabata-Pendias and Pendias 2001, Lucho-Constantino *et al.* 2005).

The elements analyzed were extracted by a leaching procedure using analytical quality HNO_3 (Papastergios *et al.* 2004, 2006). The HNO_3 extraction procedure is a very strong acid digestion that puts in solution almost all elements that could become "environmentally available" (Pickering 1986, Walsh *et al.* 1997, Quevauviller 2002, Sastre *et al.* 2002). Analytical grade HNO_3 has been selected in order to work with extreme analytical conditions, and maintain, at the same time, the compatibility of the leachate with the input solution in Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) (direct determination after dilution).

In the present work, a split of 0.1 g of each sample was placed into 14 mm diameter polyethylene tubes. Two ml 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 and Schmell 5892 white ribbon, ash-less, filter paper circles of 125 mm diameter) in 100 ml volume flasks. The volume flasks were made up volume with Milli-Q type purified water of 18.2 MΩ/cm. The final solution was placed in HDPE (high-density polyethylene) bottles, labeled, and stored in dark at 4°C until analysis (Papastergios *et al.* 2004, 2006).

2.3. Analytical methods: ICP-OES and ICP-MS analyses

The 22 trace elements analyzed were *Ag, As, B, Ba, Cd, Co, Cr, Cs, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, W, and, Zn* and the analytical methods used were Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). A PERKIN ELMER OPTIMA 3200RL with a PERKIN ELMER Autosampler AS-90+ 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. 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 ICTJA – CSIC (Institute of Earth sciences "Jaume Almera" – Spanish Council for Scientific Research), Barcelona (Spain). For reasons of quality control, the analytical repeatability, the extraction procedure repeatability, and the extraction procedure recovery were calculated. All three factors were satisfactory for the work objectives (Papastergios *et al.* 2004, 2006).

3. Results and discussion

The average, minimum and maximum elemental concentrations for the trace elements of all the samples in the present study are shown in Table 1 (for the calculation of the averages, less than detection limit values were replaced with half the detection limit value of each element).

Manganese (524 mg kg^{-1}) has the largest average concentration, and is followed, in decreasing order, by Zn (148 mg kg^{-1}), Ba (97 mg kg^{-1}), Ti (75 mg kg^{-1}), Pb (62 mg kg^{-1}), and As (55 mg kg^{-1}).

The rest of the trace elements have average concentrations below 50 mg kg^{-1}, with Sr (36 mg kg^{-1}) being the highest and Hg (0.1 mg kg^{-1}) the lowest. The concentration values for the majority of the trace elements were near expected averages, taking into account the geological setting, and the mineralizations of the study area (Filippidis *et al.* 1996). Some elements, i.e. As, Pb, and Zn are found with average values, as well as, maximum values that seem to be elevated. However, a study conducted by Kelepertsis *et al.* (2006) in a similar, nearby area (Stratoni-Chalkidiki Peninsula) found that soils near PBG sulfide mineralizations could have much higher concentrations (e.g., Pb had a mean of 895 mg kg^{-1}, As 364 mg kg^{-1} and Zn 654 mg kg^{-1}). An interesting fact though, is that the former elements in our work are found with their largest values in the vicinity of the Kavala city industrial zone whereas, in the study of Kelepertsis *et al.* (2006) the largest values are found near the ore bodies of their study area. This could possibly mean that the human activities taking place in our study area have contributed, at least partly, in these elevated values, especially since all these elements are strongly connected with the production and usage of these elements by such industries (Adriano 1986, Hesterberg 1998, Kabata-Pendias and Pendias 2001, Cui *et al.* 2005).

Table 1 - The average, minimum and maximum elemental concentrations for the trace elements of the studied soil samples (in mg kg^{-1}) and the comparison between the average values of the present work and Adriano (1986)

Element	min	max	average (this work)	USA normal soils (Adriano, 1986)	Enrichment Factor $\frac{\textit{average (this work)}}{\textit{USA normal soils}}$
Ag	<0.01	9.3	0.6	0.7	0.9
As	1.4	1634.5	55.1	7.2	***7.6***
B	0.4	84.0	8.0	30	0.3
Ba	15.9	323.8	97.2	440.0	0.2
Cd	<0.01	3.4	0.6	0.35	1.7
Co	1.0	39.4	6.8	6.7	1.0
Cr	1.0	74.3	16.1	40	0.4
Cs	0.3	8.7	1.6	4	0.4
Cu	3.2	184.3	22.3	30	0.7
Hg	<0.01	0.5	0.1	0.11	0.6
Mn	13.1	2111.2	524.2	560.0	0.9
Mo	<0.01	6.7	0.3	0.97	0.3
Ni	2.3	78.7	14.9	20.0	0.7
Pb	3.9	873.1	62.4	19	***3.3***
Sb	<0.01	2.0	0.3	0.48	0.6
Se	0.6	2.8	0.8	0.4	2.0
Sn	0.1	4.3	0.4	0.9	0.5
Sr	4.4	787.3	35.6	67.0	0.5
Ti	2.7	382.8	74.5	2400.0	<0.01
V	2.4	78.1	18.4	58.0	0.3
W	<0.01	8.7	0.4	1.5	0.3
Zn	13.4	5416.1	147.7	54.0	***2.7***

In an effort to further investigate the status of the topsoils in the Kavala area, the concentrations of the present work were compared with those cited by Adriano (1986) for normal soils of the USA, and their enrichment factors were calculated (Table 1).

The results indicate that as is enriched, in regard with its respective concentration for normal soils of the USA, almost 7.6 times, while the enrichment factors of Pb and Zn are 3.3 and 2.7, respectively. Other elements found relatively enriched are Cd (2.0 times), and Se (1.7 times), while the rest of the elements have enrichment factors around 1 or lowers (depletion). The reason for the rest of the elements having enrichment factors around 1 or lower could be attributed to either the fact that these elements have indeed lower concentrations, in total, in the topsoils of the Kavala area than those of the USA, or to the extraction method applied for this work.

4. Conclusions

The results indicate that the procedures of pedogenesis and erosion of the surrounding rocks of the study area have played an important role on the geochemical fingerprint of the surface soils studied in the present work. The majority of the elements are found in the samples of the present study with concentrations within normal ranges. However, some extreme values are noticed for As, Pb, and Zn. The comparison between the average values of the present study and the values for the USA normal soils indicates that the former elements (As, Pb and Zn) are found enriched (7.6, 3.3 and 2.7 times, respectively). Furthermore, these elements are found at their highest concentrations in the vicinity of the industrial zone of Kavala. The human activities have, also contributed to the enrichment of these elements, since they are strongly connected with the industrial and agricultural activities in the area.

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