NATURAL AND ANTHROPOGENIC EFFECTS ON THE SOIL GEOCHEMISTRY OF KAVALA AREA, NORTHERN GREECE

Papastergios G.
Filippidis A.
Fernandez–Turiel J.L
Gimeno D.
Sikalidis C.
https://doi.org/10.12681/bgsg.11637

Copyright © 2017 G. Papastergios, A. Filippidis, J.L Fernandez–Turiel, D. Gimeno, C. Sikalidis

To cite this article:

Papastergios, G., Filippidis, A., Fernandez–Turiel, J., Gimeno, D., & Sikalidis, C. (2010). NATURAL AND ANTHROPOGENIC EFFECTS ON THE SOIL GEOCHEMISTRY OF KAVALA AREA, NORTHERN GREECE. Bulletin of the Geological Society of Greece, 43(5), 2373-2382. doi:https://doi.org/10.12681/bgsg.11637
NATURAL AND ANTHROPOGENIC EFFECTS ON THE SOIL GEOCHEMISTRY OF KAVALA AREA, NORTHERN GREECE

Papastergios G.1, Filippidis A.1, Fernandez–Turiel J.L.2, Gimeno D.3, and Sikalidis C.4

1 Department of Mineralogy-Petrology-Economic Geology, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece, gpapaste@geo.auth.gr, anestis@geo.auth.gr

2 Institute of Earth Sciences “Jaume Almera”, Consejo Superior de Investigaciones Científicas (CSIC), Lluís Solé i Sabarís, s/n – 08028, Barcelona, Spain, jfernandez@ija.csic.es

3 Department of Geochemistry, Petrology and Geological Exploration, University of Barcelona, Zona Universitària de Pedralbes, Martí i Franquès, s/n – 08028, Barcelona, Spain, domingo.gimeno@ub.edu

4 Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece, sikalidi@eng.auth.gr

Abstract

A total of 65 surface soils and 8 rock samples from the area surrounding the city of Kavala, Northern Greece, was collected and analyzed for their contents in 10 major and 32 trace elements. The extraction of the elements from the < 200μm soil fraction was based on the digestion of 0.1g of each sample with 2ml HNO₃. The analytical methods used were ICP-OES and ICP-MS and the elements determined were Al, Ca, Cl, Fe, K, Mg, Na, P, S, Si, Ag, As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hg, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, Ti, U, V, W, Y, Zn and Zr. Comparisons between the concentrations of the surface soil samples and the surrounding rock samples indicate that the majority of major, as well as, of trace elements are found in the surface soils of Kavala with such concentrations that are considered as the product of natural processes such as the weathering of parent rocks and pedogenesis. However, there are some major elements (Cl, Na, S) and trace elements (Ag, As, Pb, V, Zn) that are present in the surface soils of the study area with elevated concentrations that cannot be regarded as the sole product of natural processes, but as the result of both, natural and anthropogenic activities, especially for the samples that are situated inside the industrial area of Kavala.

Key words: geochemistry, environment, soil, rock, Kavala, Greece.

1. Introduction

As it is known, soils and sediments are principal environmental sinks for both major and trace elements. Their content in soils is derived, either through natural processes such as the weathering of parent rocks, or through anthropogenic activities such as industry and agriculture. Since Potentially Toxic Trace Elements (PTTE) are regarded as one of the main sources of pollution in the environment, the study of their distribution is very important, especially from an environmental point of view, explicitly because many human activities mobilize and redistribute elements in the environment, often causing adverse effects. Elevated concentrations of PTTE in soils and sediments may re-
result in an increased uptake of PTTE by crops and vegetables which, in turn, may have a negative effect on animals and human health (Hesterberg 1998; Fernandez-Turiel et al., 2001; Georgakopoulos et al., 2001; Kabata-Pendias and Pendias, 2001; Cui et al., 2005).

The objectives of this study were to describe the chemical dataset collected and to investigate the geochemical identity of the surface soils of the Kavala area, with the intention of identifying the possible elemental sources in the area, whether natural and/or anthropogenic. In order to reach this goal, several methods where applied. However, in this paper are presented the results of the comparison between the elemental concentrations of the surface soils and the surrounding rocks of the Kavala area.

2. Study area – Geological setting

The study area is the city of Kavala, its industrial zone and their surroundings (Fig. 1). The climate of the area shows general Mediterranean characteristics. The mean temperature is 4.0°C in January and 24.5°C in July, while the prevailing wind is from SE (H.N.M.S. 1978, Petalas et al., 2004). Land uses in the area may be divided into four categories: agricultural, uncultivated, industrial and residential (Fig. 1). The main industrial activities are the Phosphoric Fertilizer Industry (P.F.I.) and the Kavala Oil land facilities. The first industry produces phosphoric fertilizers, pesticides and other similar products and its main byproduct is phosphogypsum, while in the second industry oil desulfurization takes place. Other activities include some small enterprises that exploit and market local marbles and the Xifias Fishery enterprise which terminated its activities during the undertaking of the present research. Also, near the Kavala Oil land facilities and the Xifias Fishery, several uncontrolled landfill sites exist.

The study area is a part of the Rhodope massif and it consists of metamorphic and plutonic-eruptive rocks (Fig. 2). The main rock types in the area are: a) gneisses and schists, b) limestones and marbles, c) granitic and granodioritic rocks and d) sedimentary deposits. The intense plutonism of the Rhodope is represented by granites, granodiorites, monzonites, quartz monzonites and diorites of Eocene, Oligocene, and Miocene age (Kilias et al., 1999; Christofides et al., 2001, Pe-Piper and Piper 2002). Additionally, Pyrite-Blende-Galena (PBG), Au, Cu, Mn, and Fe mineralizations and ore deposits are widespread in the study area (Filippidis et al., 1996; Vavelidis et al., 1996, 1997) (Fig. 2).

3. Methodology

3.1 Sampling and sample preparation

In total, 65 surface soil samples were collected between November 2002 and January 2003 (Fig. 1). Surface soil was selected because it is very sensitive to anthropogenic influences. This kind of samples is well suited for gaining information on the long-term impact of trace metals accumulation (Ramsey, 1997, Fernandez-Turiel et al., 2001, Kabata-Pendias and Pendias, 2001). Along with the soil samples, 8 rock samples from the surrounding rocks of the study area were collected. An effort was made so all the major rock types present in the area were represented (Tables 1 and 2).

All soil samples were dried in an oven at 40°C. After sieving, the < 200μm fraction was used due to the fact that environmentally available trace elements mainly remain in this fraction (Fernandez-Turiel et al., 2001, Kabata-Pendias and Pendias, 2001, Papastergios et al., 2009). The rock samples were crushed and pulverized in an agate mortar and followed the same procedure as the soils did.

The elements analyzed were extracted with analytical grade, concentrated (65%) HNO₃. The HNO₃
extraction procedure is a very strong acid digestion that puts in solution almost all elements that could become “environmentally available” (Walsh et al., 1997, Sastre et al., 2002). Analytical grade HNO₃ 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 ICP-MS and ICP-OES (direct determination after dilution). In the present work, a 0.1 g aliquot of each sample was placed into 14 mm diameter polyethylene tubes. Then, 2 ml of HNO₃ were added. All samples were placed in a rotary shaker for 24h. After the extraction procedure, the solution was filtered in 100 ml volume flasks. The volume flasks were made up volume with Milli-Q type deionized water of 18.2 MΩ/cm.

**Fig. 1:** Landuse/cover map of the study area and soil sample locations (modified from Papastergios, 2008).

**Fig. 2:** Simplified geological map of the study area. Locations of rock samples and mineralizations are included (modified from Papastergios, 2008).
3.2 Analytical methods

Ten major (Al, Ca, Cl, Fe, K, Mg, Na, P, S and Si), and 32 trace element (Ag, As, B, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hg, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, Ti, U, V, W, Y, Zn and Zr) concentrations were determined in all samples by 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 SCT–UB (Scientific Technical Services of the University of Barcelona), Barcelona (Spain). Details on ICP-MS analysis can be found in Fernandez-Turiel et al. (2000).

In order to check the quality of the results, the same methods were applied to the reference materials CANMET SO-1, SO-2, SO-3, SO-4, as well as to four replicates of a randomly selected sample. The methodology used, achieved precise analysis for practically all reference materials. Many elements exhibited Relative Standard Deviations (RSD) lower than 3%, and some around 1% (e.g., Ca, Mg, Fe, Al, Pb, Sr). Exceptions were Na, S, Cl, B, Cd, Ge, Hg, Sb and Se, probably due to their low concentrations (close to the quantification limits) in the reference materials. In regard to the extraction procedure’s repeatability, many elements exhibited RSD values lower than 5%. Similarly, some of the worst values could be attributed to the low concentrations of these elements. Detailed results regarding the methodology used are given in Papastergios (2008).

4. Results and discussion

Before comparing the results between the soils and the surrounding rocks, the concentrations of the surrounding rocks were compared with similar rock types, in order to disclose any unusual concentrations. The average concentrations of carbonates, shales and granites, as given by Faure (1992) were used for these comparisons. The results revealed that, only Ag (in marbles and granites) and Cd and Co (in marbles) are found with, relatively, elevated concentrations. The rest of the elements, for all rock types of the study area, are found within normal ranges (Papastergios, 2008).

4.1 Major elements

Table 1 shows the average leached concentrations for the major elements of the surrounding rocks and the surface soils of the study area. The two most abundant elements for both the surrounding rocks and surface soils are Ca and Fe, with an average concentration of 124.64 g kg⁻¹ and 27.98 g kg⁻¹ for Ca and 8.28 g kg⁻¹ and 6.35 g kg⁻¹ for Fe, respectively. This came as no surprise, as marbles are the dominant rock type and Fe mineralizations are common, in the area (Fig. 2). Concerning the surrounding rocks, Mg and Al are the next two elements with high concentrations, around 2.3 g kg⁻¹ and they are followed by P, Cl, Na, Si and S, which all have concentrations lower than 1 g kg⁻¹. The order changes slightly, for the surface soils. After Ca and Fe, the elements with the highest concentrations are Al, Mg, Na and Cl with average concentrations between 4.5 and 1.0 g kg⁻¹. The rest of the elements (P, S and Si) have concentrations below 1.0 g kg⁻¹.

A series of comparisons were generated between the surface soil samples and the surrounding rocks samples (as a total and separately with each rock type) of the study area (Table 1). The aim of the comparisons was to identify whether the surrounding rocks of the study area could provide the surface soils of Kavala with their elemental content.

The results indicate that Al, Ca, Fe, K, Mg, P and Si are found in the surface soils of the present study
as a result of natural processes, such as the weathering of parent rocks and pedogenesis, since their Enrichment Factors (EF) are lower than 3 (Table 1). On the other hand, Cl, Na and S are found in the surface soil samples with concentrations that seem to be elevated (EF larger than 3) and that could not have been provided solely by the erosion of the surrounding rocks. In the case of S, potential sources could be the PBG ore occurrences and the Kavala Oil land facilities, with the second being, most likely, the case, especially since almost all elevated values are found in its vicinity. The S deriving from the desulphurization of the oil is stacked in opencast sites inside the Kavala Oil land facilities and hence, is freely transferred by the wind. Additionally, the samples with, both Cl and Na elevated values, are found in the same area (Papastergios 2008). In fact, almost all samples that show elevated values are common. According to Kabata-Pendias and Pendias (2001) elevated Cl values are connected with the usage of mineralized waters and/or fossil fuels (i.e., oil, carbon, gas etc). Although, the transfer of sea water aerosols and the deposition of NaCl particles on the surface soils cannot be excluded.

Table 1. Average leached concentrations for the major elements (in g kg⁻¹) of the surface soils and the surrounding rocks of the study area, and Enrichment Factors (EF) of the comparisons between the leached concentrations of the surface soils and the surrounding rocks.

| Element | Rocks (total) | Marbles | Gneisses | Granites | Soils |
|---------|---------------|---------|----------|----------|-------|
| Al      | 2.11          | 0.05    | 2.65     | 3.63     | 4.50  |
| Ca      | 124.64        | 365.78  | 5.35     | 2.78     | 27.98 |
| Cl      | 0.37          | 0.90    | 0.21     | 0.02     | 1.12  |
| Fe      | 8.28          | 0.61    | 10.35    | 13.88    | 6.35  |
| K       | 1.26          | 0.01    | 1.75     | 2.01     | 1.38  |
| Mg      | 2.40          | 3.71    | 1.60     | 1.89     | 2.83  |
| Na      | 0.31          | 0.30    | 0.10     | 0.53     | 1.88  |
| P       | 0.56          | 0.53    | 0.70     | 0.44     | 0.72  |
| S       | 0.15          | 0.29    | 0.07     | 0.09     | 0.68  |
| Si      | 0.25          | 0.16    | 0.26     | 0.34     | 0.26  |

| Element | Enrichment Factors (EF) |
|---------|--------------------------|
|         | Soils vs. Rocks (total)  | Soils vs. Marbles | Soils vs. Gneisses | Soils vs. Granites |
| Al      | 2.1                       | 96.9            | 1.7              | 1.2               |
| Ca      | 0.2                       | 0.1             | 5.2              | 10.1              |
| Cl      | 3.0                       | 1.2             | 5.4              | 70.2              |
| Fe      | 0.8                       | 10.4            | 0.6              | 0.5               |
| K       | 1.1                       | 150.7           | 0.8              | 0.7               |
| Mg      | 1.2                       | 0.8             | 1.8              | 1.5               |
| Na      | 6.1                       | 6.2             | 19.6             | 3.6               |
| P       | 1.3                       | 1.3             | 1.0              | 1.6               |
| S       | 4.5                       | 2.3             | 9.6              | 7.9               |
| Si      | 1.0                       | 1.6             | 1.0              | 0.8               |

http://epublishing.ekt.gr | e-Publisher: EKT | Downloaded at 18/10/2020 13:56:25 |
4.2 Trace elements

Table 2 shows the average leached concentrations for the trace elements of the surrounding rocks and the surface soils of the study area. For the calculation of the descriptive statistics, values that were below the detection limit for each element were substituted by half its detection limit. For the surrounding rocks, only Mn had an average concentration larger than 100 mg kg\(^{-1}\) (269.45 mg kg\(^{-1}\)), while for the surface soils two elements (Mn: 524.2 mg kg\(^{-1}\) and Zn: 147.68 mg kg\(^{-1}\)) had concentrations above 100 mg kg\(^{-1}\). Elements with concentrations between 100 and 1 mg kg\(^{-1}\) were Sr, Ti, Ba, Zn, Rb, Cr, Cu, Ni, Ce, Pb, Th, Y, V, B, Li, La, Co, As, W, Cs, U, Mo, Ga and Sn, for the surrounding rocks, while the respective elements for the surface soils were Ba, Ti, Pb, As, Sr, Ce, Cu, V, Rb, Cr, Ni, La, Y, B, Co, Th, Li, Ga, Zr and Cs. The rest of the elements, either for the surrounding rocks (Se, Zr, Cd, Sb, Hg, Ag and Ge) or the surface soils (U, Se, Ag, Cd, Sn, W, Sb, Mo, Hg and Ge), had concentrations that were below 1 mg kg\(^{-1}\).

The comparisons between the surface soil samples and the surrounding rocks samples indicate that B, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hg, La, Li, Mn, Mo, Ni, Rb, Sb, Se, Sn, Sr, Th, Ti, U, W, Y, and Zr are found in soils of the Kavala area with concentrations that could have been provided through natural processes, since they have EF that are lower than 3 (Table 2). On the contrary, Ag, As, Pb, V and Zn show elevated concentrations which must not be attributed to the weathering of parent rocks, alone. The PBG ore occurrences of the study area may be regarded as possible contributors. However, with the exception of few samples located in the west part of the study area, the rest of the samples are situated far away from the PBG ore occurrences and near the industrial area of Kavala. In fact, the samples that are situated inside the industrial area of Kavala have larger concentrations than those situated outside (Fig. 1, Table 3) and, moreover, most of the samples with the elevated concentrations are found in the direction the prevailing wind blows (Papastergios et al., 2004, 2007, Papastergios 2008). Furthermore, all of the aforementioned elements have been connected to anthropogenic activities such as the ones taking place in the study area (Kabata-Pendias and Pendias 2001); therefore, these activities must have contributed to the elevated concentrations of the former elements in the surface soils of the study area. Additionally, given that the elemental content of the surrounding rocks has been found to be within normal ranges, the influence of the anthropogenic activities on the surface soils of Kavala, especially near its industrial area seems very likely, particularly, since the majority of the elevated concentrations are found near that area.

The negative influence of the local anthropogenic activities has been suggested for organic pollutants (Grigoriadou et al., 2008a, b) and heavy metals in street dust and roadside soil along the major national road in Kavala’s region (Christoforidis and Stamatis, 2009), by other researches as well. In fact, recently developed research, regarding the prefecture of Kavala, has reported that it has a higher rate of mortality (per 1000) by approximately 20% due to cancer, cardiac and pulmonary diseases than compared to the National average and that this observation could be linked to local environmental contamination activities (Theophanides et al., 2007).

5. Conclusions

The comparisons between the surface soil samples and the surrounding rocks of the study area indicate that the majority of the major elements (Al, Ca, Fe, K, Mg, P, Si), as well as of the trace elements (B, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hg, La, Li, Mn, Mo, Ni, Rb, Sb, Se, Sn, Sr, Th, Ti, U, W, Y, Zr) are found in the surface soils of Kavala with such concentrations that are considered as the product of natural processes such as the weathering of parent rocks and pedogenesis. However, there are some elements, both major (Cl, Na, S) and trace (Ag, As, Pb, V, Zn) that are present in the
Table 2. Average concentrations for the trace elements (in mg kg⁻¹) of the surface soils and the surrounding rocks of the study area, and Enrichment Factors of the comparisons between the concentrations of the surface soils and the surrounding rocks.

| Element | Rocks (total) | Marbles | Gneisses | Granites | Soils | Soils vs. Rocks (total) | Soils vs. Marbles | Soils vs. Gneisses | Soils vs. Granites |
|---------|---------------|---------|----------|----------|-------|-------------------------|-------------------|-------------------|-------------------|
| Ag      | 0.07          | 0.07    | 0.07     | 0.07     | 0.64  | 9.3                     | 9.5               | 9.0               | 9.4               |
| As      | 1.85          | 1.96    | 1.77     | 1.81     | 55.06 | 29.8                    | 28.0              | 31.0              | 30.3              |
| B       | 5.33          | 5.50    | 8.62     | 1.86     | 8.02  | 1.5                     | 1.5               | 0.9               | 4.3               |
| Ba      | 32.82         | 19.59   | 39.25    | 39.62    | 97.24 | 3.0                     | 5.0               | 2.5               | 2.5               |
| Cd      | 0.41          | 1.01    | 0.15     | 0.05     | 0.58  | 1.4                     | 0.6               | 3.8               | 12.7              |
| Ce      | 8.27          | 2.62    | 12.47    | 9.72     | 23.78 | 2.9                     | 9.1               | 1.9               | 2.4               |
| Co      | 4.13          | 6.44    | 2.66     | 3.29     | 6.83  | 1.7                     | 1.1               | 2.6               | 2.1               |
| Cr      | 17.78         | 1.26    | 20.22    | 31.85    | 16.08 | 0.9                     | 12.8              | 0.8               | 0.5               |
| Cs      | 1.60          | 0.94    | 0.62     | 4.13     | 1.55  | 1.0                     | 36.4              | 2.5               | 0.4               |
| Cu      | 15.54         | 3.47    | 19.68    | 23.47    | 32.33 | 1.4                     | 6.4               | 1.1               | 1.0               |
| Ga      | 1.43          | 0.05    | 2.12     | 2.13     | 2.58  | 1.8                     | 54.3              | 1.2               | 1.2               |
| Ge      | 0.03          | 0.02    | 0.03     | 0.04     | 0.04  | 1.2                     | 2.1               | 1.2               | 0.9               |
| Hg      | 0.09          | 0.24    | 0.02     | 0.02     | 0.07  | 0.7                     | 0.3               | 3.3               | 3.8               |
| La      | 4.74          | 4.14    | 5.18     | 4.91     | 11.91 | 2.5                     | 2.9               | 2.3               | 2.4               |
| Li      | 4.96          | 0.26    | 5.15     | 9.45     | 5.65  | 1.1                     | 21.6              | 1.1               | 0.6               |
| Mn      | 269.45        | 72.02   | 340.87   | 395.45   | 524.20| 1.9                     | 7.3               | 1.5               | 1.3               |
| Mo      | 1.44          | 0.08    | 1.76     | 2.49     | 0.28  | 0.2                     | 3.5               | 0.2               | 0.1               |
| Ni      | 11.10         | 18.08   | 6.35     | 8.85     | 14.90 | 1.3                     | 0.8               | 2.3               | 1.7               |
| Pb      | 8.08          | 4.16    | 11.63    | 8.44     | 62.36 | 7.7                     | 15.0              | 5.4               | 7.4               |
| Rb      | 18.04         | 0.22    | 22.58    | 31.32    | 16.69 | 0.9                     | 77.2              | 0.7               | 0.5               |
| Sb      | 0.12          | 0.06    | 0.15     | 0.13     | 0.30  | 2.6                     | 4.9               | 1.9               | 2.3               |
| Se      | 0.96          | 1.90    | 0.58     | 0.58     | 0.80  | 0.8                     | 0.4               | 1.4               | 1.4               |
| Sn      | 1.28          | 0.28    | 1.60     | 1.95     | 0.43  | 0.3                     | 1.5               | 0.3               | 0.2               |
| Sr      | 83.26         | 166.34  | 9.86     | 73.60    | 35.59 | 0.4                     | 0.2               | 3.6               | 0.5               |
| Th      | 6.10          | 0.40    | 10.23    | 7.68     | 5.65  | 0.9                     | 14.1              | 0.6               | 0.7               |
| Ti      | 75.31         | 1.64    | 144.85   | 79.44    | 74.52 | 1.0                     | 45.5              | 0.5               | 0.9               |
| U       | 1.52          | 0.17    | 0.49     | 3.90     | 0.90  | 0.6                     | 5.4               | 1.8               | 0.2               |
| V       | 5.57          | 1.09    | 7.75     | 7.88     | 18.42 | 3.3                     | 17.0              | 2.4               | 2.3               |
| W       | 1.85          | 5.29    | 0.18     | 0.07     | 0.43  | 0.2                     | 0.1               | 2.3               | 6.5               |
| Y       | 5.58          | 7.55    | 5.20     | 3.97     | 10.71 | 1.9                     | 1.4               | 2.1               | 2.7               |
| Zn      | 24.69         | 16.03   | 23.89    | 34.14    | 147.68| 6.0                     | 9.2               | 6.2               | 4.3               |
| Zr      | 0.74          | 0.19    | 0.39     | 1.63     | 1.99  | 2.7                     | 10.4              | 5.2               | 1.2               |
surface soils of the study area with elevated concentrations that cannot be regarded as the sole product of natural processes. In these cases, it seems very likely that the anthropogenic activities taking place in the industrial area of Kavala have contributed, at least partly, to these elevated concentrations, especially for the samples situated inside the industrial zone of Kavala. Additional statistical treatment of the data presented herein would provide further insight in the relationships between the elemental content of the surface soils and the natural and anthropogenic processes taking place in the study area.

6. Acknowledgments

The authors would like to acknowledge the technical assistance provided by the personnel of the Faculty of Geology of the University of Barcelona, the SCT–UB and ICTJA–CSIC, Barcelona (Spain). Georgios Papastergios wishes to acknowledge the support of the Greek State Scholarships Foundation (IKY). This work was partially carried out in the framework of PEGEFA 2005SGR-00795 Research Consolidated Group, funded by AGAUR-DURSI, Generalitat de Catalunya. The constructive comments of an anonymous reviewer are greatly appreciated.

Table 3. Comparison between the soil samples that are inside the Industrial Zone (IZ) and those found outside (RS).

| element | IZ average | RS average | element | IZ average | RS average |
|---------|------------|------------|---------|------------|------------|
| Al*     | 4.35       | 4.81       | Ge      | 0.03       | 0.05       |
| Ca*     | 31.96      | 19.65      | Hg      | 0.09       | 0.03       |
| Cl*     | 1.57       | 0.18       | La      | 9.94       | 16.05      |
| Fe*     | 6.36       | 6.32       | Li      | 5.88       | 5.16       |
| K*      | 1.45       | 1.24       | Mn      | 492.03     | 591.61     |
| Mg*     | 3.09       | 2.31       | Mo      | 0.36       | 0.11       |
| Na*     | 2.60       | 0.37       | Ni      | 14.98      | 14.73      |
| P*      | 0.82       | 0.51       | Pb      | 64.60      | 57.67      |
| S*      | 0.93       | 0.15       | Rb      | 15.60      | 18.99      |
| Si*     | 0.25       | 0.28       | Sb      | 0.32       | 0.26       |
| Ag      | 0.83       | 0.22       | Se      | 0.82       | 0.75       |
| As      | 66.56      | 30.96      | Sn      | 0.56       | 0.15       |
| B       | 10.70      | 2.41       | Sr      | 45.67      | 14.46      |
| Ba      | 99.63      | 92.23      | Th      | 5.14       | 6.73       |
| Cd      | 0.61       | 0.52       | Ti      | 85.68      | 51.13      |
| Ce      | 19.64      | 32.44      | U       | 0.85       | 1.00       |
| Co      | 6.56       | 7.39       | V       | 18.25      | 18.77      |
| Cr      | 16.35      | 15.50      | W       | 0.53       | 0.21       |
| Cs      | 1.59       | 1.47       | Y       | 9.65       | 12.93      |
| Cu      | 26.81      | 12.94      | Zn      | 192.73     | 53.30      |
| Ga      | 2.72       | 2.30       | Zr      | 1.98       | 2.01       |

IZ: samples inside the industrial zone. RS: samples outside the industrial zone (reference samples). Concentrations are expressed in mg kg⁻¹ except for those elements marked with asterisk, which are expressed in g kg⁻¹.
7. References

Christoforidis A. and Stamatis N. 2009. Heavy metal contamination in street dust and roadside soil along the major national road in Kavala’s region, Greece. *Geoderma*, 151: 257–263.

Christofides G., Koroneos A., Soldatos T., Eleftheriadis G. and Kilias, A., 2001. Eocene magmatism (Sithonia and Elatia plutons) in the Internal Hellenides and implications for Eocene-Miocene geological evolution of the Rhodope Massif (Northern Greece). *Acta Vulcanologica*, 13: 73-89.

Cui Y.J., Zhai R.H., Huang Y.Z., Qiu Y. and Liang J.Z., 2005. Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China. *Environment International*, 31: 784-790.

Faure G. 1992. Principles and applications of inorganic geochemistry. N.Y. Macmillan Pub. Co. 626p.

Fernandez-Turiel J.L., Llorens J.F., López-Vera F., Gómez-Artola C., Morell I. and Gimeno D., 2000. Strategy for water analysis using ICP-MS. *Fresenius’ Journal of Analytical Chemistry* 368: 601-606.

Fernandez-Turiel J.L., Aceñolaza P., Medina M.E., Llorens J.F. and Sardi F., 2001. Assessment of a smelter impact area using surface soils and plants. *Environmental Geochemistry and Health*, 23: 65-78.

Filippidis A., Georgakopoulos A., Kassoli-Fournaraki A., Misaelides P., Yiakkoupis P. and Broussoulis J., 1996. Trace element contents in composite samples of three lignite seams from the central part of the Drama lignite deposit, Macedonia, Greece. *International Journal of Coal Geology*, 29: 219-234.

Georgakopoulos, A., Fernandez-Turiel, J.L., Christianis, K., Kalaitzidis, S., Kassoli-Fournaraki, A., Llorens, J.F., Filippidis, A, and Gimeno, D., 2001. The Drama basin water: quality and peat/lignite interaction. *Environmental Geology*, 41: 121-127.

Grigoriadou A., Schwarzbauer J. and Georgakopoulos A., 2008a. Molecular indicators for pollution source identification in marine and terrestrial water of the industrial area of Kavala city, North Greece. *Environmental Pollution*, 151: 231–242.

Grigoriadou A., Schwarzbauer J. and Georgakopoulos A., 2008b. Organic geochemical parameters for estimation of petrogenic inputs in the coastal area of Kavala City, Greece. *Journal of Soils and Sediments*, 8: 253–262.

H.N.M.S. (Hellenic National Meteorological Service), 1978. Climatic data of the Greek network, period 1930 – 1975, (in Greek), 100p.

Hesteberg D., 1998. Biochemical cycles and processes leading to changes in mobility of chemicals in soils. *Agriculture Ecosystems and Environment*, 67: 121-133.

Kabata-Pendias A. and Pendias H., 2001. Trace elements in soils and Plants, 3rd ed., CRC Press, New York, 413p.

Kilias A.A., Falalakis G and Mountrakis D.M., 1999. Cretaceous – Tertiary structures and kinematics of the Serbomacedonian metamorphic rocks and their relation to the exhumation of the Hellenic hinterland (Macedonia, Greece). *International Journal of Earth Sciences*, 88: 513-531.

Papastergios G., Georgakopoulos A., Fernandez –Turiel J.L., Gimeno D., Filippidis A., Kassoli-Fournaraki A. and Grigoriadou A., 2004. Heavy Metals and Toxic Trace elements contents in selected areas of the Kavala Prefecture, Northern Greece, Bulletin of the Geological Society of Greece, 36(1): 263-272.

Papastergios G., Filippidis A., Christofides G., Kassoli-Fournaraki A., Fernandez-Turiel J.L., Georgakopoulos A. and Gimeno D., 2007. Trace elements contents in uncultivated surface soils in the Kavala area, northern Greece, Bulletin of the Geological Society of Greece, 40(3): 1491-1498.

Papastergios G., 2008. Environmental geochemical study of soils and sediments in coastal areas, east of Kavala (Macedonia, Greece) and production of geochemical maps via the use of GIS. (in Greek, with English summary), PhD, Aristotle University of Thessaloniki, Greece, 224p.

Papastergios G., Fernandez–Turiel J.L., Georgakopoulos A. and Gimeno D. 2009. Natural and anthropo-
pogenic effects on the sediment geochemistry of Nestos River, northern Greece. Environmental Geology, 58: 1361–1370.

Pe-Piper G. and Piper D.J.W., 2002. The igneous rocks of Greece, The anatomy of an orogen, Gebrüder Borntraeger, Berlin; 573p.

Petalas C., Pliakas F., Diamantis I. and Kallioras A., 2004. Study of the distribution of precipitation in District of Eastern Macedonia and Thrace for the Period 1964-1998, (in Greek with English abstract), Bulletin of the Geological Society of Greece, 36(2): 1054-1063.

Ramsey M.H., 1997. Sampling and sampling preparation. In: Gill, R., (Editor), Modern Analytical Geochemistry, An introduction to Quantitative Chemical Analysis Techniques for Earth, Environmental and Materials Scientists, Pearson Education Limited, England, 329p.

Sastre J., Sahuquillo A., Vidal M. and Rauret G., 2002. Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. Analytica Chimica Acta, 462: 59-72.

Theophanides M., Anastassopoulou J., Vasilakos C., Maggos T. and Theophanides T., 2007. Mor-tality and pollution in several Greek cities. Journal of Environmental Science and Health, Part A, 42: 741-746.

Vavelidis M., Christofides G. and Melfos V., 1996. The Au-Ag bearing mineralization and placer gold of Palea Kavala (Macedonia, N. Greece), Terranes of Serbia, The formation of the geologic framework of Serbia and the adjacent regions, Eds: Knežević V. and Krsić B., Belgrade 1996, 311-316p.

Vavelidis, M., Melfos, V. and Eleftheriadis, G., 1997. Mineralogy and microthermometric investigations in the Au-bearing sulphide mineralization of Palea Kavala (Macedonia, Greece). In: Papunen H. (Editor). Mineral deposits: Research and exploration, where do they meet? Balkema, Rotterdam, 343-346.

Walsh J.N., Gill R. and Thirwall M.F., 1997. Dissolution procedures for geochemical and environmental samples. In: Gill, R., (Editor), Modern Analytical Geochemistry, An introduction to Quantitative Chemical Analysis Techniques for Earth, Environmental and Materials Scientists, Pearson Education Limited, England, 329p.