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Heavy Metals in Agricultural Soils of the Mouriki-Thiva Area (Central Greece) and Environmental Impact Implications

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The heavy metal content of 51 surface soil samples from the agricultural region of Mouriki-Thiva (central Greece) was investigated by a combination of mineralogical (X-ray diffraction and scanning electron microscopy) and geochemical (aqua regia and 0.5 M HCl extractions) methods in order to determine the levels of contamination, as well as the origin, distribution and mobility of selected metals. The geology of the area includes ultrabasic rocks, and consequently the soils have anomalous values in Ni (621-2639 mg/kg) and Cr (134-856 mg/kg). Whereas Cr is mainly hosted in the crystal structure of chromite, Ni is primarily mobilized from olivine and serpentine. Nickel, and to a lesser extent Cr, were also found to be absorbed in Fe oxides. The results of a single 0.5 HCl leach revealed significant differences in the mobility and potential bioavailability of Ni and Cr in representative soil samples; Nickel is substantially more labile, and as a result a potential amount of this metal is readily available to the plants. The whole area is heavily contaminated by Ni and Cr and consequently the monitoring of the agricultural products of the region for their heavy metal content is strongly recommended.

Keywords Ultrabasic rocks, soil contamination, heavy metals, Ni and Cr, Greece

1. Introduction

Soil is a dynamic system, resulting from the weathering of the parent rocks, and is subjected to a number of pollutants from both natural and anthropogenic sources. Monitoring the levels of heavy metals in soil materials and the knowledge of their sources constitute a crucial undertaking, due to their effects on human health (Soylak and Türkoglu, 1999; Soylak et al., 2001). Furthermore, in contrast to most organic contaminants, heavy metals do not decay with time and are always present in soils at a background level of non-anthropogenic origin (Facchinelli et al., 2001). Ultrabasic rock weathering normally produces a high geochemical background with Ni and Cr anomalies in the soil horizons (Caillaud et al., 2009). Specifically, Ni content in most agricultural soils averages less than a hundred mg kg^{-1} (McGrath, 1995), but in the presence of ultramafic bedrock it can reach more than 10,000 mg kg^{-1} (Brooks, 1987).

Heavy metal content in soils is of major significance regarding fertility and nutrient status. Chemical elements such as Zn, Co, Cr, and Cu are necessary or beneficial

to plants and living organisms at certain levels, but they can be toxic when they are present in high concentrations (Alloway and Ayres, 1993). Other metals, which are not considered to be essential, like Pb and Cd, even in low concentrations, may become harmful.

To assess soil contamination, the total heavy metal concentration is often compared with some threshold limits and guideline values, fixed by legislation of various countries. However, high total concentrations of heavy metals do not always pose a threat to the environment and are usually determined when examining the degree and extent of contamination and mass balance of metals in the soil system. Heavy metals in soils are present in different mineralogical—geochemical phases, which determine their mobilization capacity and bioavailability to plants (Li and Thornton, 2001). For instance, heavy metals that are bound in silicate structures are only released extremely slowly into the environment and are not considered bioavailable.

Several digestion methods are used in order to determine the heavy metal levels in soils. Each of them "attacks" specific portions of metals that are associated with particular mineralogical forms. Among the common extraction methods, the hot aqua regia digestion is routinely applied to environmental studies and is usually available in geoanalytical laboratories, representing a strong partial leach, but it overestimates the amount of bioavailable heavy metal concentrations. Dilute 0.5 M HCl is recommended for the determination of the potential amount of metals that is transferred to the plants as it satisfies the essential requirement of minimal dissolution of the silicate detrital lattice and produces the highest contrast between anomalous and background samples (Agemian and Chau, 1976). Sutherland and Tack (2008) also stated that this single partial leach represents an effective, inexpensive, and rapid approach for heavy metal contamination assessment. Regarding the chemical analyses, flame atomic absorption spectrometry is widely used for the determination of toxic elements in various geochemical media, due to its selectivity, speed, and low cost (Saracoglu and Soylak, 2010; Khani and Shemirani, 2010).

The present geochemical-environmental study was carried out as a preliminary survey on soil contamination at a regional scale in Thebes area (central Greece), located some 100 km north of Athens, with the following objectives: a) to determine the mineralogical composition and heavy metal concentrations (released by aqua regia and 0.5 HCl extraction methods) of agricultural soils; b) to assess the levels of soil contamination with respect to the world average soil composition and the Dutch target and intervention values for soil remediation; and c) to identify possible factors that can explain the geochemical element variability.

2. Site Description

The studied area is situated in the prefecture of Viotia, Central Greece (Figure 1), covering an area of about 150 km^2. More specifically, its northern geographical boundary is the Mouriki village next to the Iliki lake, while the Thiva town lies southwards. Morphologically, the region is a part of the wider Thiva–Malakasa–Oropos Neogene basin, which is a composite of a plain surrounded by hills.

2.1. Geological Setting

The study area consists of the geological formations of the Sub-Pelagonian unit (Tataris et al. 1966; Papanikolaou, 1988; Papanikolaou, 2009), comprising Triassicmiddle Jurassic
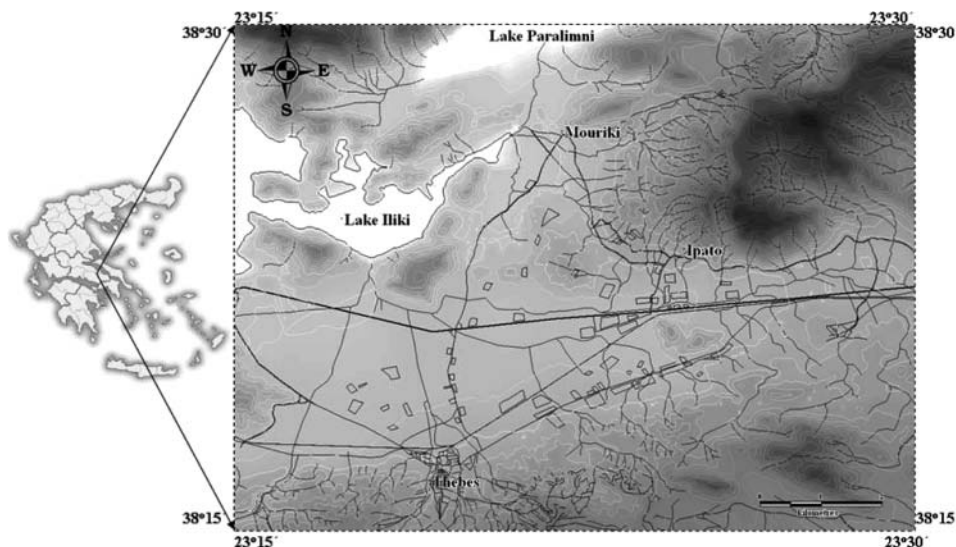
Figure 1. Map of Greece depicting the studied area.

carbonate rocks, overlain by the late Jurassic schist-hornstein formation (Figure 2). The latter is composed by a mixture of ophiolites, shales, limestone layer intercalations and other materials. The ophiolites are mainly serpentinized and are composed by peridotites, and other basic and ultrabasic rocks. The post-alpine formations are represented by alluvial deposits covering the Thiva plain, and an elluvial mantle of considerable thickness, mainly formed above the schist-hornstein formation.

2.2. Land Use

The agricultural sector represents one of the most important economic activities of the region, covering the majority of the total available land surface. Potatoes, carrots, cotton, grain, and beans are mainly cultivated in the plain area while, moving towards the Thiva town, farming becomes less intense and low-scale industrial activities exist. The use of fertilizers and pesticides is prolonged and intensive farming methods, such as ploughing and harvesting, are visible in the whole area.

3. Materials and Methods

3.1. Sampling Collection and Preparation

During October 2009, a total of 51 soil samples were collected, north and south of the Athens Lamia National Highway. The sampling points are depicted in Figure 3. The surface of each sampling location was cleaned from superficial debris and vegetation before digging to a depth of 10 cm. In each sampling location, representative composite samples were received by collecting material over an area of 1 m^2. Samples were put in
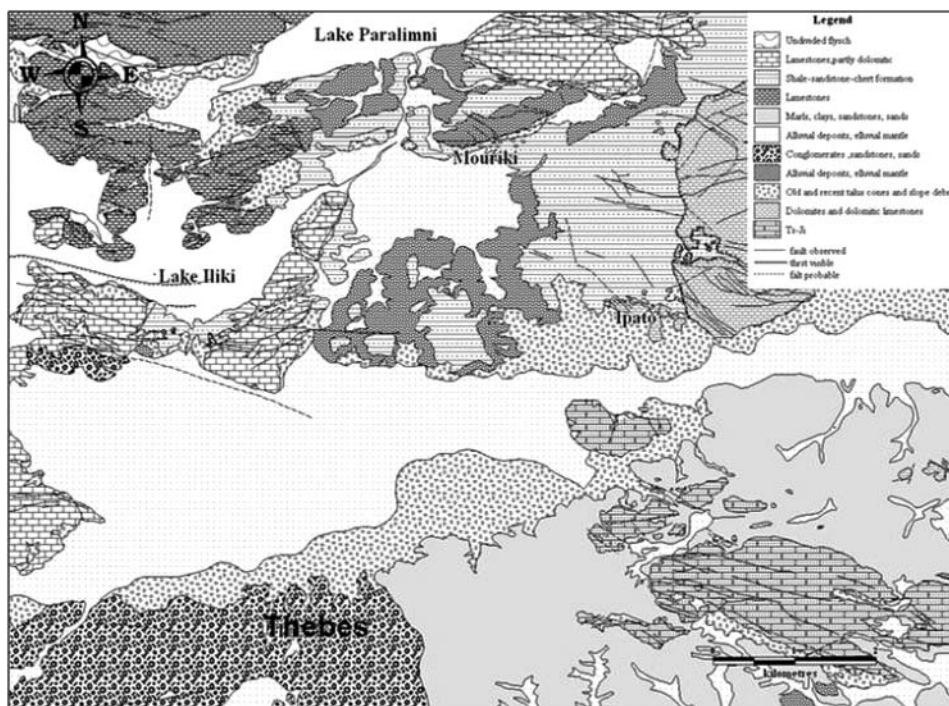
Figure 2. Geological map of the area under study (Tataris et al., 1966).

clean polyethylene bags for transport, and were processed at the Laboratory of Economic Geology and Geochemistry, Department of Geology and Geoenvironment, University of Athens. In particular, samples were oven-dried at a constant temperature of 40°C for three days, sieved to <2.00 mm fraction, then pulverized in an agate mortar to approximately <0.075 mm and stored in polyethylene bags for routine mineralogical and chemical analyses. This fraction was preferred for chemical analyses since different studies have shown that heavy metals, either of natural or anthropogenic origin, accumulate more extensively in the finer grain-size fractions (Salomons, 1980; Groot et al., 1982).

3.2. *Mineralogical Analysis*

Methods used to determine the mineralogical composition of soil samples included X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction patterns were obtained for 14 representative samples covering the whole area using a Siemens D5005 Diffractometer with Cu-Ka radiation, operating at 40 kV and 40 mA. Each powdered sample was scanned from 3° to 65° 2θ with a one counting time per step. The diffraction patterns were evaluated using the software EVA 2.2. Microscopic observations were conducted using a Jeol JSM-5600 instrument, equipped with an energy dispersive X-ray spectrometer for microanalysis (EDS, Oxford Link ISIS 300). Five representative
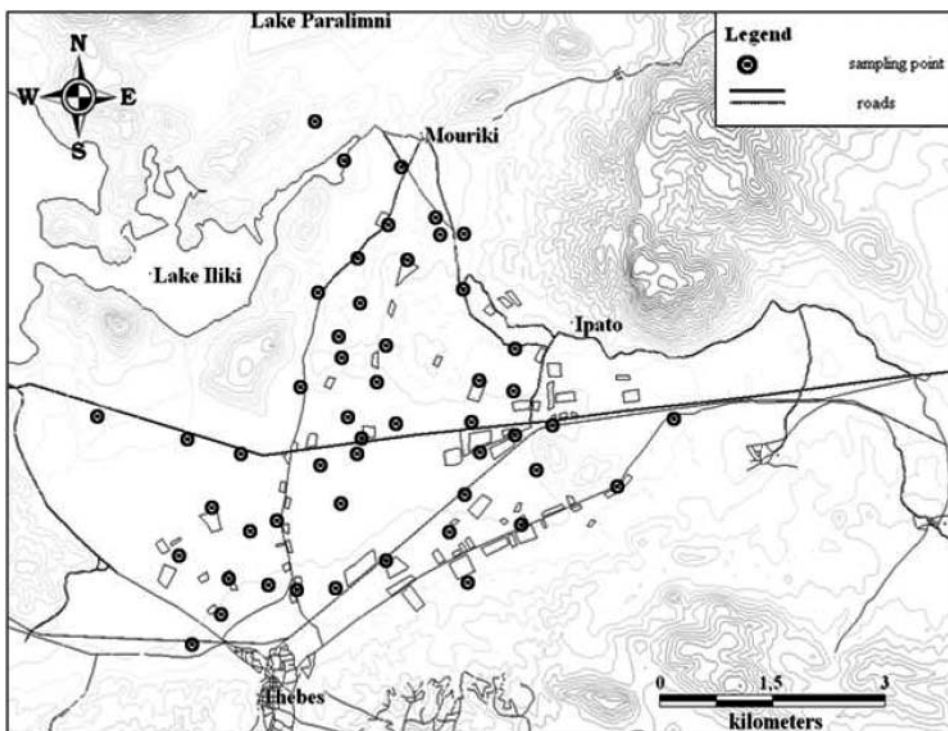
Figure 3. Map of the studied area showing the sampling locations.

carbon-coated metallographic sections were prepared by mixing the powdered material with an appropriate resin and were studied with operating conditions such as acceleration voltage 20 kV, beam current 0.5 nA, beam diameter 2 μm, and acquisition time 80 sec.

3.3. Chemical Methods

The major chemical parameters pH (for 21 representative samples) and organic matter (for all 51 samples) were determined. Both of them strongly influence metal mobility and bioavailability. The pH values were after mixing 8 gr of the surface soil sample (the <2.00 mm fraction) with 20 ml distilled water using the Jenway 3040 Ion Analyser. The determination of organic matter was made according to the Walkey–Black adaptation of volumetric method (Walkley and Black, 1934), which is is based on the oxidation of organic substances with $K_2Cr_2O_7$ and H_2SO_4.

In order to determine the metal content, samples were digested into hot aqua regia (4 ml HCl and 1 ml HNO_3), which only extracts a fraction of the major elements (pseudo-total analysis), since some phases are not completely dissolved with this method. Generally, the digestion by modified aqua regia is suitable for the dissolution of metals bound in carbonates, most sulphide minerals, some silicates like olivine and trioctahedral micas (the

darker colored ferromagnesian-rich silicates), clay minerals, and primary and secondary salts and hydroxides (Tarvainen and Kallio, 2002; Albanese et al., 2007). As a result, most of the environmentally concerned components are efficiently dissolved, which are indicative for the assessment of toxicity. After dilution to 15 ml with distilled water, solutions were analyzed for Pb, Zn, Ni, Cr, Cu, Mn, Co, Fe, and Mg, by flame atomic absorption spectroscopy (FAAS), Perkin Elmer 1100B. Additionally and according to the obtained results of the aqua regia extraction, 21 representative samples were also digested into 0.5 M HCl solution in order to determine the potential leachability of Ni and Cr. The 0.5 M HCl can extract water soluble, exchangeable, carbonate, and a part of oxide fractions in the soil (Adriano, 1986). Therefore, this method may be related to the long-term potentially bioavailable concentrations of the previously mentioned metals, determining their labile forms (Sutherland, 2002).

3.4. Quality Control

The analytical precision of the aqua regia digestion method, as the relative percent difference, was checked by duplicate analyses of 10 random samples. The analytical precision was found within the international standards, being lower than 14%, while prepared blanks were always below the instrumental detection limits. Accuracy was determined by the simultaneous analysis of two certified reference materials: SRM 2709 San Joaquin soil and SRM 2711 Montana Soil, covering low and intermediate concentrations of heavy metals. The obtained results indicate a good agreement between the measured data and the reference values, with the percent difference being lower than 10% in most of the cases. As expected, high differences were observed for the rock-forming elements Fe and Mg, which were not totally released during the aqua regia extraction.

3.5. Statistical Analysis and Use of MapInfo

The statistical technique of R-mode factor analysis was applied for the interpretation of the geochemical data. Factor analysis characterises different groups of chemical elements with approximately similar geochemical patterns, aiming to reduce the complex pattern of correlations among many variables to simpler sets of relationships between fewer variables (Kelepertsis et al., 1982; Kelepertsis et al., 2001). The different factors obtained were studied and interpreted according to their presumed origin (natural or anthropogenic). MapInfo (version 9.5) and Vertical Mapper were used to create a simplified geological map showing the outcropped lithological types and faults in the studied area. The source of this information was a published geological map (Tataris et al., 1966) of scale 1:50,000. The spatial database developed was completed by plotting the collected soil samples using size symbols indicating the levels of measured metal concentrations.

4. Results and Discussion

4.1. Mineralogical Composition

According to the XRD results, the soil samples present similar mineralogical composition consisting of carbonate minerals (calcite, dolomite, ankerite) stemming from the carbonate rocks, whereas the presence of quartz and feldspars (albite,
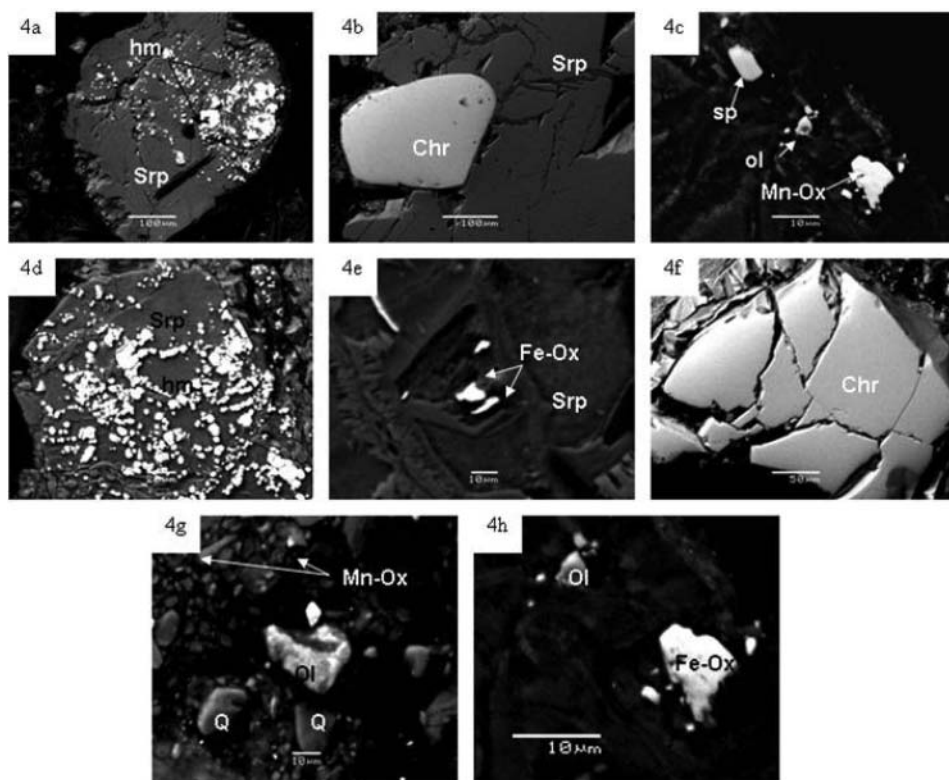
Figure 4. Selected back-scattered photomicrographs of the examined samples (abbreviations: Srp:serpentine, hm: hematite, sp: spinel, chr: chromite, ol: olivine, Mn-ox: Mn oxide, Fe-ox: Fe-oxide, Q: Quartz).

anorthite, microcline) reflects the schist-hornstein chert formation. The influence of ultramafic rocks on soil mineralogy becomes apparent from the existence of olivine and serpentine. Clay minerals include chlorite, as well as illite and/or montmorillonite.

Scanning electron microscopy studies have additionally revealed the presence of Fe and Mn oxides, revealed the presence of Fe and Mn oxides and chromite. (Figure 4). The previously mentioned oxides are characterized by their strong tendency to bind and trap metals, primarily Ni and to a lesser extent Cr. Nickel is also associated with serpentine formed by original olivine, whereas the Cr-carriers phases are chromite and olivine. Table 1 presents representative semi-quantitative chemical analyses of the identified main mineral phases. The determined chemistry of the minerals shows a deviation from the ideal chemistry (Deer et al., 1992), due to the nature of the sample (soil) consisting of altered minerals and the presence of fine-grained minerals as a matrix.

4.2. Physicochemical Properties of the Studied Soils

Soil pH values vary between 7.5 and 8.7, suggesting neutral to alkaline conditions (85% of samples are characterized by pH > 8.0), which derive from the carbonate and ultrabasic parent materials. According to Rodriguez et al. (2008), pH is an essential factor that influences cation mobility and regulates the solubility of heavy metals in soils. Most of the

Table 1

Chemical analyses of the identified main mineral phases

Figure 4a	Figure 4b	Figure 4c	Figure 4d
Srp: SiO_2 35.79%, μgO 27.03%, Fe_2O_3 4.95% **hm:** Fe_2O_3 92.18%, SiO_2 1.39%, NiO 0.49%	**Srp:** SiO_2 65.19%, MgO 39.95%, Fe_2O_3 6.28%, Al_2O_3 1.56%, CaO 0.72%, Cr_2O_3 0.67% **Chr:** MgO 13.47%, Al_2O_3 22.52%, Cr_2O_3 49.82%, Fe_2O_3 21.58%	**Sp:** Al_2O_3 40.14%, Cr_2O_3 20.31%, MgO 27.03%, FeO 15.17%, SiO_2 19.89% **Ol:** SiO_2 33.67%, MgO 59.00%, Fe_2O_3 15.89% **Mn-Ox:** MnO 85.16%, Fe_2O_3 5.67%, NiO 2.05%	**Spr:** SiO_2 65.71%, MgO 32.77%, Fe_2O_3 6.66% **hm:** Fe_2O_3 92.56%, SiO_2 2.30%, MgO 0.75%, CaO 0.21%

Figure 4e	Figure 4f	Figure 4g	Figure 4h
Srp: SiO_2 41.52%, MgO 32.47%, Fe_2O_3 5.21% **Fe-Ox:** Fe_2O_3 83.23%, SiO_2 4.15%, MgO 3.69 %, NiO 3.14%	**Chr:** Cr_2O_3 37.01%, Al_2O_3 27.40%, Fe_2O_3 16.62%, MgO 12.87%	**Ol:** Fe_2O_3 43.46%, SiO_2 26.79%, Al_2O_3 14.01%, MgO 4.26%, K_2O 2.12%, Cr_2O_3 1.98%, CaO 0.79%, NiO 1.77% **Mn-Ox:** MnO 74.34%, Fe_2O_3 5.23%, NiO 0.76%	**Ol:** SiO_2 39.00%, MgO 45.22%, Fe_2O_3 5.98%, NiO 1.59% **Fe-Ox:** Fe_2O_3 85.16%, MnO 2.05%, MgO 1.62%, SiO_2 1.87%, NiO 4.58%

Table 2

Main descriptive statistics of the analyzed metals (values in mg/kg, except for Fe and Mg that are presented in %)

Elements	Mean Value	Median	Standard Deviation	Minimum	Maximum
Pb	24	23	9.9	5	55
Zn	67	63	26.3	44	234
Ni	1591	1549	616.9	621	2639
Cr	277	237	115.6	134	856
Cu	32	31	7.3	20	53
Mn	1010	1008	176.6	685	1307
Co	54	46	21.9	23	97
Fe	4.66	4.57	8063	2.78	6.35
Mg	4.28	3.89	1.05	1.1	10.28

metals tend to be available in acid pH; the higher soil pH values do not favor the transfer of heavy metals to crops. Organic content ranges from 0.01% to 0.39%, indicating that organic matter is not a crucial factor that determines metal mobility and bioavailability in the collected soils.

4.3. Results of Chemical Analysis

4.3.1. Metal content evaluation and levels of soil pollution. Table 2 presents the main descriptive statistics of the studied elements released by the aqua regia extraction method. The average range in soil composition and published mean metal values for soils developed on geological formations, including ultrabasic rocks (peridotites and serpentinites) from Greek areas, are shown in Table 3 for comparison purposes. Additionally, since in Greece there are not any legal standards for soil chemistry evaluation, Table 3 displays

Table 3

Average range in soil composition, published mean metal values for soils developed on geological formations including ultrabasic rocks from Greek areas, and the Dutch guidelines (values in mg/kg, except for Fe and Mg that are presented in %)

	Pb	Zn	Ni	Cr	Cu	Mn	Co	Fe	Mg
Mean in Thebes soils	24	67	1591	277	32	1010	54	4.66	4.28
Average range in soil composition[1]	10	50	40	100	20	850	10	3.8	*
Mean in Susaki soils[2]	33	95	994	920	23	831	54	3.73	5.09
Mean in Agia soils[3]	15	87	189	299	73	1394	29	4.7	2.2
Mean in Triada soils[4]	35	74	2160	1040	24	954	108	7.2	*
Netherlands[5]	85	140	35	100	36	*	20	*	*
Netherlands[5]	530	720	210	380	190	*	240	*	*

1) Siegel, 1974.
2) Kelepertsis et al., 2001.
3) Skordas and Kelepertsis, 2005.
4) Vardaki and Kelepertsis, 1999.
5) Target and intervention limits established by Dutch law (VROM, 2000).

the target and intervention values in use by Dutch authorities. The use of Dutch standards has been proposed on the basis that they are long established while concurrently they have been based on extensive studies on both human and eco-toxicological effects of soil contaminants. The Dutch target values indicate the level at which there is a sustainable soil quality whereas the intervention values indicate the concentration levels of metals above which the functionality of the soil for human, plant and/or animal life may be seriously damaged.

A comparison of the metal concentrations with the global average soil composition reveals that all the studied samples present Ni, Cr, Fe, and Co concentrations significantly higher than the values of the average soil composition given by Siegel (1974), while high concentration of Mn is met in 80% of the samples of Thiva soils. The metals Pb, Zn, and Cu, which are good indicators for metal pollution caused by human activities, are characterized by slightly higher concentrations than the ones given by Siegel (1974). The elevated concentrations of Ni, Cr, Co, Fe, and Mn are attributed to the presence of ultrabasic rocks of the schist-hornstein formation, indicating a natural case of metal pollution. Various authors in Greece (Vardaki and Kelepertsis, 1999; Kelepertsis et al., 2001; Skordas and Kelepertsis, 2005) have reported soil pollution by ultrabasic rocks, resulting in high concentrations of the previously mentioned elements (Ni, Cr, Co, Fe, and Mn) due to the weathering and dispersion of the parent materials, in which these metals are predominant. The slightly higher than the average soil composition values of Pb, Zn, and Cu in the studied soils can be ascribed to the ferromagnesian minerals of the ultrabasic rocks. In respect to the published mean metal values, Thiva soils present lower Ni, Cr, Co, and Fe mean values than the reported mean values for the Triada area, located on Euboea Island, but this is mainly attributed to the nickeliferous mineralization that occurs on the weathered surface of the serpentinites and peridotites, which are considered the parent rocks of the mineralization (Vardaki and Kelepertsis, 1999). Nickel content in the studied soils is considerably higher than both the corresponding mean values reported for Agia (Skordas and Kelepertsis, 2005) and Susaki (Kelepertsis et al., 2001) soils, while Cr concentrations are similar to the concentrations determined in the soils from Agia area, but significantly lower than the levels measured in Susaki soils.

Regarding the quality criteria derived from the Netherlands, all the studied samples have Ni concentrations that significantly exceed the corresponding value of 210 mg/kg (minimum value 621 mg/kg), whereas Cr levels for eight samples also exceed the limit of 380 mg/kg.

4.3.2 Data processing. The chemical elements Pb, Ni, Mn, and Fe display a normal distribution while the rest have skewed distributions. For this reason, a log_{10} transformation was applied to the data before the performance of the parametric statistical tests presented below. Table 4 shows the Pearson's correlation coefficients between the element pairs. Concentrations of Ni, Co, Fe, and Mn display good to strong positive correlation, indicating a common source for these metals, i.e. the occurrence of the ultramafic rocks. The lack of correlation for the rest of the elements signifies that they do not have the same origin and therefore their concentrations cannot be attributed to one particular source.

The correlation coefficient between Ni and Cr is of great interest since it is quite poor (0.24), and requires interpretation. Due to the geological environment area and particularly the existence of the ultrabasic formations, a higher correlation coefficient between these two metals was expected. If the parent rock was of uniform composition, i.e. ophiolites, Ni and Cr should be characterized by similar geochemical behavior. The poor correlation between

Table 4

Pearson correlation matrix for the soil data

	Pb	Zn	Ni	Cr	Cu	Mn	Co	Fe	Mg
Pb	1								
Zn	0.22	1							
Ni	−0.15	−0.08	1						
Cr	0.26	0.17	0.24	1					
Cu	0.17	0.58	−0.39	0.09	1				
Mn	−0.20	0.25	0.39	0.45	0.18	1			
Co	−0.22	−0.07	0.94	0.26	−0.33	0.58	1		
Fe	−0.07	−0.04	0.67	0.43	−0.15	0.53	0.70	1	
Mg	0.03	−0.23	0.41	0.26	−0.26	−0.44	0.19	0.21	1

Ni and Cr in the studied soils is due to the different sources providing the soil formation. A common source is evident for Ni and Cr and this is represented by the ophiolite blocks of the schist-hornstein formation, while the non-common sources are the schists, cherts, and the limestone intercalations.

Additionally and according to the scanning electron microscopy observation studies, the Ni-bearing minerals are represented by the olivine, serpentine, and the Fe and Mn oxides, which are dissolved and release their trace metal content during the aqua regia digestion. On the contrary, Cr is bound to chromite, olivine, and Fe oxides. Aqua regia is inefficient in releasing the portion of Cr that is incorporated in the crystal structure of chromite, resulting in the underestimation of the real Cr content in the studied soils. Numerous studies have manifested low Cr recovery by aqua regia due to the presence of insoluble Cr-carriers minerals, such as chromite (Liu et al., 1996; Medved et al., 1998; Chen and Ma, 2001).

Furthermore, R-mode factor analysis was applied to the data. Rotated factor loadings, communalities and the proportion of the variance explained by three factors are presented in Table 5. The three-factor model, accounting for 76% of the data variability, was deemed

Table 5

Varimax component loadings of three factors, communality and percentage of variance explained for the studied elements

Variable	Factor 1	Factor 2	Factor 3	Communality
Pb	−0.22	−0.02	0.81	0.70
Zn	0.04	−0.87	0.12	0.78
Ni	0.90	0.27	−0.06	0.88
Cr	0.39	−0.03	0.69	0.62
Cu	−0.28	−0.59	0.34	0.54
Mn	0.67	−0.67	−0.05	0.89
Co	0.94	0.16	−0.13	0.92
Fe	0.82	0.02	0.20	0.71
Mg	0.25	0.80	0.23	0.76
% Variance	34.9	25.6	15.1	75.6

appropriate for the soil data of the studied area. Specifically, Factor 1 includes Ni, Fe, Co, and Mn with high positive loadings and Cr and Mg with low positive loading, reflecting the signature of the ultrabasic rocks on the soil chemistry. The second factor, explaining 26% of the total variance, is controlled by Zn, Cu, and Mn with negative factor loadings, indicating their association with the aluminosilicate minerals of the schist-hornstein formation. The second factor also comprises Mg with high positive loadings, suggesting that the source of this metal is both the ferromagnesian minerals and the dolomitic limestones. The third factor, which accounts for 15% of the total variability, includes Pb and Cr, possibly reflecting their association with chromite grains.

4.3.3. Spatial distribution and implications for bioavailability. The maps produced by MapInfo and Vertical Mapper computer programs display the spatial distribution of Ni and Cr in the Thebes soils (Figure 5). The highest concentrations of Ni (>1000 mg/kg with a maximum of 2639 mg/kg) are detected in the northeast part of the studied area where the schist-hornstein formation outcrops, but notable levels of this metal are still accounted for at the south part, around the Thiva town. Chromium levels display a different spatial distribution. The highest concentration for this element (856 mg/kg) was measured close to Iliki Lake, while an area with relatively high values (around 450 mg/kg) is located south of the national highway Athens-Lamia.

The study area—the Thiva plain—has been subject to intense agricultural activities. The plants are the intermediate reservoirs for heavy metals through which they move from soils to man and animals. Thus, it was considered necessary to perform a comparison of the metal values of Thiva soils with the phytotoxic levels as they are given by Kabata-Pendias and Pendias (1992) (Table 6). Apparently, the potentially toxic elements Ni, Cr, and Co are characterized by higher concentrations than the corresponding levels presented by the same authors.

The potentially bioavailable concentrations of Ni and Cr for 23 representative samples, as determined by 0.5 M HCl extraction, are presented in Table 7. Nickel values range from 15 to 735 mg/kg, with 15 out of 23 samples showing concentrations that exceed the Dutch guideline limit of 210 mg/kg, which is referred to the total content of this metal in the soil, as already mentioned. On the contrary, Cr levels extracted by 0.5 M HCl are low, ranging

Table 6

Phytotoxic levels of chemical elements in comparison with the concentration range in Thiva soils (values in $\mu g\ g^{-1}$)

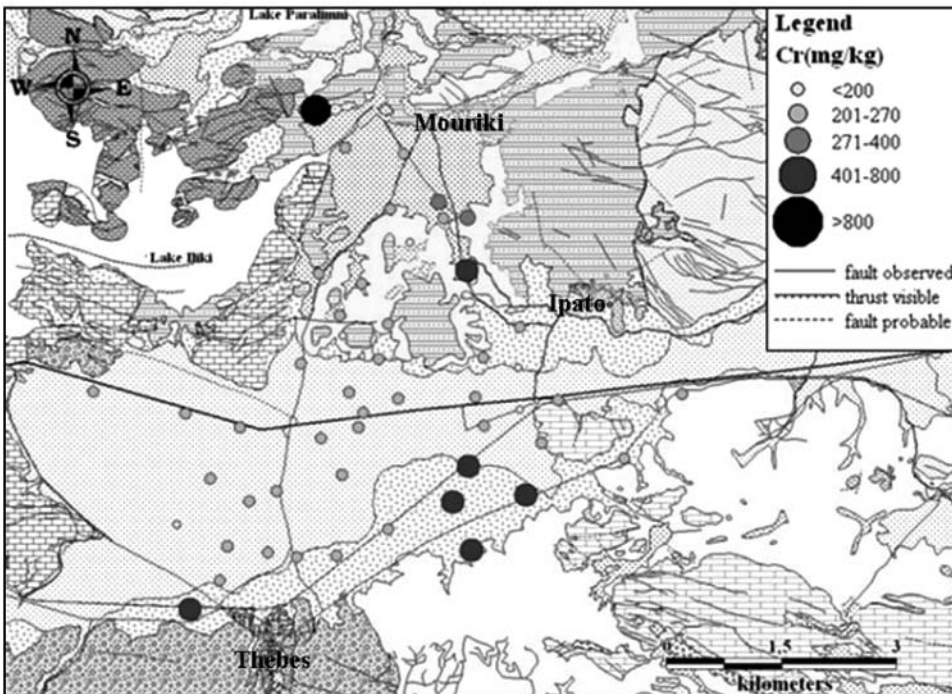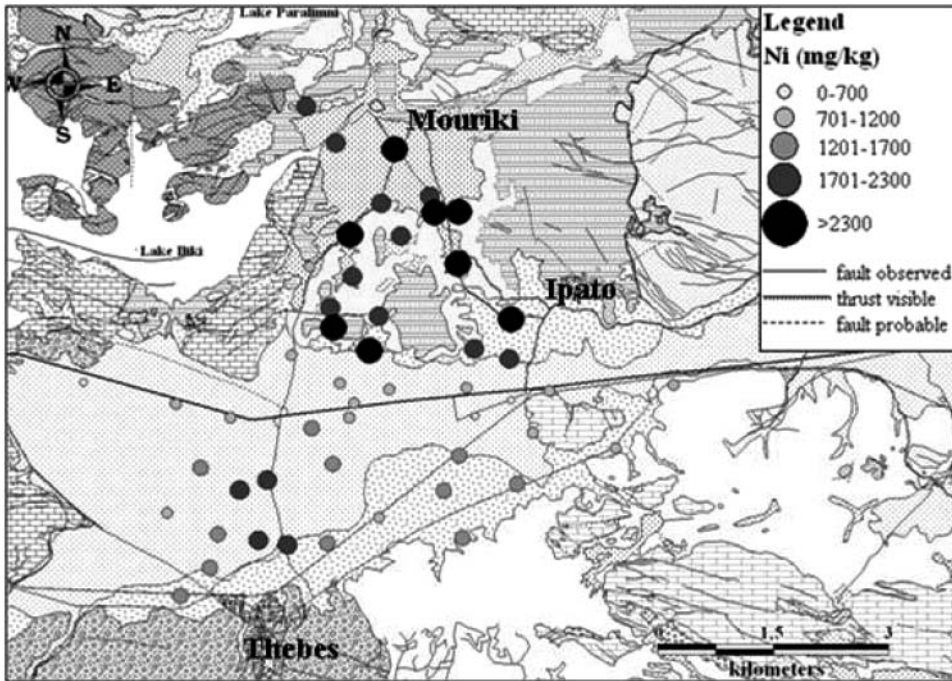| Chemical Elements	Concentrations Range in Thebes soils	Phytotoxic Levels
Pb	5–55	100–400
Zn	44–234	70–400
Ni	621–2639	100
Cr	134–856	75–100
Cd	0–1.8	3–8
Cu	20–53	60–125
Mn	685–1307	1500–3000
Co	23–97	25–50
Fe	27780–63524	—

Figure 5. Spatial distribution of Ni and Cr in the Thiva soils.

Table 7

Concentrations of Ni and Cr extracted by 0.5 M HCl in the Thiva soils (in μg g^{-1}), and percentage of the extractable Ni and Cr for individual samples

Sample	Cr	Cr % extracted	Ni	Ni % extracted
Th1	6	0.7	285	14
Th2	17	5.72	387	17.80
Th3	12	5.29	485	20.47
Th4	13	3.95	389	19.08
Th7	13	5.18	501	24.31
Th9	7	2.54	416	18.08
Th11	12	6.19	678	25.85
Th13	5	2.14	15	1.27
Th16	8	4.02	128	5.44
Th20	13	5.88	160	19.18
Th23	26	17.45	735	32.81
Th26	13	6.16	136	15.83
Th28	10	4.93	114	18.27
Th29	8	3.76	127	15.97
Th30	14	5.56	322	26.66
Th33	19	6.48	334	28.79
Th36	16	3.98	270	17.43
Th40	14	5.91	406	22.22
Th42	15	5.34	368	21.02
Th45	10	3.76	261	16.13
Th48	11	2.55	253	18.02
Th50	29	12.24	135	14.79
Th51	6	2.09	1.49	16.06

from 5 to 29 mg/kg, reflecting the low bioavailability of this element, as a result of its existence into the crystalline structure of insoluble mineral particles.

The correlation coefficient between pseuso-total (aqua regia) and bioavailable (0.5 M HCl) concentrations for Ni (Figure 6) is significant (+0.75), suggesting that a substantial amount of Ni in the soils is transferred to the plants. Such a satisfactory correlation indicates that 0.5 M HCl extraction method should be conducted to better determine the risk to the environment regarding the Thiva agricultural soils.

5. Conclusions

1) The soils of the Mouriki-Thiva area showed elevated concentrations of Ni, Cr, Co, Fe, and Mn, due to the presence of ultrabasic rocks of the shale-sandstone chert formation of the Sub-Pelagonian zone.
2) The studied soils are significantly contaminated by Ni, presenting concentrations that are extremely higher than the Dutch proposed guideline value. This chemical element is also characterized by high mobility and bioavailability, and a substantial amount of its total concentration in the soil is potentially transferred to the plants. The geochemical
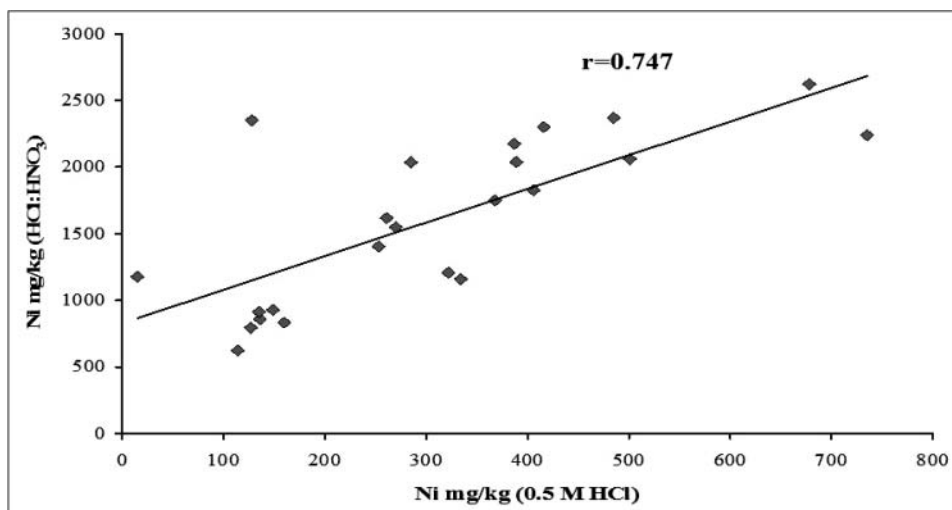
Figure 6. Diagram showing the relationship between pseudo-total (aqua regia) and potentially bioavailable (0.5 M HCl) concentrations of Ni.

map of Ni defines specific heavily polluted areas where various agricultural products are cultivated, posing a threat for the human health.

3) The low correlation between Ni and Cr is attributed to the different sources of these metals, reflecting the heterogeneity of the parent rock materials.

4) The 0.5 M HCl weak extraction method can be effectively applied to the Thebes soils in order to determine the potentially bioavailable concentrations of Ni.

Acknowledgements

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