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Spatial distribution and concentrations of Fe, Mg, Co, Cr and Ni in topsoils of central Greece as affected by parent rocks

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Abstract. The spatial distribution of five potentially toxic elements (Fe, Mg, Co, Cr and Ni) was studied in topsoils of Agia district, central Greece and their concentrations were measured and correlated to the underlying geological formations of the study area. The investigation was focused on mapping the areas with elevated concentrations and evaluating the contribution of the geological formations to these concentrations. A total of 173 surface soil samples (0-30 cm) were collected and the total concentration of the former elements was measured by ICP-AES after treatment with $HClO_4$, HNO_3, HCl and HF mixture. The analysis revealed that the average concentrations of Fe, Mg, Co, Cr and Ni were higher than those of global ones for the earth's crust. However, the soils of the present study, compared with similar soils in Greece or ultramafic rocks, demonstrate similar or lower concentrations, respectively. The spatial distribution of the metal concentrations seems to be strongly correlated to the presence of ophiolithic and metamorphic rocks in the region. A comparison with international regulation guidelines (Dutch list) indicated that Co, Cr and Ni have average concentrations above the suggested optimum level.

Key words: Spatial distribution, Potentially Toxic Element (PTE), ultramafic rock, Agia, Greece

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Константинос Скордас, Димитриос Патерас, Георгиос Папастергиос, Алексиос Лолас, Анестис Филипидис. Пространствено разпределение и концентрации на Fe, Mg, Co, Cr и Ni в повърхностни почви от централна Гърция, повлияни от коренните скали

Резюме. Пространсвеното разпределение на пет потенциално токсични елемента (Fe, Mg, Co, Cr и Ni) беше изучено в повърхностни почви от района Агия, централна Гърция и техните концентрации бяха измерени и съпоставени с тези в подстилащите геоложки формации в изучавания район. Изследването беше фокусирано върху картиране на областите с повишени концентрации и оценяване на приноса на подлежащите формации за това повишение. Бяха събрани бщо 173 проби от повърхностния почвен слой (0-30 см) и съдържанието на изследваните елементи беше определено с ICP-AES след разтваряне в смес от $HClO_4$, HNO_3, HCl и HF. Анализите показаха, че средните концентрации на Fe, Mg, Co, Cr и Ni в изследваните почви са по-високи от средните за земната кора, но сравнени с подобни почви в Гърция или такива свързани с ултрамафични скали, показват подобни или по-ниски концентрации.

Пространственото разпределение на металите изглежда силно корелирано с присъствието на офиолитови или метаморфни скали. Сравнението с международните норми (Холанския списък) показва, че концентрациите на Co, Cr и Ni надхвърлят указаните там оптимални стойности.

Introduction

Elevated concentrations of Potentially Toxic Elements (PTE) in soils, in regions where geological formations are highly enriched with these elements, are a widespread and noteworthy problem (Chatsigeorgiou-Stauraki 1998; Kelepertsis et al. 2001, 2006; Skordas & Kelepertsis 2005; Vardaki & Kelepertsis 1999). The concentration of PTE in soils is highly affected and differentiated by the nature of parent materials. The latter controls, along with other factors (i.e., soil pH, Eh, absorptive power of soil constituents etc.) the level of the element availability and their uptake from plants and animals in sufficient and, in some cases, even toxic levels (Alloway 1995; Alloway et al. 1988; Hesterberg 1998; Kabata-Pendias & Pendias 2001; Newman & Unger 2003; Siegel 2002; Simmons et al. 2005; Thorton & Abrahams 1983).

In such cases soil geochemical surveys are undertaken in order to reveal the existence of extremely high concentrations or so called positive geochemical anomalies in the soils, formed on such geological material and to attribute their existence either to mineralization or to environmental pollution (Bölviken et al. 1996; FOREGS 2005; Kelepertsis et al. 2006; Papastergios et al. 2010; Papastergios et al. 2010a). The methods to identify the aforementioned geochemical anomalies as well as the analytical procedure and data manipulation are those employed in the geochemical prospection for mineral detection. The latter is used to map the natural sources that influence the presence of metals as well as to identify any anthropogenic pollution of the related elements (Carranza 2009; Kelepertsis 2000).

In several regions of Greece there are ultramafic rocks, which contain PTEs that could end up, through weathering and pedogenesis processes, in soils and the environment, in general (FOREGS 2005; Petrotou et al. 2010; Vardaki & Kelepertsis 1999). For example, soils formed on ultramafic igneous rocks such as olivine basalts or pickrites inherit high concentrations of Co, Cr and Ni. These metals are commonly contained in minerals constituting these rocks, such as forsterite (Co, Ni), chrome-diopside and chromite. Flora growing in soils deriving from ultramafic igneous rocks or their metamorphic equivalent (i.e., serpentinites) can accumulate the latter elements in proportion to their natural baseline contents (Anderson et al. 1999; Brooks 1983; Reeves & Brooks 1983; Shallari et al. 1998; Siegel 2002).

The aim of the present study was to delineate the areas in Agia district with high concentrations of five PTEs (Fe, Mg, Co, Cr and Ni) and map these areas that fall into a certain range of concentrations. At the same time, it was interesting to see the relation of the measured concentrations with the geological formations of the region and present a model of the metal dispersion.

Study area – Geological setting

The study area of the present research lays inside the Amyros river watershed, situated in the eastern part of Larissa prefecture, central Greece (Fig. 1a). It consists of a plain area with hills that rise up in certain regions. Kissavos Mountain lies north of the area while low hills surround its eastern and southern parts.

The area belongs to the Pelagonian zone and consists of metamorphic rocks (Fig. 1a). The stratigraphic column of the area is made up of the following formations (IGME 1981, 1984; Katsikatos et al. 1980, 1982; Migiros 1983):

1. Quaternary sediments: consisting of unconsolidated material with sand and rounded and angular pebbles in the torrent beds, and alluvial sediments.

2. Neogene sediments: They are composed of marly limestones, marls, and conglomerates.
3. Marbles of Agia (Upper Cretaceous).
4. Pre-Upper Cretaceous tectonic cover. It is wholly metamorphosed with a thickness of 1000 m. It includes a variety of mixture formations and an ophiolithic complex.
5. Middle Upper Cretaceous – Upper Jurasic marbles.
6. Neopaleozoic – Lower Mesotriasic formations. They include a variety of metamorphic rocks of sedimentary origin and coarse-grained marble and cipolines.
7. Paleozoic (Pre-Carboniferous) crystalline basement of the Pelagonian zone. It includes gneisses-schists, amphibolite schists and amphibolites.

In the southeast part of the area many occurrences of iron oxides and hydroxides as well as copper, antimony and arsenic exist. Arsenic occurs as arsenopyrite, antimony as stibnite and copper as malachite. Manganese oxide outcrops are also, common. All the above ore occurrences are found within the metamorphic rocks of the basement and the ophiolite complex (Migiros 1993). Although some of the ore deposits show economic interest, no mining activity has been reported.

Materials and methods

A total of 173 soil samples were collected covering an area of 65 km^2, approximately. During the sampling procedure the initial regular sampling grid of 500x500 m was not possible to be followed accurately because of the cultivated and in some parts mountainous terrain, but care was taken to preserve a uniform distribution of sampling sites over the study area. The sampling locations are presented in Figure 1a.

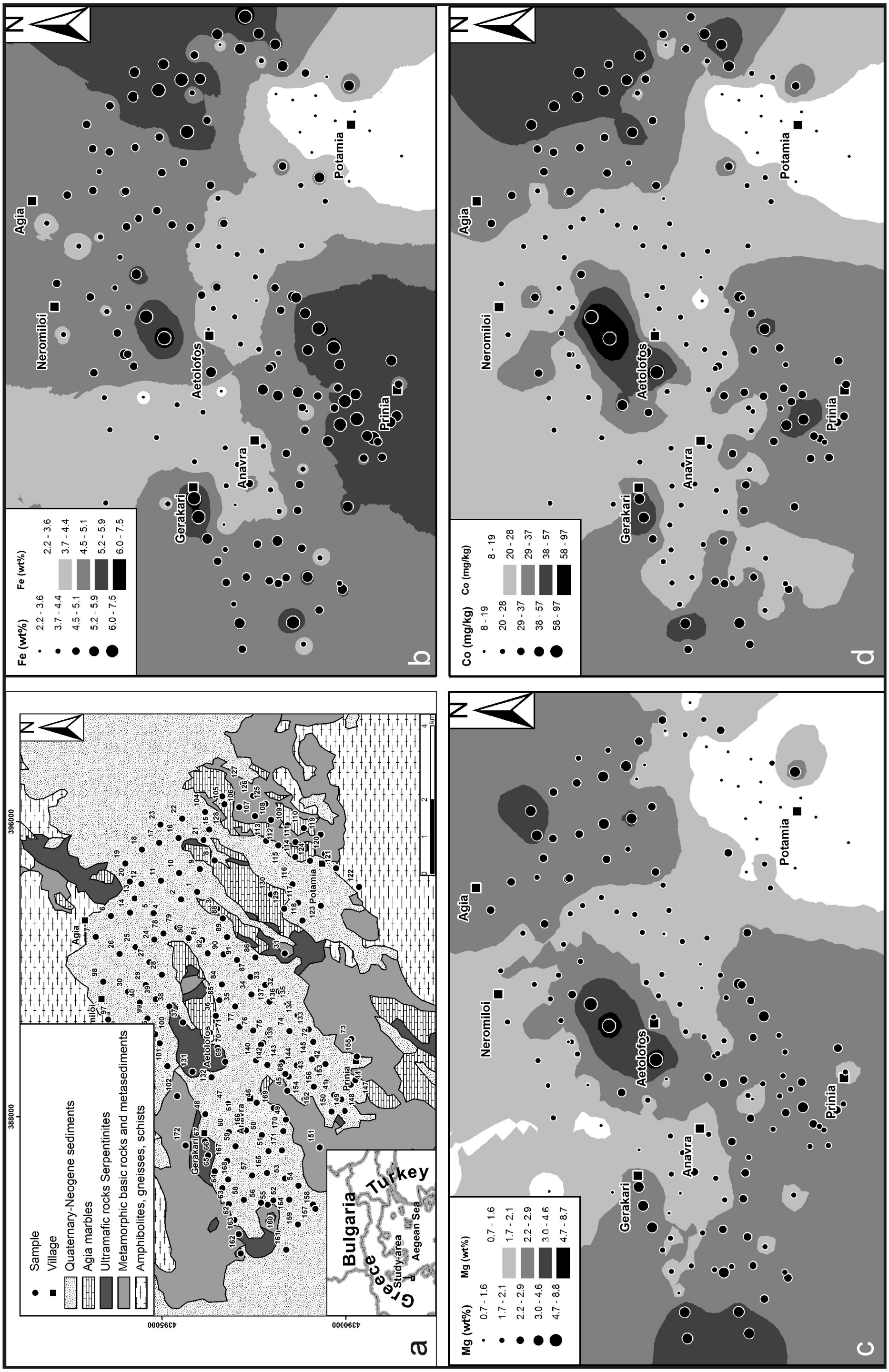
The surface of each sample location was cleaned from superficial debris, vegetation and O-soil horizon material before digging to a depth of 10 cm. The samples were oven dried at 40^oC, disaggregated in an agate mortar and sieved through nylon screens of 2 mm. The finer fraction (<2 mm) was homogenised and pulverised to <0.075 mm in an agate mill. Then the soil samples were digested with a mixture of $HClO_4$–HNO_3–HCl–HF and analysed for Fe, Mg, Co, Cr, Ni and Zr by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

Analytical data quality was assured by introduction of internal reference samples in randomised positions within the analytical batch and by duplicate analysis of a proportion of the samples (Ramsey et al. 1987). Analytical precision was calculated from these duplicate samples and it was found within the international standards.

Results and discussion

Descriptive statistics regarding the elements determined in the present study are given in Table 1. Compared to the earth's crust, all elements have average concentrations above those cited in the literature. However, compared to concentrations cited for ultramafic rocks their average concentrations are lower. These differences may be due to erosion and pedogenesis processes or differences in the applied methodologies. Petrotou et al. (2010) studied the concentrations for several elements in the Kozani-Ptolemais basin (Greece) and reported similar average values for Fe, Mg and Co and a little higher for Cr and Ni.

The distribution of the elements focused in the present study seems to be strongly controlled by the regional geology, especially from the presence of ultramafic rocks in which Fe, Mg, Co, Cr and Ni are predominant (Skordas & Kelepertsis 2005). Graduated symbol maps, along with interpolation maps (Fig. 1b-f) were created, with the aid of GIS software (ArcGIS 9.2), for the concentrations of the studied elements and projected on the simplified geological map of the study area in order to visualise the spatial relationship between the latter elements and their sources in the Agia region. The concentrations of the elements were divided into five classes (for the graduated symbol maps, as well as the interpolation maps) using the "natural breaks"


a
Sample
Village
Quaternary-Neogene sediments
Agia marbles
Ultramafic rocks Serpentinites
Metamorphic basic rocks and metasediments
Amphibolites, gneisses, schists
Bulgaria
Turkey
Greece
Study area
Aegean Sea
b
Fe (wt%)
2.2 - 3.6
3.7 - 4.4
4.5 - 5.1
5.2 - 5.9
6.0 - 7.5
c
Mg (wt%)
0.7 - 1.6
1.7 - 2.1
2.2 - 2.9
3.0 - 4.6
4.7 - 8.8
4.7 - 8.7
d
Co (mg/kg)
8 - 19
20 - 28
29 - 37
38 - 57
58 - 97
Agia
Neromiloi
Aetolofos
Gerakari
Anavra
Prinia
Potamia
N

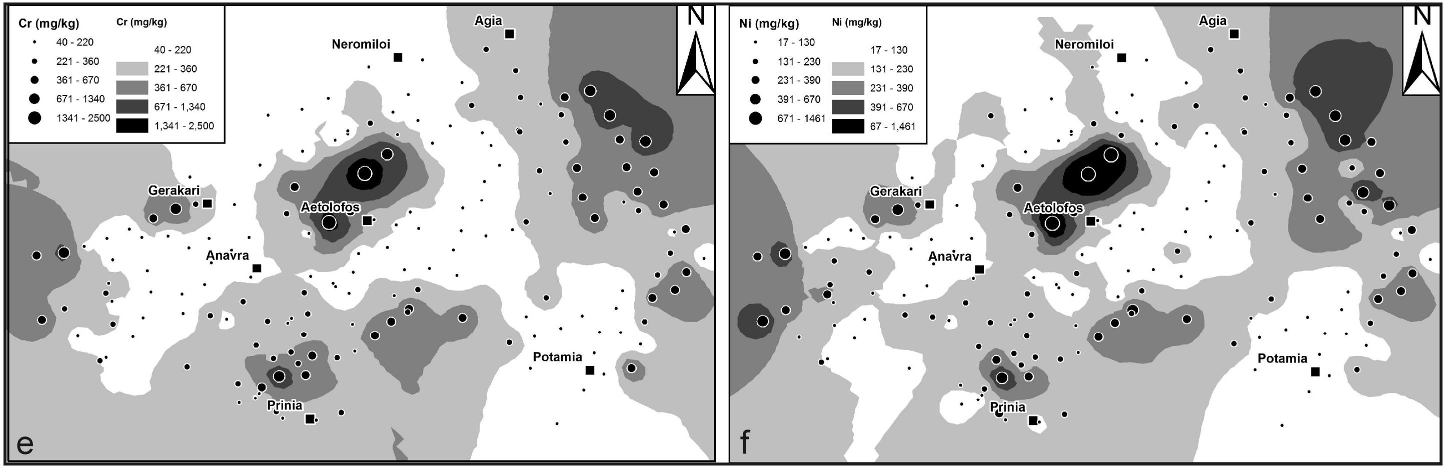


Fig. 1a) Simplified geological map of the study area and sample locations. b) –f) Graduated symbol plots and interpolation maps of the spatial distribution in the study area for the elements, given in the respective legends

Table 1. *Summary statistics for the soils of the present study and comparison with the earth's crust, ultramafic rocks (Umaf) and similar soils from Greece*

Element	Fe	Mg	Co	Cr	Ni
Units	wt%	wt%	mg/kg	mg/kg	mg/kg
Minimum	2.2	0.7	8	40	17
Maximum	7.5	8.8	97	2500	1461
Average (present study)	4.7	2.2	29	299	189
Average (earth's crust)[1,2]	3.8	1.3	10	43	17
Average (Umaf)[3]	9.4	-	110	2980	2000
Average (Umaf)[4]	-	-	150	2000	2000
Average (Greek similar soils)[5]	5.2	2.4	22	346	287

[1] Connor & Shacklette 1975, [2] Siegel 2002, [3] Rose et al. 1979, [4] Bowie & Thornton 1985, [5] Petrotou et al. 2010

method provided by ArcGIS software. The interpolation method applied was "Inverse Distance Weighted" (IDW) as it provided smoother lines that were easier to interpret.

High concentration values of Fe have been found throughout the region. Substantially high values were spotted in areas where ophiolithic rocks are present (Fig. 1b). Less extreme concentrations show a wide distribution and this is attributed to the presence of Fe in the metamorphic rocks of the study area.

The largest Mg concentration values were found in the northern part of Aetolofos village area, in the south-east area of Agia, in the area of Prinia and Gerakari village, as well as in the western border of the basin (Fig. 1c). The presence of Mg in the soil is related to the weathering of ophiolithic rocks and marly limestones.

Cobalt concentration values, substantially high, were spotted in the central part of the region and especially close to the northern area of Aetolofos village, in the eastern border of the basin, in the western and southern area of Gerakari village, as well as in the northern area of Prinia village (Fig. 1d). These high concentration values are attributed to the presence of ophiolithic rocks.

Chromium appears with elevated values in the areas where ultramafic rocks are present (Anderson et al. 1973; Kabata-Pendias & Pendias 2001). Concentration values, substantially high, were spotted in the surrounding region of Aetolofos village, in the eastern-northeastern part of the study area, in the area of Gerakari and Prinia village, as well as in the southern border of the study area (Fig. 1e). Chromium in the soils derives from the weathering of ultramafic rocks in the region. The high Cr concentration values appeared, as it was expected, in areas where serpentinized peridotites appeared. The highest ones belong to the serpentinized dunites and pyroxenites while the lowest ones to the metabasalts (Migiros 1986).

The highest Ni concentrations were found in the centre of the study area and northern of Aetolofos village. Elevated concentrations were also found in the eastern-northeastern edges of the basin, in the western part of the Gerakari village area and in the western border between Gerakari village and that of Prinia in the southern end of the study area (Fig. 1f). The elevated concentrations are strongly correlated with the presence of ultramafic rocks in the region.

Because the variables (elements) under study demonstrated a skewed distribution (the average was larger than the median) they were log-transformed ($\log_{10}$). The calculation of the Pearson Product Moment Correlation Coefficients (r) has shown that strong positive correlation exists between the elements focused in the present study (Table 2). This observation suggests common sources for the elements with high correlation coefficients and is attributed to the presence of ultramafic rocks predominating in the area.

In Europe, it is well known that the Netherlands has clear, comprehensive legislation regarding contaminated land and the environment (Boekhold 2008; Breure et al. 2008). As a result, many researchers use the values suggested by the Netherlands (Dutch List) as guidelines for comparisons with their own datasets (i.e., Papastergios et al. 2010b; Schulze et al. 1997; Wilcke et al. 1998). A comparison between the average values of Co, Cr and Ni in the present study and those proposed as optimum and action values by the Dutch list indicated that all three elements have average concentrations above their proposed optimum concentrations. However, only Cr and Ni approached the proposed action value (Table 3).

Table 2. *Pearson correlation coefficient matrix for the data of the present study*

	Ni	Cr	Co	Fe	Mg
Ni	1				
Cr	0.956	1			
Co	0.912	0.891	1		
Fe	0.502	0.514	0.749	1	
Mg	0.881	0.853	0.838	0.570	1

Table 3. *Comparison between the average concentrations of Co, Cr and Ni of the present study and the Dutch list*

Element	Present study	Dutch list	
(mg/kg)	average	optimum	action
Co	29	20	240
Cr	299	100	380
Ni	189	35	210

Conclusions

The soil analysis data of the present research revealed elevated concentrations of Cr and Ni in relation to their respective global mean values but similar values when compared to similar soils from other areas in Greece. The elevated concentrations of the latter elements emanate from the weathering of the ophiolithic rocks of the Agia district. Furthermore, high Fe concentrations may, also derive from the altered rocks that are present in the area. The spatial distribution of the elements discussed in the present research, throughout the study area, is unbreakably connected with the areas where ophiolithic rocks are present. When compared to international guidelines Cr and Ni average concentrations approach the proposed action limits. Further assessment, regarding the bioavailability of the studied elements is required in order to estimate the potential risk that these elements pose on human health.

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