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Geochemical Characterization of Greek Ophiolitic Environments Using Statistical Analysis

N. Bompoti[1] · M. Chrysochoou[1,2] · D. Dermatas[2]

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Abstract The presence of elevated Cr and Ni levels in the geoenvironment may be attributed to both anthropogenic sources and natural weathering processes of ultramafic rocks. Understanding the origin of these metals is important in environmental management. This study employed statistical methods, such as factor analysis and Pearson correlations, and specialized diagrams, in order to determine the origin of elevated metal levels as a function of the geologic background in five areas in Greece.

Factor analysis indicated that each area had distinct geochemical characteristics with three geological background types involved: ultramafic, carbonate and silica rich rocks. Vergina has the strongest ultramafic background, while Thermi consists mostly of rocks with high silica content. Avlonas has a mixed ultramafic background with silica enrichment and Thiva has admixtures of ultramafic with carbonate rocks components. Inofita consists of primarily carbonates, with silica rocks contribution in the surficial samples and ultramafic components in the deeper samples. Accordingly, the highest Cr (up to 12,000 mg/kg) and Ni (up to 3140 mg/kg) concentrations in soil were observed in Vergina and the lowest in Thermi.

In groundwater, Cr(VI) levels in Inofita exceeded 500 μg/L and are considered anthropogenic, as they are accompanied by high Cl$^-$ levels and not justified by soil Cr levels. Cr(VI) in groundwater was below 200 μg/L in all other areas. In Vergina, with only agricultural activity and pure ultramafic background, half of the groundwater samples were at or above the 50 μg/L threshold for Cr in drinking water. Also there is evidence of Ni concentrations exceeding 20 μg/L in the groundwater of Inofita and Thermi, both of which are attributed to the high ionic strength of groundwater.

✉ N. Bompoti
nefeli.bompoti@uconn.edu

1 Department of Civil and Environmental Engineering, School of Engineering, University of Connecticut, 261 Glenbrook Road, Storrs, CT 06269, USA

2 Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Zografou Campus, 9 Iroon Polytexneiou, 15780 Athens, Zografou, Greece

1 Introduction

Chromium is a common metal and exists in the environment in mostly its trivalent (Cr(III)) and hexavalent (Cr(VI)) state. Cr(III) is considered insoluble in most environmental conditions (pH>5) and is an essential element of human metabolism, while Cr(VI) is highly mobile, toxic and carcinogenic (ATSDR 2012). Cr(VI) presence in the geoenvironment (i.e., soil and groundwater) is commonly related to anthropogenic sources, but recent investigations have shown that Cr(VI) can also be derived from the natural geological background (Izbicki and Ball 2004; Fantoni et al. 2002; Dermatas et al. 2015). Ultrabasic or ultramafic rocks contain substantial concentrations of Cr(III), which can be oxidized to Cr(VI) by high-valence manganese oxides and mobilized in groundwater under favorable pH conditions. Ultramafic rocks and their weathering products occur in several populated areas globally including Greece (Oze et al. 2004; Bonifacio et al. 1997; Caillaud et al. 2009; Kelepertzis et al. 2013) and are characterized by elevated levels of Ni, Cr and Co compared with the more common silicate rich rocks.

Reported Cr(VI) concentrations in the surface and groundwater of such areas occasionally exceed the World Health Organization's maximum contaminant level for total Cr in drinking water (50 μg/L) (ATSDR 2012) and have several socio-economic impacts (Tentes and Damigos 2012). For example, spring water in Italy was reported to have up to 73 μg/L Cr(VI) (Fantoni et al. 2002), groundwater in the Mojave desert up to 60 μg/L Cr(VI)) (Izbicki et al. 2008) and in several areas in Greece groundwater concentrations up to 150 μg/L (Tziritis et al. 2012; Dermatas et al. 2015; Panagiotakis et al. 2015). In certain cases, e.g., in Thiva, Greece, the origin of Cr(VI) in soil and groundwater may be ambiguous, as both anthropogenic and geogenic sources are present in the area (Panagiotakis et al. 2015) This has important implication with respect to responsibility for remediation. As such, understanding the source and behavior of Cr and associated metals in the geoenvironment is important. Accordingly, the aim of this paper is to employ statistical analyses of the geochemical characteristics of soil and groundwater in ultramafic areas in Greece, in order to identify characteristics that may be used to distinguish between the geogenic and anthropogenic origin of Cr and Ni.

2 Materials and Methods

2.1 Sample and Data Collection

The study took place in five areas in Greece (Fig. 1) that have known Cr(VI) occurrences in ground- or surface waters. Three of the areas, Thiva, Avlonas and Inofita, are in Viotia, Central Greece, which is located in an ophiolitic zone (Sup-Pelagonian zone) (Mountrakis 1986). This is an area with intense industrial activity, where previous investigations have shown both geogenic and anthropogenic Cr contamination (Kelepertzis et al. 2013; Economou-Eliopoulos 2003). The other two areas studied, Vergina and Thermi, are located in Central Macedonia, Northern Greece and both have a broader geologic background of serpentinized ultramafics (Vardar zone) (Mountrakis 1986). Both chosen sampling locations are far from anthropogenic
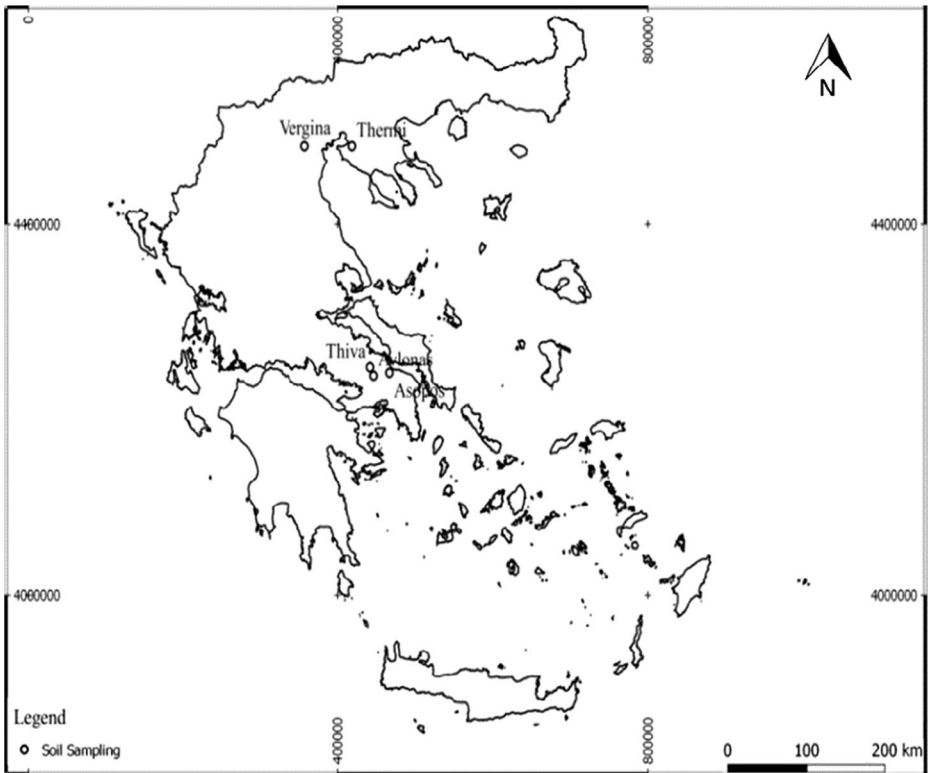
Fig. 1 Map of Greece with areas of investigation

activities, with the exception of agriculture, which is intensive in Vergina. Table 1 and Table S1 in Supplemental material presents an overview of the number and type of soil and groundwater samples collected from the 5 areas, along with information on the specific local geology derived from geologic maps. Additional information on the Thiva samples is provided by Panagiotakis et al. (2015) and on the Vergina samples by Dermatas et al. (2015). In total, the dataset included chemical analysis data for 111 soil and 157 groundwater samples.

2.2 Elemental Analysis

Analysis of surface soil and drill core samples included pH and total elemental analysis. Soil pH was measured according to the SW-846 method 9045C and total concentrations of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Si, Sr, Ti, Y, Zn in all samples were determined by X-ray fluorescence spectrometry (XRF). Sample preparation involved drying at 103 °C for 24 fours, sieving at 2 mm and crushing to 100 μm. The XRF spectrometer used was calibrated up to 0.3 % for NiO (2357 mg/kg Ni), so that this was the upper limit for the reported concentrations for this element. The XRF detection limits are shown in Table S2 in the Supplemental material.

Groundwater samples were analyzed for pH, temperature, redox potential (with an Ag/AgCl electrode (3 M KCl)) and Cr(VI) was measured with the diphenylcarbazide method (US EPA method 7196A with DL 0.5 mg/L in Inofita, Avlonas, Vergina and Thermi and DIN

Table 1 Overview of geologic background, soil and groundwater samples obtained from the five Greek areas

	Geology[a]	Topsoil	Soil boring samples	Groundwater samples
Thiva	Alluvial deposits of various materials, marls, clays, sandstones and rock slides of Jurassic limestone, adjacent to ophiolitic complex	14	None	61 existing wells (Panagiotakis et al. 2015)
Avlonas	Fluvial-terrestrial deposits, calcareous cobbles, limestone, ultramafic rocks and sandstones in the broader area	5	None	4 existing wells
Inofita	Marls, clays, loams, cobbles, sand, limestone, ultramafic rocks and sandstones in the broader area	11	38 (6 borings to 45 m depth)	59 (51 samples from 6 new borings+8 from existing wells)
Vergina	Unconsolidated, unsorted rubbles and cobbles of carbonate and schist rocks, adjacent to mass of strongly serpentinized and weathered ultramafic rocks	3	17(1 boring to 98 m depth)	8 (4 discrete in new boring and 4 existing wells)
Thermi	Valley deposits of sandy clay, broader areas geology includes gneiss, gabbro and ultramafic rocks	8	15 (1 boring to 98 m depth)	25 (12 from existing wells and 13 from new borings)

[a] Obtained on the basis of geologic maps provided by the Greek Institute of Geology and Mineral Exploration

38405-D24 with DL 1 μg/L in Thiva). The Atomic Absorption Spectrophotometer was used for the elemental analysis (PERKIN ELMER 2100; using flame) for Ca, K, Na, Mg, Si analysis in Inofita, Avlonas, Vergina and Thermi while in Thiva Cr(VI) measured with Inductively Coupled Plasma, atomic emission spectroscopy ICP-AES (EN ISO 11885). In all areas, chlorides (Cl$^-$) were measured with the EPA 325.1 colorimetric method and the EPA 375.4 turbidimetric method was used for determination of sulfates (SO$_4^{2-}$). The HCO$_3^-$ concentration was calculated based on the alkalinity (as mg CaCO$_3$/L), which was measured by titration with H$_2$SO$_4$ (0.01 - 0.1 N) at pH equal to 4.5 with the assumption that it was the only base contributing to the alkalinity. Both soil and groundwater samples were analyzed at the ISO-certified, Laboratory of Metallurgy, NTUA with the exception of groundwater samples in Thiva area, where the analyses were performed by Intergeo – Environmental Technology Ltd.

2.3 Statistical Analysis

Pearson's correlation coefficients were determined and R-mode factor analysis was applied in order to examine elemental associations that can be correlated to the geochemical background. The statistical package used is SPSS statistics 17.0. Multivariate analysis and especially factor analysis has been used in several case studies processing geochemical data (Reimann et al. 2002; Kumru and Bakac 2003; Antibachi et al. 2012; Kelepertsis et al. 2001; Stamatis et al. 2011) as it investigates and evaluates common factors in a group of variables in order to reduce dimensionality, compare variables with different units and explain correlations among data (Karlis 2005). Factor analysis focused on soil samples; and more specifically 18 variables for the 111 soil samples were analyzed, including depth, pH, Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti and Y. Trace elements that had more than 30 % of the values below the

instrumental detection limit (IDL) were excluded. For the remaining variables, data below the IDL were assigned a value corresponding to 50 % of the detection limit. The data distribution was generally positively skewed, so data were log-normalized, as factor analysis is a sensitive method to non-normally distributed data and could lead to biased results (Reimann et al. 2002). The dataset satisfied the criterion of Kaiser-Meyer-Olkin Measure of Sampling Adequacy (0.785) and considered correlated enough to apply the statistical analysis. Also, Bartlett's Test of Sphericity was significant for $p < 0.001$ and the R-matrix was not an identity matrix. The factors extracted based on the Kaiser criterion according to which the covariance of the factors has to be>1. Finally, the Varimax rotation was applied in order to minimize the number of variables that have high loadings on each factor.

3 Results and Discussion

3.1 Soil Characteristics

3.1.1 Trace Metal Concentrations

All 111 soil samples exhibited levels of Cr exceeding the global average 70 mg/kg for Cr and only 8 samples in Thermi and 2 samples in Inofita were at or below the global average of 50 mg/kg for Ni (Sparks 2003). The distribution of concentrations for the 5 areas is shown in Fig. 2 while Table 2 summarizes the mean, min and max concentrations encountered in each area. For both elements, the Thermi samples had median concentrations well below the overall median (1400 mg/kg for Cr and 1200 mg/kg for Ni). In contrast, Vergina was the area with the highest median values for both elements. It should be noted that the median Ni concentration is skewed downwards because of the upper detection limit of the XRF calibration for Ni (2357 mg/kg). Twelve samples from Vergina and one sample from Inofita exceeded this concentration. Inofita and Thiva had median concentrations close to the overall median, while Avlonas exhibited a unique behavior in that the Cr concentration was close to the median,
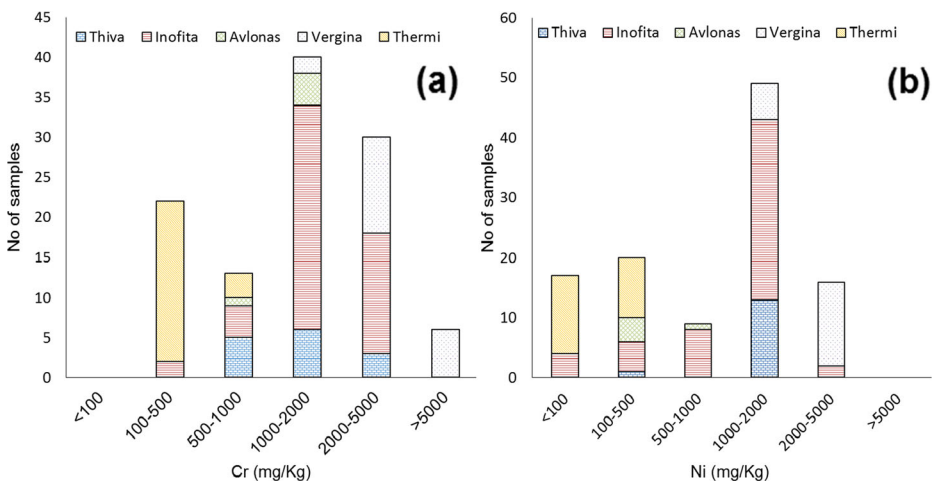

Fig. 2 Histograms of Cr (**a**) and Ni (**b**) concentrations (mg/kg) in soils

Table 2 Descriptive statistics of soil parameters examined

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation	Variance
Depth	111	0.050	98.250	19.892	25.861	668.805
pH	111	5.980	9.450	8.282	0.486	0.236
%						
Al	111	0.050	15.830	5.604	4.117	16.949
Ba	111	0.002	0.058	0.016	0.013	0.000
Ca	111	0.290	60.140	13.307	12.057	145.368
Co	111	0.001	0.190	0.016	0.018	0.000
Cu	111	0.001	0.018	0.004	0.002	0.000
Fe	111	0.060	12.400	7.072	2.613	6.827
K	111	0.060	3.300	1.033	0.805	0.647
Mg	111	0.400	38.400	10.879	10.181	103.649
Mn	111	0.005	0.390	0.128	0.061	0.004
Ni	111	0.002	0.400	0.143	0.104	0.011
Si	111	0.520	71.390	38.119	13.327	177.619
Sr	111	0.001	0.080	0.014	0.011	0.000
Ti	111	0.001	0.759	0.348	0.186	0.035
Y	111	0.000	0.004	0.001	0.001	0.000
Zn	111	0.001	0.030	0.007	0.003	0.000
Cr (mg/kg)	111	102.600	12110.300	1810.698	1771.426	3137950.330

while the Ni concentration was much lower. This indicates potential differences in the mineralogical composition of the analyzed samples.

The overall range of Cr concentrations reported for serpentine soils is between 200 and 60,000 mg/kg, with the higher values reported in New Caledonia (Oze et al. 2004). Deschamps et al. (2013) reported an average concentration of 2900 mg/kg Cr and 2300 mg/kg Ni in serpentinite rocks in subducted zones, as the one present throughout Europe. Depending on the pedogenetic processes and the sample depth, these concentrations may increase, as Cr and Ni accumulate in surficial weathered ophiolitic horizons, or decrease due to the presence of other soil types (Oze et al. 2004). Previous studies in Greek areas with ophiolitic background identified similarly high Cr and Ni concentrations in soil (Lilli et al. 2015). More specifically, in Thiva soil samples obtained from an area with serpentinite outcrops, Cr was 2400–3400 mg/kg and Ni 3350–3800 mg/kg (Kelepertzis et al. 2013. In Central Euboea, Cr and Ni in topsoil obtained near Ni-laterite deposits had a mean value of 1300 mg/kg and 2800 mg/kg, respectively (Megremi 2010). Finally, in a Ni-laterite deposit in mount Vermio, near Vergina, Cr ranged from 5500 to 21,900 mg/kg and Ni from 5200 to 15,000 mg/kg (Economou-Eliopoulos 2003). Thus, all areas except Thermi exhibited levels of Cr and Ni that are consistent with previous studies on soils derived by weathering of ultramafic rocks in Greece. Vergina showed the highest levels of Cr and Ni, and it may be inferred that the strongest ophiolitic presence is in this area. Additionally, given the absence of industrial activity in the area, it follows that Cr levels in soil alone may be used to infer its origin, in areas with known occurrence of serpentinites.

3.1.2 Major Elements

The major chemistry of the soil samples, including oxides of Si, Fe, Al, Mg and Ca are shown in Fig. 3 Substantial differences are observed between the chemistry of the various areas, which reflects variable geology, as also derived from the Ni and Cr levels. Vergina samples are rich in Mg (30 wt.%), and depleted in Si and Al. In comparison, the average concentrations of soils globally are 70 % Si, 13.4 % Al, 0.8 % Mg and 2.1 % Ca (Sparks 2003). The substantial enrichment in Mg and depletion in Si is typical of ultramafic rocks (Oze et al. 2004), so that the Vergina samples show characteristic chemistry of serpentinite-derived soils. In contrast, Thermi samples resemble more to the average global soil composition, which implies that they are likely dominated by silicate minerals of granitic rocks. The Inofita dataset exhibits high Ca (23 wt.% on average) concentrations, while the highest soil Ca content reported is approximately 45 % Ca (Sparks 2003). High Ca concentrations in soils reflect the existence of carbonate/limestone geologic background (Graf 1960). Thiva soils have intermediate concentrations for both Ca and Mg (11 % and 12 %, respectively), indicating partial influence of carbonate and serpentinite geologic background. Finally, Avlonas has elevated Ca (12 %) indicating some influence of carbonates. Distinguishing between ophiolites and carbonates as the geological origin for high Mg concentrations may be performed utilizing the Ca/Mg ratio, which is very low for serpentine soils, typically between 0.1 and 1 (Lee et al. 2001). All samples in Inofita and Avlonas presented Ca/Mg ratio above 1, with average well above this value (9.4 and 5.8, respectively), which reflects the prevalence of carbonate influence in these areas. In Thiva, the average Ca/Mg ratio was 1.3, with 3 out 14 samples exceeding 1. The geology of this area is influenced by both ophiolite complexes in the north and carbonates in
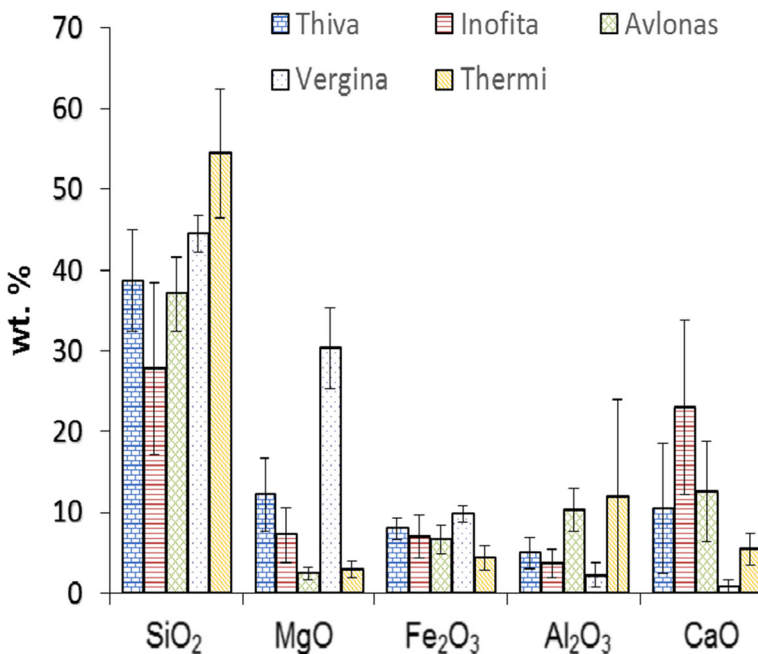

Fig. 3 Average percentage and standard deviation of major elements (oxides of Si, Fe, Al, Mg and Ca) in all areas

the south, so that the influence is mixed in the various sampling locations. Finally, the average Ca/Mg ratio in Vergina is 0.02, which shows that serpentine soils are practically exclusively responsible for the observed Mg contents.

Using the Mg content and the Ca/Mg ratio as an indicator for the presence of ultramafic rocks and/or soils, the five areas may be classified as Vergina >>Thiva>Inofita>>Avlonas= Thermi, with the latter two showing only marginal influence of ultramafic rocks with 3 % average Mg concentration.

The geochemical background and soils and rocks were also explored using triangular diagrams obtained using Microsoft Excel (Fig. 4a and b) (Kierczak et al. 2007; D'Amico et al. 2008; Quantin et al. 2008; Bulmer and Lavkulich 1994). These illustrate the relative contribution of major elements, given that the ratio of elements is controlled by the dominant minerals in a particular type of rock or soil. The Vergina samples plot closest to the point representing pure serpentinite rock (Bonifacio et al. 1997). The majority of Inofita samples and especially surface samples have lower Mg levels and higher Si, Fe and Al, a common trend exhibited in weathered soil horizons compared to the parent rock composition in ultramafic rocks (Bonifacio et al. 1997; Kelepertzis et al. 2013; Caillaud et al. 2009; D'Amico et al. 2008). Thiva samples have the same composition with soils of similar studies in the area (Kelepertzis et al. 2013) which identifies the origin of Ni and Cr enrichment being the transport of weathered parent rock fragments from upslope ultramafic sources. Furthermore, Thermi and Avlonas plot near soil samples derived from a higher degree of serpentinization studied by Bulmer and Lavkulich (1994). The aforementioned Mg index of ultramafic rocks can be supplemented by the slight increase in Fe and Al, signifying another geological background or a higher degree of ultramafic rock weathering. Taking into account trace metal concentrations,
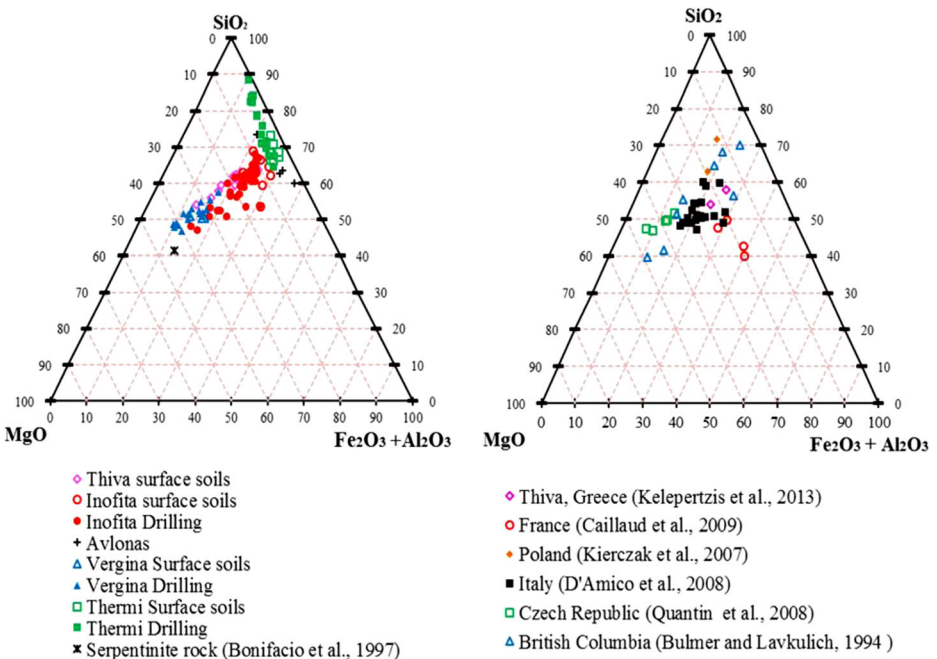

Fig. 4 Triangular diagrams for soil samples in this study (**a**) and data from other studies with ultramafic soils (**b**)

Thermi likely has a non-ophiolitic background while Avlonas possibly has some serpentines, subject to a higher degree of weathering.

3.1.3 Pearson's Correlation Factors

In order to examine the source of metals in soils, correlations between major and trace elements were evaluated for the entire dataset (Fig. 5) with a p–value of 0.05 and lower, including pH and depth as additional parameters.

Mg exhibits very good correlation with Cr, Ni and Fe (R for Mg-Ni 0.8, Mg-Cr 0.7 and Mg-Fe 0.6) in agreement with previous studies on serpentine soils (Oze et al. 2004; Kelepertsis et al. 2001) Positive correlations between these elements and Mn and Co have also been previously reported (Kelepertsis et al. 2001), but in this study the R factors were quite low ($R=$ 0.3–0.4), indicating that these elements were not exclusively linked to the serpentinite geologic environment. Another group of positively correlated elements is Al, Si, K, Ba and Y, which are also anti-correlated with Mg and the other associated elements. This reflects the existence of a different geological background, presumably that of silicate minerals. An interesting observation is that, in contrast to the findings of Prokisch et al. (2000), Y does not correlate with Cr nor other elements associated with ophiolitic rocks, and therefore, cannot be considered a general indicator to assess the geogenic or anthropogenic origin of Cr.

Examining the correlations for individual areas (not shown), Thiva has the strongest correlation among Cr and Mg, Ni and Co (R for Cr/Mg 0.8, Cr/Ni 0.9, Cr/Co 0.68) compared to the other areas while Cr/Fe (0.4) correlation is lower. Thiva only has surficial samples from varied locations so that a more heterogeneous background may be expected. The negative correlation between Mg and Al, K, Ti, Ba and Y (Mg/Al −0.7, Mg/K −0.8, Mg/Ti −0.7, Mg/Ba −0.7, Mg/Y −0.6) indicates the admixture of non-ultramafic material.

While the other areas have an inverse or negligible correlation between Mg and Al, Thermi has low positive correlation (Mg/Al 0.4) which shows its different geologic background.
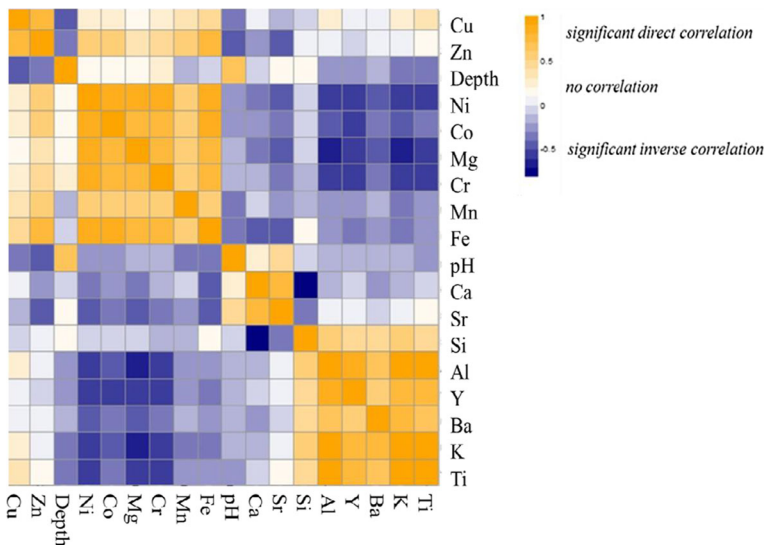

Fig. 5 Graphical representation of Pearson's correlation factor among pH, depth, major and trace element pairs

Although positive correlations among Mg, Fe, Ni and Mn are apparent (Mg/Ni 0.9, Mg/Fe 0.7, Mg/Mn 0.6) showing the ultramafic existence, Al is also correlated with these elements (Al/Ni 0.5, Al/Fe 0.9, Al/Mn 0.6). Also in Thermi, there is no significant correlation between Cr and other elements.

In Inofita, the correlation among Cr and Mg, Ni and Co is lower (R for Cr/Mg 0.4, Cr/Ni 0.6, Cr/Co 0.68) while a very strong correlation of Fe and Ni, Co and less with Cr is evident (R for Cr/Fe 0.61, Fe/Ni 0.9, Fe/Co 0.9). A negligible correlation between Mg with Al and K as well as a slight correlation of Fe with Al (0.48) is apparent, indicating the intense weathering of the parent material. As it is shown in the triangular diagrams, surface soils in Inofita exhibit a slight increase in Fe and Al, while Mg is depleted.

In contrast with Inofita and Thermi, in Vergina the inverse correlation of Mg/Al (−0.85) and Mg/K (−0.8) is stronger, manifesting the existence of non-ultramafic materials, especially in the aquifers (Dermatas et al. 2015).

3.1.4 Factor Analysis

Factors Analysis explained 72 % of the total variance of 111 soil samples for the 3 factors. The 3-factor loadings and the communalities of each variable are given in Table 3. Important loadings accounting for each factor are bolded. Communalities display the proportion of the variable's variance that is common to others in the set (Kumru and Bakac 2003).

Table 3 Factor analysis loadings and communalities for each variable

Variables	Factor 1	Factor 2	Factor 3	Communalities
Depth	−0.12	0.40	**−0.74**	0.72
pH	−0.21	−0.24	**−0.72**	0.62
MgO	**−0.49**	**0.78**	−0.03	0.84
Al$_2$O$_3$	**0.97**	−0.11	0.02	0.94
SiO$_2$	**0.66**	**0.61**	−0.25	0.87
K$_2$O	**0.97**	−0.09	0.00	0.95
CaO	**−0.46**	**−0.85**	0.00	0.94
TiO$_2$	**0.87**	−0.19	0.28	0.88
MnO	−0.30	0.24	**0.46**	0.36
Fe$_2$O$_3$	−0.31	**0.68**	**0.51**	0.81
NiO	**−0.62**	**0.66**	0.26	0.88
CuO	0.03	−0.08	**0.65**	0.43
ZnO	0.03	0.29	**0.72**	0.61
SrO	−0.16	**−0.80**	−0.26	0.72
BaO	**0.77**	−0.01	0.03	0.60
CoO	−0.27	**0.46**	0.00	0.29
Y	**0.88**	−0.11	0.05	0.80
Cr	**−0.47**	**0.65**	0.00	0.64
% of Variance	32.50	23.87	15.34	
Cumulative %	32.50	56.37	71.71	

Bold numbers represent the important loadings for each factor

The first factor, accounting for 33 % of total variance, includes a group of variables with high positive loadings (Al, Si, K, Ti, Ba and Y) and a group with high negative loadings (Mg, Ca, Ni and Cr). One may derive that: a) elements within each group are positively correlated (as also indicated by the correlations analysis); and b) samples with high concentration of the positive group have low concentrations of the negative group and vice versa. Considering the typical chemical composition of various rock types, it is possible to relate this grouping of elements to geologic background. Table 1 shows that the geologic background encountered in the five areas include rocks that are rich in Ca and Mg (limestone, dolomites and the metamorphic products marls), rocks that are rich in Si (sandstone, gneiss, schist) and basic (gabbro) and ultrabasic (serpeninite, ophiolites) rocks that have lower contents of Si and higher contents of Mg (Oze et al. 2004). Given the variability in the actual type of geology present, especially with respect to the Si-rich ones, we will discuss the results in terms of three broader categories: carbonate, silica-rich and ultramafic geologic background.

The second factor, explaining 24 % of the total variance, includes Mg, Si, Fe, Ni, Co and Cr with positive loadings, while Ca and Sr exhibit high negative loadings. Ca and Sr are derived from carbonate-rich geology, so that a highly negative second factor indicates samples with carbonate background, that are poor in other elements from both silica-rich and ultramafic (Mg, Ni, Fe, Cr) geology.

The third factor accounts for a small percentage of the variance (15 %). It is positively affected by Cu, Zn, Fe and Mn, with high negative loadings of depth and pH. Interestingly, pH and depth are independent from all other variables, and only correlated with each other. The latter is because deeper samples exhibit a slight increase in pH values which can be explained by the effect of hydrolysis reactions on percolating rainwater (Oze et al. 2004). However, there is no association between pH, depth and a particular geologic background in the analyzed dataset. The correlation of Cu and Zn has received different interpretations in the literature, the prevalent one being that these elements are associated with either industrial pollution or the use of phosphate fertilizers, sewage sludge and pesticides in agriculture (Alloway 2013). Given the low overall concentrations of Cu and Zn (<100 mg/kg in soil borings, respectively, and< 240 mg/kg in topsoils), they are most likely natural background values, as natural occurrence of Cu and Zn in basic rocks is 30–160 mg/kg and 48–240 mg/kg, respectively, while the positive correlation of Cu with Fe indicates the existence of mafic igneous rocks (Alloway 2013).

Based on this analysis, the geologic origin of individual samples was evaluated by pairwise plotting the scores for the three factors (Fig. 6). The geologic background of each sample is interpreted through the position along each axis. In Fig. 6a, the x-axis depicts silica-rich (in the positive) and ultramafic background (in the negative), while the y-axis corresponds to ultra-mafic background in the positive and carbonates in the negative. In Fig. 6b, the x-axis is the y-axis in Fig. 6a, while the positive of y-axis denotes higher Zn and Cu concentrations and the negative of y-axis is related to the sample pH and depth. It is apparent from Fig. 6 that samples from different areas plot in clusters that correspond to a distinct geology.

In Fig. 6a, all Thermi samples are plotted on the positive of the x-axis and have y-values near zero, indicating an exclusively silica-rich background. Avlonas samples are also plotted in this area but have negative y-values, denoting some influence of carbonate rocks. Samples in the third quadrant (negative in both axes) are primarily influenced by carbonate and ultramafic rocks, including the majority of the Inofita samples. All surface soil samples from Inofita are plotted below the samples from soil borings, indicating that the relative influence of ultramafic rocks is overall higher in deeper samples. The second (negative x, positive y) quadrant denotes
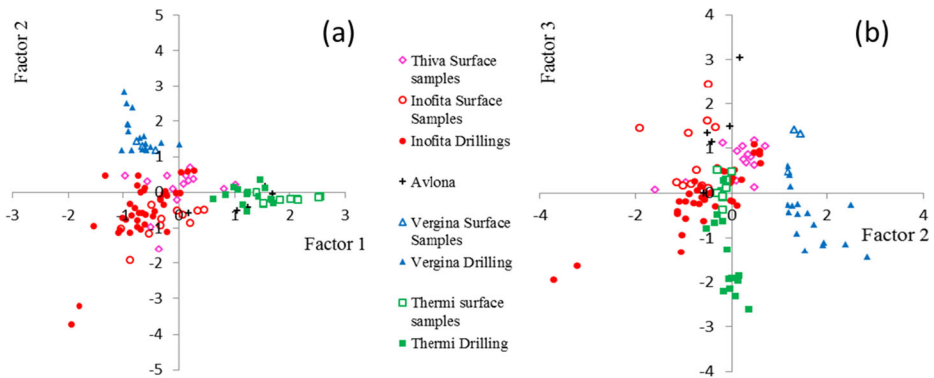
Fig. 6 First and Second (**a**) and Second and Third (**b**) Factor scores for all soil samples

a strong ultramafic influence and includes most samples from Vergina, a few from Inofita and Thiva, which shows a mixed ultramafic background with some silicate-rich influence and a single sample with strong carbonate influence. Topsoils in all areas have more silica-rich background influence compared with deeper samples.

In addition to the general characterization of the geologic background in each area, plotting individual values is also useful in order to identify locations with particular characteristics, i.e., outliers. For example, the two Inofita points that plot in the bottom left of the third quadrant in Fig. 6a were obtained from the deeper layers of a single boring, which have exclusively Ca and very little of any other element. Selection of individual samples for more detailed analysis (e.g., X-ray Diffraction, Electron Microscopy) may also be done on this basis.

The evaluation of the second plot in Fig. 6b shows two main observations. First, there is a positive linear correlation ($R^2=0.75$) between factors 2 and 3 values for the Inofita borehole samples and Thiva ($R^2=0.38$), and a negative one for the Thermi ($R^2=0.51$) and Vergina ($R^2=0.39$) borehole samples. The examination of the Inofita data shows that this is driven primarily by pH, i.e., samples with lower (i.e., more negative) factor 3 values have higher pH. In other words, in Inofita higher pH is associated with more carbonate and less ultramafic contribution. In Vergina, where carbonate geochemistry does not influence soil properties, the opposite is true. pH and depth are positively correlated and both influence factor 3. Deeper samples with higher pH contain more unweathered ultramafic minerals, so that the correlation between factors 2 and 3 is inverse. Finally, in Thermi factor 3 is primarily driven by depth; this indicates that deeper samples have slightly higher factor 2 values, or more ophiolitic contribution. However, the phenomenon for the Thermi samples is not pronounced, since factor 2 values are close to zero (neither carbonate nor ophiolitic contribution is significant).

The positive correlation in Inofita implies that the superficial samples (which also have slight lower pH) and in general exhibit higher Cu and Zn content, have more of the ultramafic component and less carbonate. This trend is attributed to two facts: a) that Inofita topsoils are enriched in Cr, Zn and Cu due to industrial activity that affects mostly the upper zone of soil; and b) that topsoils are transferred from upslope weathered rock fragments. The latter is the case for Thiva as it has been identified by other studies (Kelepertzis et al. 2013).

3.2 Groundwater Analysis

The geochemical origin of groundwater was investigated using Piper diagrams obtained by GW_Chart (Version 1.28.0.0). For each area one or two characteristic samples were plotted (Fig. 7). All samples except Thermi's new well plot fall on the left corner of the diamond. Water in this area is characterized by temporary hardness with high levels of Ca^{2+}, Mg^{2+} and HCO_3^-. Specifically, samples from Vergina and Thiva are Mg-CO_3 type, which is typical of groundwater in serpentinite geology (Fantoni et al. 2002). Groundwater in Avlonas is Ca-CO_3, which is in agreement with the carbonate background derived from the soil analyses. The Inofita samples are of mixed type which is in accordance with previous findings (Stamatis et al. 2011), and is likely to be due both to the mixed geologic background and the location of the borings, in an area with high anthropogenic influence. The same applies to the existing Thermi well. Finally, evidence of sea water contamination is apparent in Thermi's new well, as the water is characterized saline. High Na^+, K^+ and Cl^- is an indication for saline waters (Kelepertsis et al. 2001; Brezonik and Arnold 2011). It should be noted that the groundwater pH was very similar in all areas, with most samples between 7 and 8; Vergina and Thermi had the most alkaline samples with the average pH exceeding 8.0, while Avlonas had the lowest, with no sample exceeding pH 7.5.

Groundwater analysis revealed that chromium in groundwater occurs mostly as hexavalent chromium, indicated both by the Cr(VI)-Cr(tot) correlation ($R^2=0.97$) and the Cr(VI)/Cr_{tot} ratio (0.70). This is in agreement with several other studies in serpentinite environments (Fantoni et al. 2002; Megremi 2010; Ball and Izbicki 2004). The distribution of measured Cr(VI) concentrations in groundwater of all areas is shown in Fig. 8a. Values exceeding 500 µg/L are attributed to anthropogenic sources and restricted to the Inofita sampling location, which is surrounded by industrial activities. Interestingly, the samples with Cr(VI) concentrations exceeding 500 µg/L in Inofita, had also very high Cl^- concentrations (100–300 mg/L), without correspondingly high Na^+ concentrations as in the Thermi sample. Cl^- is considered of anthropogenic input as usually it is the least abundant anion groundwaters located away from coastal areas (Brezonik and Arnold 2011). Excluding samples with high Cl^- and Cr(VI)>500 µg/L, shows that Cr(VI) in the remaining samples is below 200 µg/L, with the highest frequencies observed in the ranges <10 and 10–50 µg/L. (Fig. 8a). The average Cr(VI) concentration in the reduced dataset is 23 µg/L and the median value 16 µg/L.

It should be noted that anthropogenic influence cannot be excluded in the dataset excluding the >500 µg/L values. Specifically, Panagiotakis et al. (2015) studied high Cr(VI) levels in Thiva and showed that while Cr was most likely of geologic origin, the old uncontrolled landfill of Thiva created high alkaline conditions that can favor Cr(III) oxidation to Cr(VI). Vergina is the only area with purely serpentinite background and anthropogenic influence limited to agriculture (which, however, can impact Cr levels in groundwater). In Vergina, 3 out of 8 groundwater samples were at and above the 50 µg/L threshold (49 µg/L, 61 µg/L, 74 µg/L) for drinking water. Avlonas and Thermi groundwater samples are consistent with the lower Cr levels in soil, as Cr(VI) concentrations are lower than 50 µg/L.

The Ni concentrations in groundwater were also investigated (Fig. 8b). Thiva, Avlonas and Vergina had Ni concentrations below the 20 µg/L (Ni threshold for groundwater), while Inofita (30 % of samples) and Thermi (50 % of samples) exceeded this limit. This is a surprising finding, given that the Ni levels in the Thermi soil were the lowest of the five areas. In both cases, this exceedance is likely to be related to the high ionic strength caused by high salt concentrations, which favors desorption of Ni^{2+} at the alkaline pH of the samples.
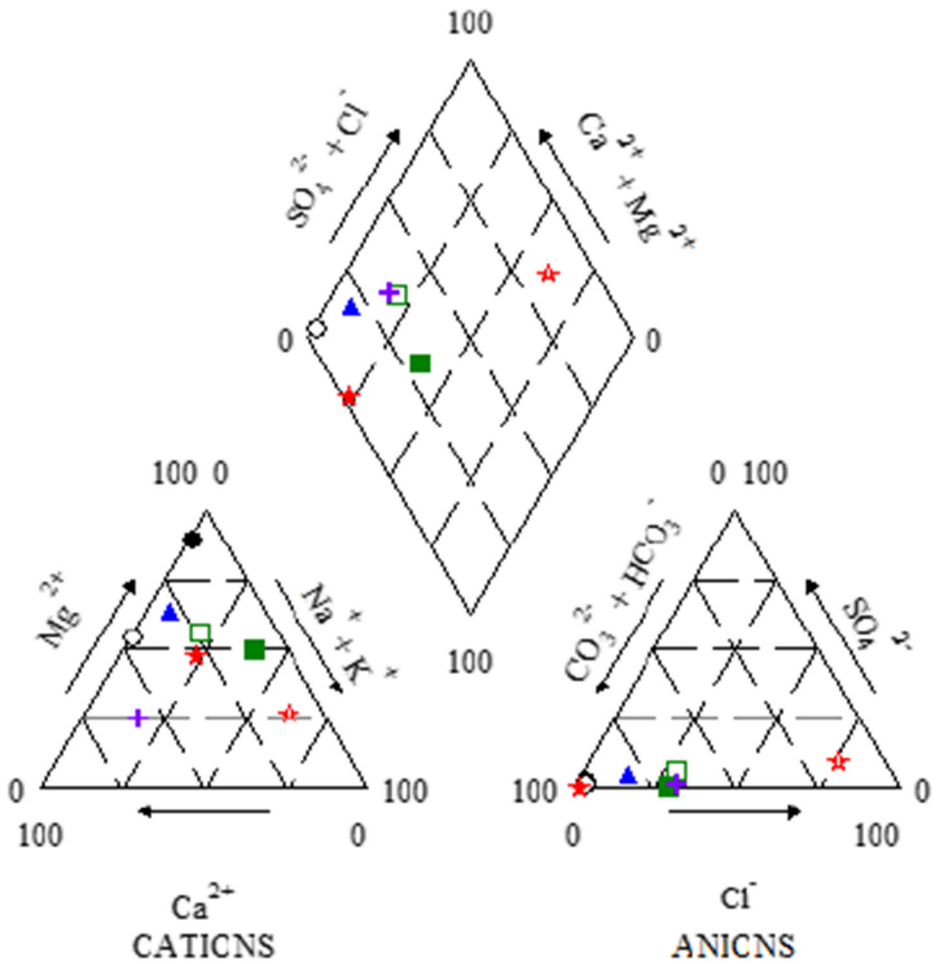
Fig. 7 Piper diagram of groundwater samples in all areas
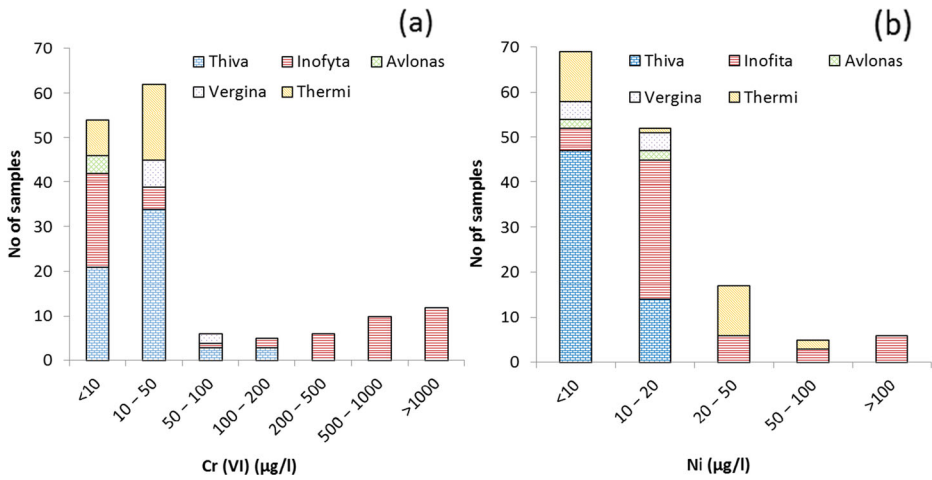
Fig. 8 Histogram of hexavalent chromium (Cr(VI) (μg/L)) (**a**) and nickel (Ni (μg/L)) (**b**) in groundwater of the areas studied

4 Conclusions

The geochemical background of soil and groundwater samples from five areas in Greece (Thermi, Vergina, Avlonas, Thiva and Inofita) with known occurrences of Cr(VI) in groundwater was investigated using meta-analysis of chemical composition data. While all areas are located in broader geologic zones in Greece that include ultramafic rocks, the particular background in each sampling location was not precisely known. Evaluation of the geochemical and geological background was performed using two approaches: use of characteristic indices and statistical analyses.

The Cr and Ni levels in the soil were the characteristic elements associated with ultramafic geology and four out of five areas (except Thermi) had levels consistent with ultramafics, with Vergina exhibiting the highest levels and presumably the strongest ultramafic presence. In addition, the Mg content and Ca/Mg ratio are known to be indicative of ultramafic background, while Fe_2O_3 and Al_2O_3 enrichment shows either a different geological background or a higher degree of ultramafic rock weathering. According to these indices, Vergina resembles most to pure serpentinite geology, Inofita and Avlonas are influenced by carbonate rocks, Thiva is influenced by both serpentinite and carbonate geology, while Thermi has neither character.

Factor analysis of soil chemical parameters yielded 3 factors that explained 72 % of the variance in sample composition. The first factor groups Al, Si, K, Ti, Ba and Y as positive loadings. These elements are known to be associated with rock types that are rich in silicate minerals, such as sandstones, schists and gneiss that are present in some of the areas. The negative loadings included a group of elements prevalent in ultramafic rocks (Mg, Cr and Ni). The second factor yielded Ca and Sr as representative of carbonate minerals (Ca, Sr) and also grouped Si, Mg, Ni, Fe and Cr as representative of non-carbonate geology. Finally, the third factor represents elements related with natural occurrence of Cu and Zn in mafic rocks along with an indication of agricultural/industrial activity in topsoils, as an inverse trend of pH and depth. Plotting the scores of individual samples showed that points from the different areas

grouped together depending on the geologic background. According to this classification, Thermi has a silica - rich geologic background, while Vergina exhibits the strongest ultramafic presence, consistent with the individual indices. Avlonas and Thiva have a mixed ultramafic background, the former with silica-rich rocks and the latter with carbonates. Inofita geology consists of primarily carbonate rocks, with the deeper samples exhibiting a more pronounced ultramafic contribution. Topsoils in all areas have a silica enrichment compared with deeper samples, the latter of which comprise unweathered ultramafic material. In Thermi, depth is not a controlling factor as neither carbonate nor ophiolitic contribution is significant.

The type of groundwater was examined in all areas and was found to be consistent with the identified geology. In general, the type of groundwater is Ca-Mg-HCO$_3$ with the exception of Thermi's new well, which is characterized as saline. Vergina and Thiva waters are of Mg-CO$_3$ type, typical of serpentinite environment, while Avlonas is of the Ca-CO$_3$ type, in accordance with the findings of soil analysis. In Inofita, where the anthropogenic activity is apparent, the type of water is mixed.

Groundwater analysis revealed that Cr in the groundwater is mostly hexavalent (Cr(VI)), with Cr(VI) concentrations in Inofita exceeding 500 μg/L. High Cr(VI) concentrations in Inofita are accompanied by high Cl$^-$ concentrations signifying that the elevated Cr(VI) levels are of anthropogenic source. All other areas had Cr(VI) below 200 μg/L. The geogenic levels of Cr(VI) can be isolated in Vergina, which is the only area with a pure ultramafic background and without industrial activities. In Vergina almost half of the samples were nearing or exceeding the limit of 50 μg/L total Cr for drinking water. Finally, Ni concentrations exceeding 20 μg/L were observed in the groundwater of Inofita and Thermi, both of which are attributed to the high ionic strength of groundwater. In Inofita, this is due to anthropogenic contamination, while in Thermi it is due to the natural salinity.

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