Spatial diversity of Cr distribution in soil and groundwater sites in relation with land use management in a Mediterranean region: The case of C. Evia and Assopos-Thiva Basins, Greece

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HIGHLIGHTS

- Spatial distribution of Cr and other elements in an area of Greece investigated
- Maps of land use and element contents in soil and groundwater were developed.
- GIS and multivariate statistics were applied to assess the origin of Cr contamination.
- Maps help distinguish Cr of geogenic and anthropogenic origin and salinization.
- These provide information for sustainable land management.

GRAPHICAL ABSTRACT
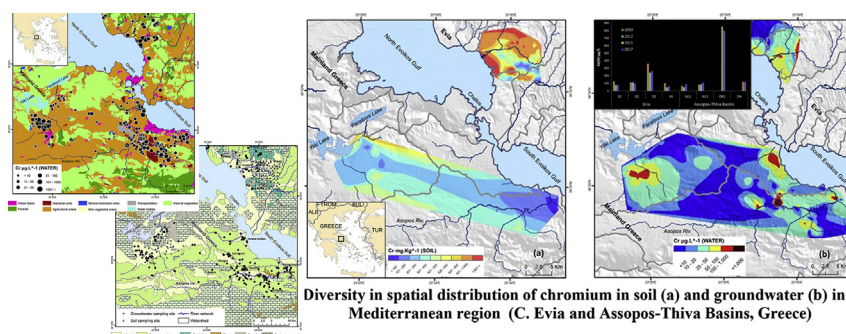
Diversity in spatial distribution of chromium in soil (a) and groundwater (b) in a Mediterranean region (C. Evia and Assopos-Thiva Basins, Greece)

ARTICLE INFO

ABSTRACT

The present study compiles new and literature data in a GIS platform aiming to (a) evaluate the extent and magnitude of Cr contamination in a Mediterranean region (Assopos-Thiva and Central Evia (Euboea) Basins, Greece); (b) combine spatial distribution of Cr in soil and groundwater with land use maps; (c) determine geochemical constraints on contamination by Cr; and (d) provide information that will be useful for better management of land use in a Mediterranean type ecosystem in order to prevent further degradation of natural resources.

The spatial diversity of Cr distribution in soils and groundwater throughout the C. Evia and Assopos-Thiva Basins is considered. It is attributed to both natural Cr sources (Cr-bearing peridotites, affecting primarily soil) and human (industrial) activities (the dominant source of groundwater contamination).

A combination of the spatial distribution of metals in soil and land use maps was used to define the specific areas of agricultural land use with elevated heavy metal contents.

Furthermore, the combination of the spatial distribution of Cr in groundwater and land use maps allows for definition of specific areas of industrial land use with elevated Cr concentrations (Inofita, south Assopos-Thiva Basin). Despite the good correlation ($r = 0.75$) between Cr(VI) and the strong oxidant NO_3^- in C. Evia, the lower standard potential (E^0) values for NO_3^- compared to those for $Cr_2O_7^{2-}$ (the latter is a stronger oxidant than the former) suggest that NO_3^- is not an oxidant of Cr.

This detailed assessment and presentation of the available analytical data for soil and groundwater in Assopos-Thiva and C. Evia Basins on a land use map provides information for land management decision makers.

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1. Introduction

Current knowledge based on the European Soil Data Centre indicates that metals are frequent soil contaminants (Liedekerke et al., 2014). The term 'Contaminated Site' refers to a well-defined area where the presence of soil contamination has been confirmed, and this presents a potential risk to humans, water, ecosystems or other receptors. The term 'Potentially Contaminated Site' refers to sites where unacceptable soil contamination is suspected, but not verified, and where detailed investigations need to be carried out to determine whether there is an unacceptable risk of adverse impacts on receptors (Liedekerke et al., 2014). The most abundant species of chromium (Cr) in nature are Cr(III), that is a required nutrient, and the highly toxic and very soluble oxidized Cr(VI), which causes serious health problems in the form of chromate oxyanions such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ (ATSDR, 2000; Losi et al., 1994; Shock et al., 1997).

Soil management, food, and water security are among the currently major issues of the ongoing Land Degradation and Restoration Assessment (LDRA) (Keesstra et al., 2016). The provision of the irrigation water is of global significance, since the amount of 92% of freshwater is of agricultural use (Hoekstra and Mekonnen, 2012). Water resources of proper quality are crucial for irrigation of crops, and for water supply in areas of increasing urbanization and growing tourism. The need to protect groundwater in the European Union, including Greece, has been recognized though the Water Framework Directive on groundwater. Council Directive 98/83/EC has established a maximum permissible limit for various potentially toxic elements. Among them Cr_{total} in drinking water, is regulated in a maximum permissible limit of 50 μg/L or ppb.

Soil contamination by Cr, and the consequent contamination of groundwater, is a risk in many countries of Europe, due to industrial activities and/or natural processes, related to Cr-bearing minerals and ores (Salunkhe et al., 1998; Eliopoulos and Economou-Eliopoulos, 2000; Fantoni et al., 2002; Oze, 2003; Becquer et al., 2003; Ball and Izbicki, 2004; Oze et al., 2004, 2007, 2016). Untreated or poorly treated industrial wastes from approximately 700 industrial plants, (concerning activities such as the production of chromic acid, Cr-pigments, leather tanning, corrosion control) in the Assopos-Thiva Basin, and the widespread occurrence of ophiolites and Fe-Ni-laterite deposits in C. Evia (Euboea) are considered to be the major contamination sources of Cr for soil and water, and in other regions in Greece (Giannoulopoulos, 2008; Vasilatos et al., 2008, 2010; Megremi, 2009, 2010; Megremi et al., 2013; Economou-Eliopoulos et al., 2011, 2012, 2013, 2014, 2016, 2017; Dermatas et al., 2015; Dimitroula et al., 2015; Dokou et al., 2015).

This work combines measurement of the spatial distribution of Cr and other potentially toxic elements with land use maps for soil and groundwater in a Geographical Information System (GIS). A Hot Spot Analysis for Cr distribution in soils and groundwater, in C. Evia and Assopos-Thiva Basins was applied. The main scope was (a) to evaluate the extent and magnitude of Cr contamination in those Basins, and (b) to contribute to a sustainable management of land use in Mediterranean type ecosystems (prevention of soil from further degradation and protection of local water resources in respect to the established agricultural activities and human consumption).

2. Methods of investigation

Hundreds of soil samples (N = 254) were collected from the Assopos-Thiva Basins and C. Evia, Greece (Fig. 1), during the period 2007 to 2012, and data reported for previous studies during this time are presented here. The elements Al, B, Ba, Cr, Cu, Fe, K, Li, Mn, Na, Ni, P, S, Se, Si, V, and Zn in soils were measured by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS), at ACME Analytical Laboratories in Canada, after Aqua Regia digestion. Detection limits and the results for the quality control samples, the precision of the analyses of the minor and trace elements is in good agreement with international standards (<10%) (Supplementary table). Also, the mineralogical composition and mineral chemistry

of representative soil samples have been investigated using reflected light microscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) analysis, at the National and Kapodistrian University of Athens (Megremi, 2009, 2010, Economou et al., 2011, Economou et al., 2012; Atsarou and Economou-Eliopoulos, 2012; Theodoratou and Economou-Eliopoulos, 2012).

Almost two hundred groundwater samples (N = 204) were collected from domestic and irrigation wells covering the C. Evia and Assopos-Thiva Basins (Fig. 1), during the period from 2007 to 2017, and analyzed for major and trace elements by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) (Giannoulopoulos, 2008; Megremi, 2009, 2010; Moraki, 2010; Atsarou and Economou-Eliopoulos, 2012; Megremi et al., 2013). Detection limits, quality control samples and the precision of the analyses is in agreement with international standards (<10%) (Supplementary table).

All the data were imported into two separate spatial geodatabases (one for soil and a second for water samples), and were processed in a GIS platform (ESRI's ArcGIS v.10.3). Several layers of geographic information were combined in order to visualize the physiographical and geological properties of the studied areas in relation to the sampling sites. Geostatistical analysis using a variety of spatial tools was carried out in order to interpolate the point data measurements and create continuous information data layers covering the studied areas with the calculated values as much as close to the reality. The location of the sampling sites led us to use the 'Nearest Neighborhood' geostatistical method that proved to yield the most realistic results for both soil and groundwater data. The main concept of this method is to find the closest subset of the samples to a query point and interpolate a new value, after applying proportional weights to the measured values (Sibson, 1981). The Nearest Neighbor method (as used in ESRI's ArcGIS v.10.3) handles large numbers of sample points efficiently and is the most acceptable method for spatial prediction when sample data points are distributed with uneven density (Ver Hoef and Temesgen, 2013). On the other hand, geostatistical methods e.g. 'Kriging' (Cressie, 1990), in cases of irregular spatial sampling locations causes interpolated values to be different (either higher or lower) than the real measured values, as the predicted locations do not coincide with any of the real sampling locations during the resampling procedure (Corona et al., 2014). The geostatistical processing between mainland Greece and Evia point locations had been run independently since the sea water body of the Evia Gulf lies in between. Furthermore, a Hot Spot Analysis was applied in order to spatially identify any clustering between the sampling locations and highlight the areas of geostatistical significance. The spatial resolution of the output raster layer was set to 100 m taking under consideration the spatial arrangement and the average distances between the sampling sites.

Multivariate statistics were applied to the water dataset in order to explain the observed variability in elemental concentrations in groundwater. The computer program MINITAB_ 15 for Windows was used for multivariate (Factor) analysis (Howarth and Govett, 1983). The input has focused on seven elements, namely Na, B, As, K, Li, Mg, Ca, and Cr. Data were processed by means of R-mode factor analysis, applying the varimax-raw rotational technique. This technique can simplify a complex data set by identifying one or more underlying 'factors' that might explain the dimensions associated with data variability. The 'loading' of each factor, i.e. the degree of association between each variable and each factor, allows the recognition of clusters. A varimax rotation was applied to the initial factor loadings in order to maximize the variance of the squared loadings. The correlation matrix was computed for 204 groundwater samples (47 from central Evia and 157 from Assopos-Thiva Basin), after normalization of their concentrations by transforming the arithmetic values to their normal scores. This transformation was necessary to ensure the normal distribution for all the elements and reduce the influence of high values on the output results. Principal Component Factor Analysis with a Varimax rotation was subsequently applied to the data in order to create factors, each representing a cluster of interrelated variables within the data set.
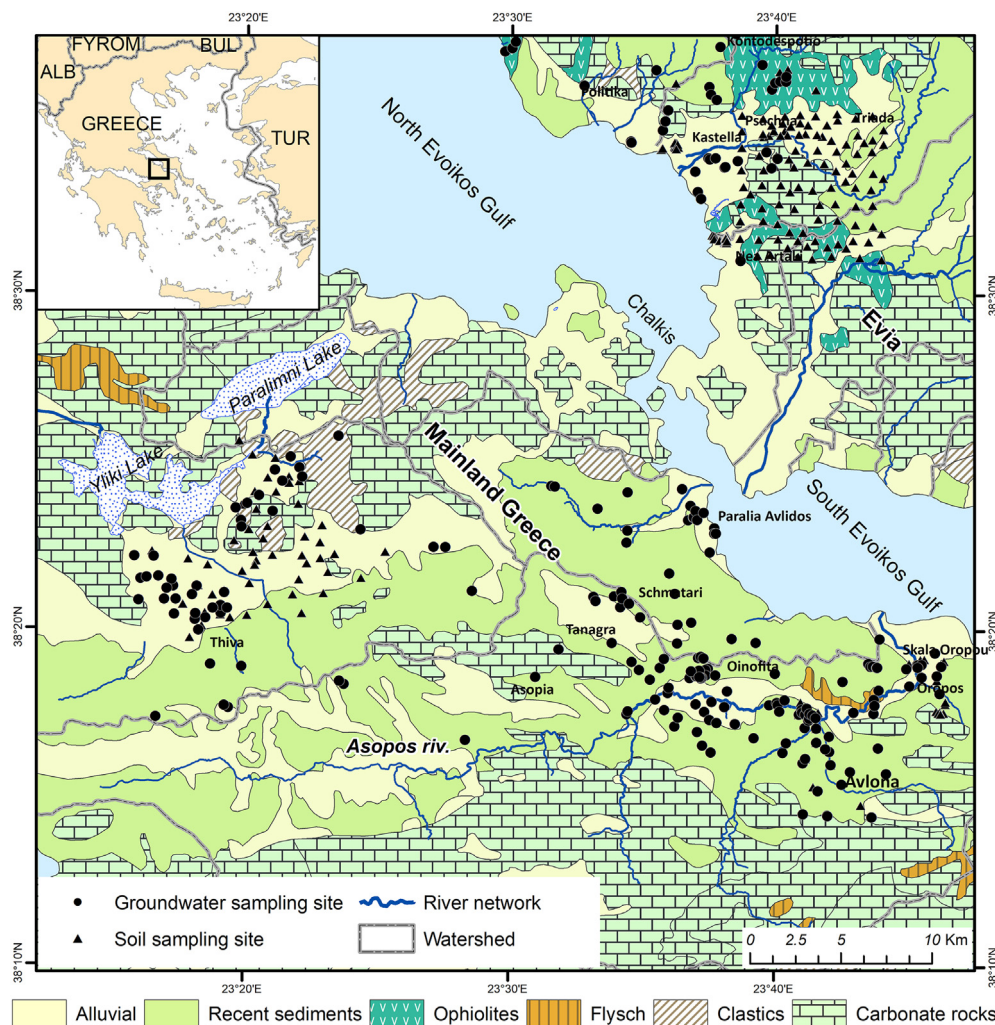
Fig. 1. Geological map presenting the rock and water sampling sites. The formation of the Assopos and Thiva basins are composed by, alternations of marls and marl limestones at the lowest parts, and continental sediments consisting of conglomerates (pebbles derived from carbonates, basic and ultramafic rocks) with small intercalations of marl, marly limestone, metaclastic schist, sandstone, clays and flysch, at the uppermost horizons (Papanikolaou et al., 1988). Central Evia apart from Quaternary alluvial formations, covering lowland areas, is characterized by widespread masses of ophiolites and Ni-laterite deposits (Megremi, 2010).

3. Assessment of the available data

3.1. Spatial distribution of Cr and other metals in soils

Average metal values in soils range from 50 to 190 mg/kg Cr in the Oropos area and from 130 to 520 mg/kg at the Avlona area (Fig. 1) in the Assopos-Thiva Basin, 230 to 310 mg/kg Cr (occasionally 800 mg/kg) in the north part of the basin (Thiva area), with an increasing trend from south to north that is in a close proximity with Ni-laterite deposits (Atsarou, 2011; Theodoratou and Economou-Eliopoulos, 2012; Economou-Eliopoulos et al., 2013). The wide range of Cr content in soil in Evia Basin has been related to Ni-laterite ores and ophiolites (Megremi, 2009, 2010).

A wide variability in metal contents in the aforementioned soils and a relation between Cr, Fe, Mn, and Co (all components of ophiolites and Fe-Ni-laterites) are visualized in Fig. 2. Furthermore, Hot Spot Analysis for Cr in soil indicated remarkable differences between Assopos-Thiva and Evia Basins.

3.1.1. Reference soils

Due to the presence of chromite and/or Cr-bearing Fe-hydroxides and silicates (serpentine, chlorite), and the relatively high Cr content in soils of Neogene Basins throughout C. Evia and Assopos-Thiva regions (Megremi, 2009; Atsarou, 2011; Theodoratou and Economou-Eliopoulos, 2012; Kampouroglou and Economou-Eliopoulos, 2016) the reference material was not collected from formations composed those basins. Thus, the natural background level (NBL) was established using soil samples from south Peloponnese (Messenia) that is characterized by the absence of any ophiolitic Cr-bearing rocks and exhibited much lower mean (n = 2) contents of metals: 35 mg/kg Cr; 7.5 mg/kg Co, 198 mg/kg Mn; 1.69 wt% Fe and 18 mg/kg Ni (Economou-Eliopoulos et al., 2011).

3.2. Spatial distribution of Cr and other metals/metalloids in groundwater

Groundwater from domestic and irrigation wells throughout the Assopos-Thiva, and C. Evia Basins are mostly hosted in a depth ranging from 11 to 200 m. Samples from the shallow Neogene aquifers exhibit concentrations over the maximum acceptable level for Cr_{total} in drinking water (50 μg/L, according to the EU Directive, 1998). Irrigation wells, hosted mostly in deeper ultramafic rocks (peridotites), exhibit lower Cr concentrations compared to those located at shallower depths within alluvial (unconfined) sediments. In addition, groundwater from karst-type aquifers is characterized by negligible Cr concentrations (lower than 2 μg/L) (Megremi et al., 2013). In Assopos–Thiva Basin concentrations of Cr(VI) ranges from <2 to 850 μg/L, while in Central Evia they range from <2 to 360 μg/L. New published data from the monitoring of the heavily contaminated area of Oinofita (Inofyta), near the Assopos
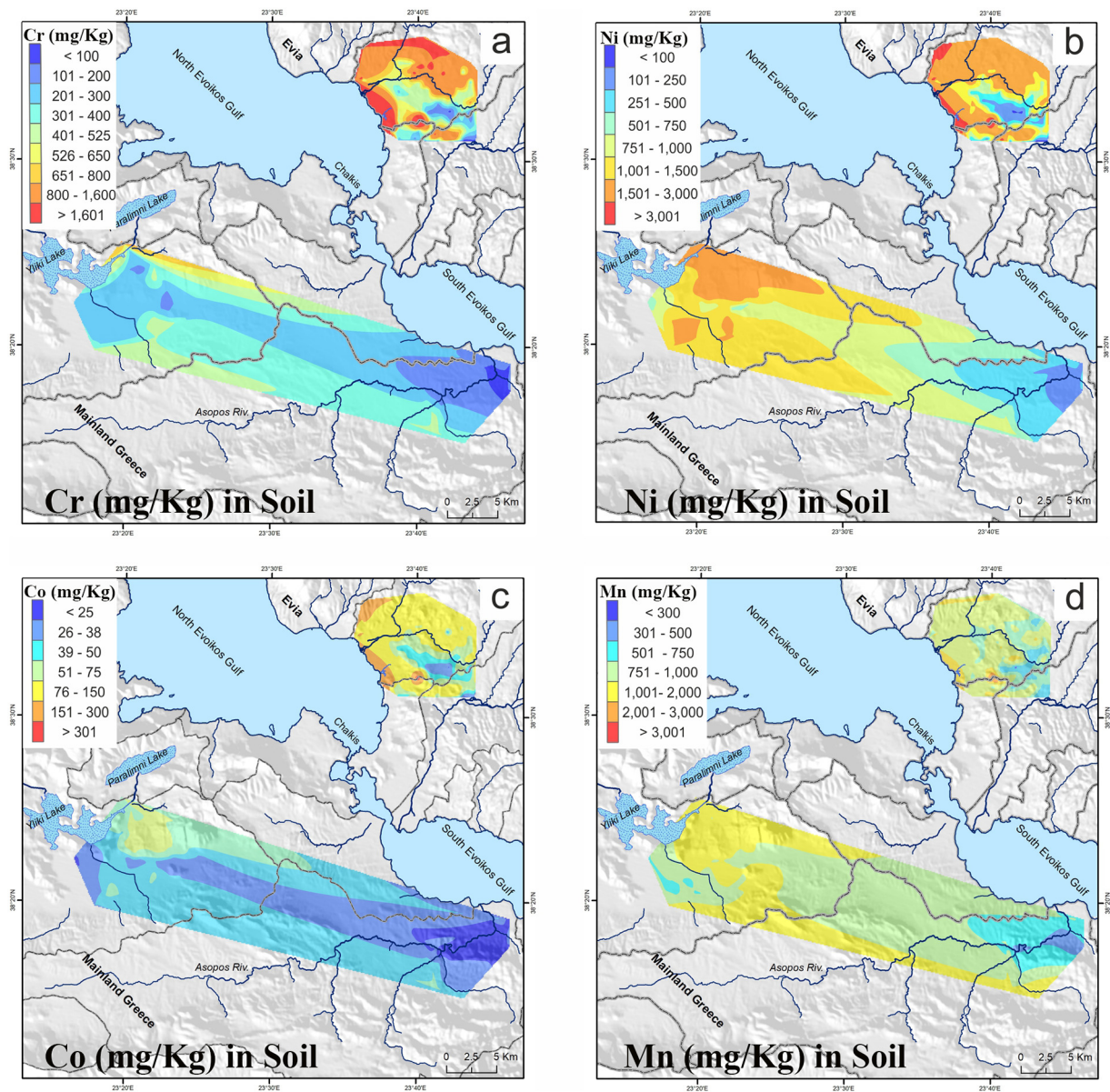
Fig. 2. Maps of Cr, Ni, Co and Mn (a–d) spatial distribution in soils of the Evia and Assopos-Thiva basins.
Data from Megremi (2009, 2010), Atsarou and Economou-Eliopoulos (2012), Theodoratou and Economou-Eliopoulos (2012) and Economou-Eliopoulos et al. (2014).

river, exhibit much higher concentrations, up to 8000 μg/L (LIFE10 ENV/GR/000601, 2015; Michalakis, 2015; Zygogianni et al., 2017).

Since toxic and mobile Cr(VI) in groundwater exhibits high concentrations, geostatistical and geospatial techniques were applied, in order to determine the spatial extent and magnitude of Cr and other potentially toxic element contaminations (Fig. 3).

3.3. Multivariate statistics

Rotated factor loadings, communalities, and the proportion of the variance for groundwater concentrations explained, are presented in Table 1. The first factor contains K, Na, B, Li, and As with high positive loadings and is considered as the most important factor accounting for 43% and 34% of the total variance in Evia and Assopos-Thiva Basins respectively, indicating the influence of seawater intrusion in groundwater aquifer. The second factor is comprised of Cr and Mg with high positive loadings, that is indicative of the influence of Cr-bearing Mg-

silicate minerals. This factor explains 30% and 26% of the total variance in Evia and Assopos-Thiva Basins, respectively. The third factor is Ca with highly loading, suggesting the influence of carbonate rocks on the water composition. This factor explains ~14% and 15% of the total variance in Evia and Assopos-Thiva Basins respectively.

3.4. Temporal variability of the Cr(VI) concentrations

Selected groundwater samples with relatively high Cr concentrations (higher than the parameter value of 50 μg/L) were analyzed several times during the 2007–2017 period in order to define the temporal variability of chromium content. In the Assopos-Thiva Basin neither a seasonal nor any temporal variation in contaminated water is clear (LIFE10 ENV/GR/000601, 2015; Michalakis, 2015). However, in the majority of wells from C. Evia the recorded variability of Cr concentrations in water seems to exhibit a decreasing trend (Fig. 4).
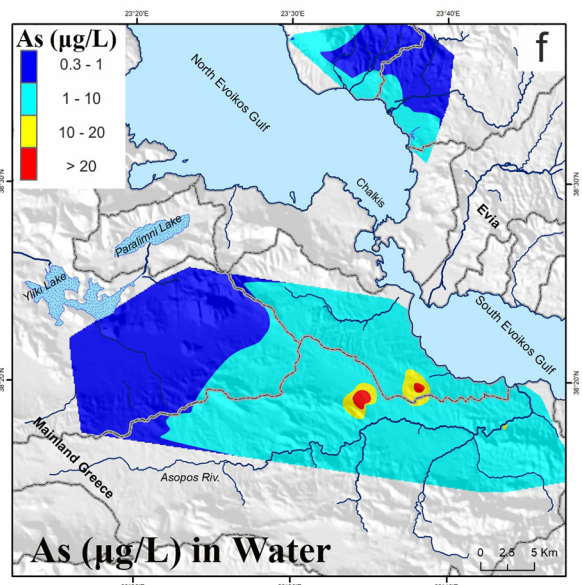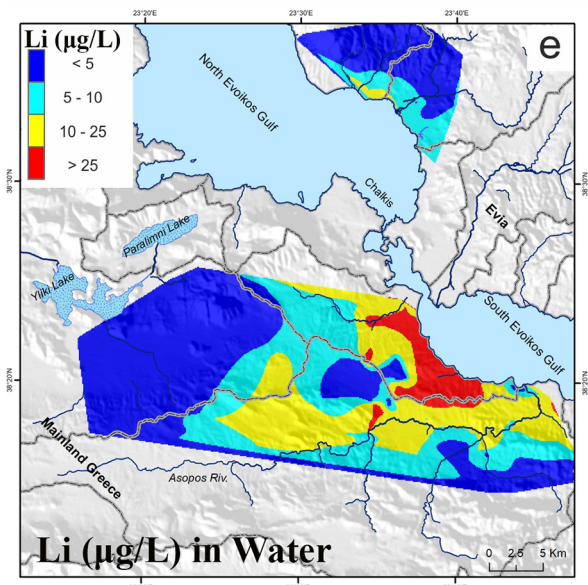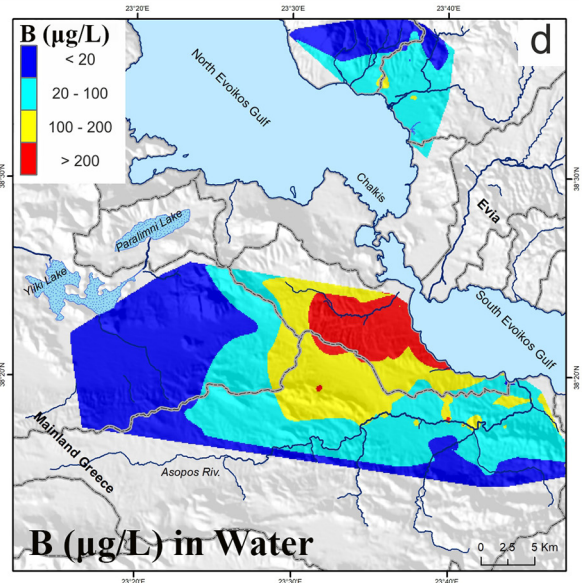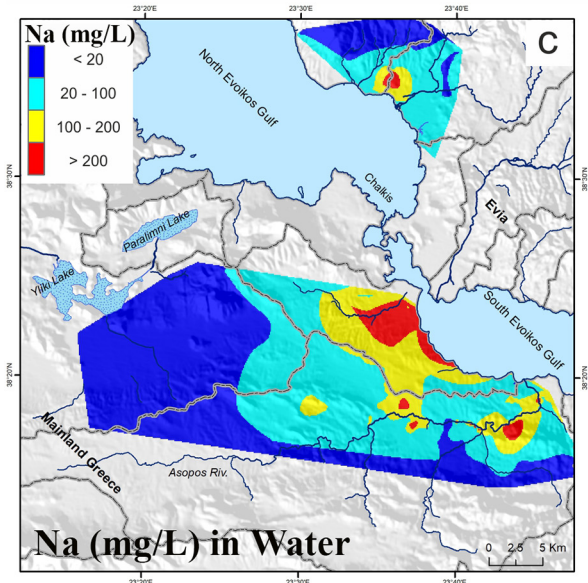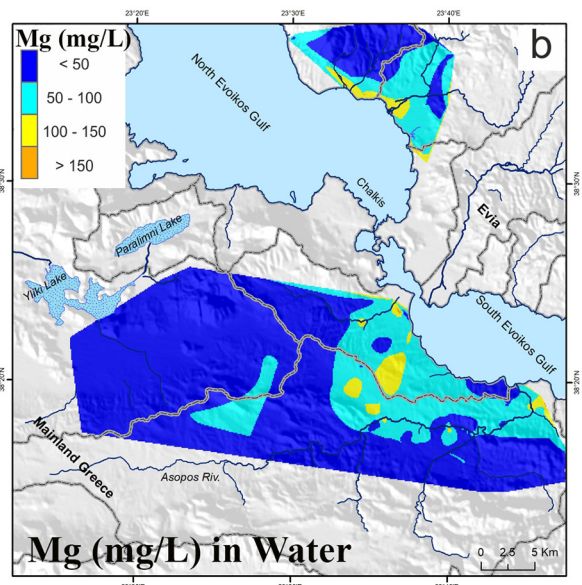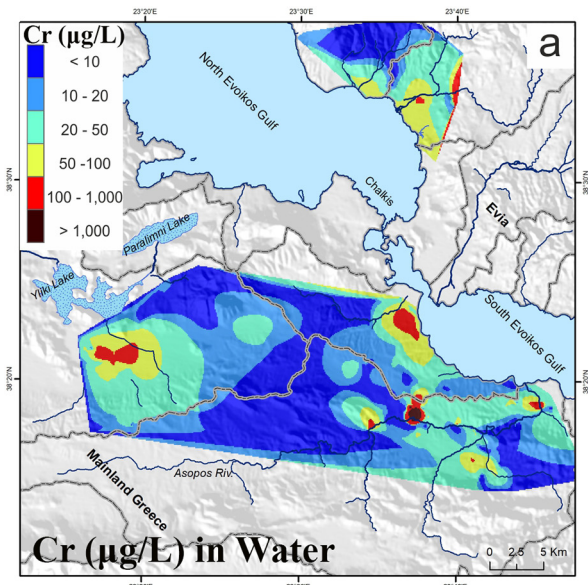
Table 1
Varimax component loadings of three factors controlling the chemical composition of groundwater in Evia and Assopos-Thiva Basins. Percentage of variance is explained for eight variables.

Central Evia (N = 47)				
Variable	Factor1	Factor2	Factor3	Communality
Cr	0.007	−0.930	0.108	0.877
Ca	0.106	0.103	−0.956	0.937
Mg	0.327	−0.884	0.074	0.893
K	0.850	0.006	−0.229	0.774
Na	0.834	−0.42	−0.177	0.903
B	0.788	−0.477	−0.219	0.896
Li	0.707	−0.599	−0.106	0.870
As	0.871	−0.038	0.261	0.828
Variance	34.148	2.421	11.429	69.787
% variance	0.427	0.303	0.143	0.872

Assopos-Thiva basin (N = 157)				
Variable	Factor1	Factor2	Factor3	Communality
Cr	0.031	0.882	−0.192	0.816
Ca	0.003	−0.086	0.954	0.918
Mg	0.374	0.723	0.174	0.693
K	0.774	0.244	0.169	0.688
Na	0.833	0.376	−0.108	0.847
B	0.764	0.333	−0.37	0.831
Li	0.505	0.665	−0.216	0.743
As	0.668	0.01	0.038	0.447
Variance	27.176	20.631	12.026	59.833
% variance	0.34	0.258	0.15	0.748

3.5. Land use and Cr spatial distribution

Using multiple elements and land use maps (Fig. 5a, b) show widespread elevated potentially toxic element contents in hundreds of topsoil samples compared to the aforementioned natural background values for the Cr, Ni, Mn, and Co in samples from the Messenia area (Peloponnese, Greece). These are associated with agricultural areas (Fig. 5a, c), where the soil content is contaminated by the transfer of weathered material from the surrounding ultramafic basement rocks, especially at Evia island. Also, spatial element distribution derived from hundreds of groundwater samples, coming from shallow (10–40 m) and deep (180 to >200 m) domestic and irrigation wells, along with land use maps show a wide variation in the Cr and other elements throughout the C. Evia and Assopos-Thiva Basins (Figs. 3a, 5b). However, water samples with the highest Cr concentrations are found in areas of active industrial units at Oinofita (Fig. 5d).

4. Discussion

The available database and maps for European countries by GEMAS (geochemical mapping of agricultural soils and grazing land of Europe) and LUCAS (Land use and land cover survey) for the main harmful elements: As, Cd, Cr, Cu, Hg, Pb, Zn, Sb, Co, and Ni, although of very low density, provide valuable evidence for the presence of highly contaminated areas (De Vos et al., 2006; Tóth et al., 2016/ LUCAS survey; Reimann et al., 2014). These data demonstrate a wide spatial distribution in top soils throughout European countries for many elements. In addition, the guideline values have been defined on the basis of either ecological or health risks, for the decision makers and scientists (De Vos et al., 2006; Tóth et al., 2016/LUCAS survey; Reimann et al., 2014). Also, hydrogeochemical databases provide an excellent resource on the bottled water for European countries (Birke et al., 2010). Furthermore, detailed studies at a local scale provide mineralogical and geochemical evidence suggesting that Cr in ultramafic rocks and Fe-

Ni-laterites is mainly hosted in chromite, which is thermodynamically stable, and within silicate minerals and Fe-hydroxides (goethite), which are more easily weathered than chromite and are potential contributors to environmental contamination by chromium (Navrotsky et al., 2008; Fantoni et al., 2002; Oze, 2003; Ball and Izbicki, 2004; Izbicki, 2004; Oze et al., 2007, 2016; Vasilatos et al., 2008; Megremi, 2010; Rajapaksha et al., 2013; Economou-Eliopoulos et al., 2011, 2012a, 2016, 2017).

4.1. Distribution of Cr in soil and water and potential sources

The composition of top soil that varies temporarily and spatially may be a result of climate change, geomorphology, presence of organic matter, potential transfer of sediments from weathered rocks and ores (Komnitsas and Modis, 2009; Nadal-Romero et al., 2008; García-Ruiz et al., 2013). The projection of available analytical data for soil and irrigation water in cultivated soil, on land use maps (Figs. 2, 3 and 5) reveals elevated contents for Cr compared to defined parameter values (De Vos et al., 2006; Tóth et al., 2016; Reimann et al., 2014).

In Greece, the high contents of Cr and other metals (Ni, Fe, Mn and Co) in C. Evia soil samples (Megremi, 2009, 2010; Economou-Eliopoulos et al., 2013) are related to the widespread occurrence of peridotites. The mobility of chromium through rocks and soils is dependent upon oxidation state and pH (Bartlett and James, 1979; Richard and Bourg, 1991; Banerjee and Nesbitt, 1999). Field observations and experimental data, have demonstrated that H_2O_2 is present in fluids related to serpentinization systems and acts as a potential oxidant of Cr in chromite under alkaline conditions (Oze et al., 2016). In addition, the recharge, due to the return of Cr(VI) by irrigation, particularly in shallow aquifers with limited groundwater flow paths, may contribute to elevated Cr(VI) content as well. Returned water from irrigation, has also been identified in water samples from wells having high Cr(VI) concentrations in an agricultural region of California (Mills et al., 2011; Manning et al., 2015; Izbicki et al., 2015).

Fig. 3. Maps of Cr, Mg, Na, B, Li and As (a–f) spatial distribution in groundwater from the Evia and Assopos-Thiva basins.
Data from Vasilatos et al. (2008), Giannoulopoulos (2008), Megremi et al. (2013), LIFE10 ENV/GR/000601 (2015), Michalakis (2015), Zygogianni et al. (2017) and Economou-Eliopoulos et al. (2017).
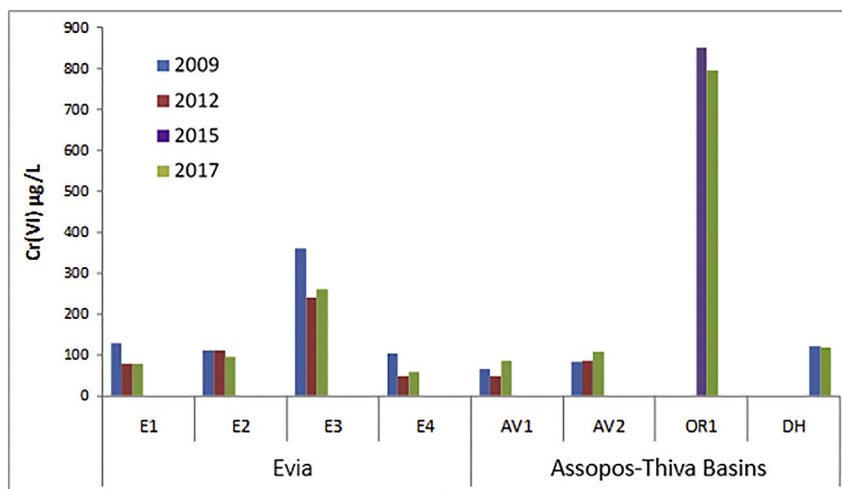
Fig. 4. Temporal variability of the Cr(VI) concentration, all in μg/L (Y axis), in groundwater wells during the period 2009 to 2017. Data: Present data, Vasilatos et al. (2008), Megremi et al. (2013) and Economou-Eliopoulos et al. (2014, 2016).

The role of nitrate (NO_3^-) in highly cultivated areas is a topic of interest, but its relationship with (Cr(VI) is still uncertain (Burland and Edwards, 1999; Middleton et al., 2003; Kourtev et al., 2009; Vasileiou et al., 2014). Recently, on the basis of the nitrogen isotope data, it has been concluded that the septic and industrial zones of the Assopos-Thiva Basin are characterized by the most enriched $\delta^{15}N–NO_3$ values, indicating that septic and industrial wastes were likely the main sources of nitrate contamination (Matiatos, 2016). A salient feature is the presence of commonly elevated NO_3^- concentrations in groundwater of C. Evia, showing a positive correlation with Cr(VI) (Vasileiou et al., 2014; Remoundaki et al., 2016), a negative correlation in groundwater from the area of both Avlona (Assopos sub-basin) (Atsarou, 2011) and Thiva sub-basin (Koilakos, 2017) while no clear relationship was found in the wider Assopos and Thiva Basin (Giannoulopoulos, 2008; Tziritis, 2009). Furthermore, the binary plot of available data for Cr(VI) and NO_3^- concentrations in groundwater (Fig. 6) from C. Evia, reveals a positive correlation (r = 0.75, p = 0.000), while data from the Assopos-Thiva Basin is not (r = 0.2, p = 0.024). Two different fields with different trends can be also observed in Fig. 6. Defining the sources of contamination, Cr(VI) presence in groundwater from C. Evia has been related to ultramafic rocks (Megremi, 2010), whereas NO_3^- concentrations are correlated to intensively soil cultivation (Vasileiou et al., 2014). The relatively low NO_3^- and the extremely high Cr(VI) values in the samples from Assopos-thiva Basin (Fig. 6) are associated with intense industrial activities (Vasilatos et al., 2008, 2010; Economou-Eliopoulos et al., 2011, 2012, 2014; Megremi et al., 2013; Matiatos, 2016; LIFE10 ENV/GR/000601, 2015). Even though the above mentioned fields overlap, the trends may provide evidence for the discrimination of the origin of contamination.

Despite the good correlation between Cr(VI) and the strong oxidant NO_3^- in Evia, the role of the NO_3^- to the oxidation of Cr(III) to Cr(VI) could not be established (Burland and Edwards, 1999; Vasileiou et al., 2014). In addition, due to the comparable redox potential values for NO_3^- and $Cr_2O_7^{2-}$ (slightly lower for the former than the later) (Reimann and Filzmoser, 2000; Appelo and Postma, 2005) the role of NO_3^- to the oxidation and preservation of Cr(VI) remains unclear. In contrast, hydrogen peroxide, H_2O_2, high-valent Mn-oxides, and MnO_4^- may act as oxidants of Cr(III) (Rock et al., 2001; Fantoni et al., 2002; Ball and Izbicki, 2004), as their higher standard potentials favour that reaction (Reimann and Filzmoser, 2000; Appelo and Postma, 2005).

Assuming that the effect of additives (e.g. fertilizers and compost) is on a similar level in the cultivated land of C. Evia and the Assopos-Thiva Basins, the recorded differences between the Hot Spot Analysis results in groundwater and soil (Figs. 2, 3 & 5), points to an industrial origin of Cr in water and a geogenic one in soil.

4.2. The effect of salinization

Salinization is a common process recorded not only in coastal land of Greece, but in many coastal countries (Metternicht and Zinck, 2003; Shrivastava and Kumar, 2015), due to irrigation of agricultural land by groundwater being mixed with seawater. This can be identified based on groundwater chemical composition. For example, the elevated concentrations of Na, Li, B, and As in water samples are characteristic of seawater composition (Rose et al., 1979; Smedley and Kinniburgh, 2002; Megremi et al., 2013; Economou-Eliopoulos et al., 2013). The first factor derived from the multivariate statistics containing K, Na, B, Li and As with high positive loadings in both Evia and Assopos-Thiva Basins (Table 1), suggests the influence of seawater intrusion. An increase of the Cr(VI) in water wells appear to be strongly effected by seawater intrusion (Fig. 3c–f). However, chromium is not derived from seawater based on the low (<1 μg/L) Cr(VI) concentration and the relatively low $\delta^{53}Cr$ ‰ (Campbell and Yeats, 1981; Bonnand et al., 2013; Economou-Eliopoulos et al., 2017).

4.3. Environmental risk and natural attenuation of Cr(VI) in groundwater

Metals may remain in the environment for years, posing long term risks to life well after sources of contamination have been removed. Accurate estimation of the environmental risk for human health and ecosystems depends on the analytical methods used, as well as the type of the samples, the sampling period, the origin and the chemistry of contaminants, the variation of climatic conditions, and the mechanisms of contaminant migration (Korre et al., 2002; Koutsoyiannis and Montanari, 2007; Komnitsas and Modis, 2009; García-Ruiz et al., 2013).

Assuming that Cr-bearing ultramafic rocks and ores, such as in orogenetic zones of the Earth's crust, are widespread on a global scale (Oze et al., 2007), chromium may be a common component in agricultural soils. An overview of the environmental impact and pathways of potentially toxic elements from the soil to terrestrial ecosystems, apart from the reduction or loss of fertility and productivity of agricultural soils, reveals that those metals can be leached and transferred into shallow aquifers, during an interaction with the soil components and a continuous element recycling, as contaminated irrigation wells may be used in cultivated areas and be transferred into the food chain (De Vries et al., 2007; Megremi, 2009, 2010; Demetriades, 2011; Economou-Eliopoulos et al., 2011, 2012a, 2012b, Kanellopoulos et al., 2015).

Besides a slight temporal variability of the Cr(VI) concentrations in groundwater wells recorded during the dry periods of 2007–2017, Cr

concentrations in water exhibit a decreasing trend in wells from C. Evia (Fig. 4). In order to evaluate the efficiency of natural attenuation of the toxic hexavalent Cr(VI) to the less harmful Cr(III) in the groundwater, using a Rayleigh distillation model and different fractionation factors of Cr(VI) reduction valid for aqueous Fe(II) and Fe(II)-bearing minerals,

more than ~53%, but maximum ~94%, of the originally mobile Cr(VI) pool was calculated to be reduced in the groundwater from C. Evia and Assopos-Thiva Basins (Economou-Eliopoulos et al., 2014, 2017; Frei et al., 2014; Koilakos, 2017). Recently chromium isotopes (δ^{53}Cr) and Cr(VI) concentrations investigated in shallow aquifers at four
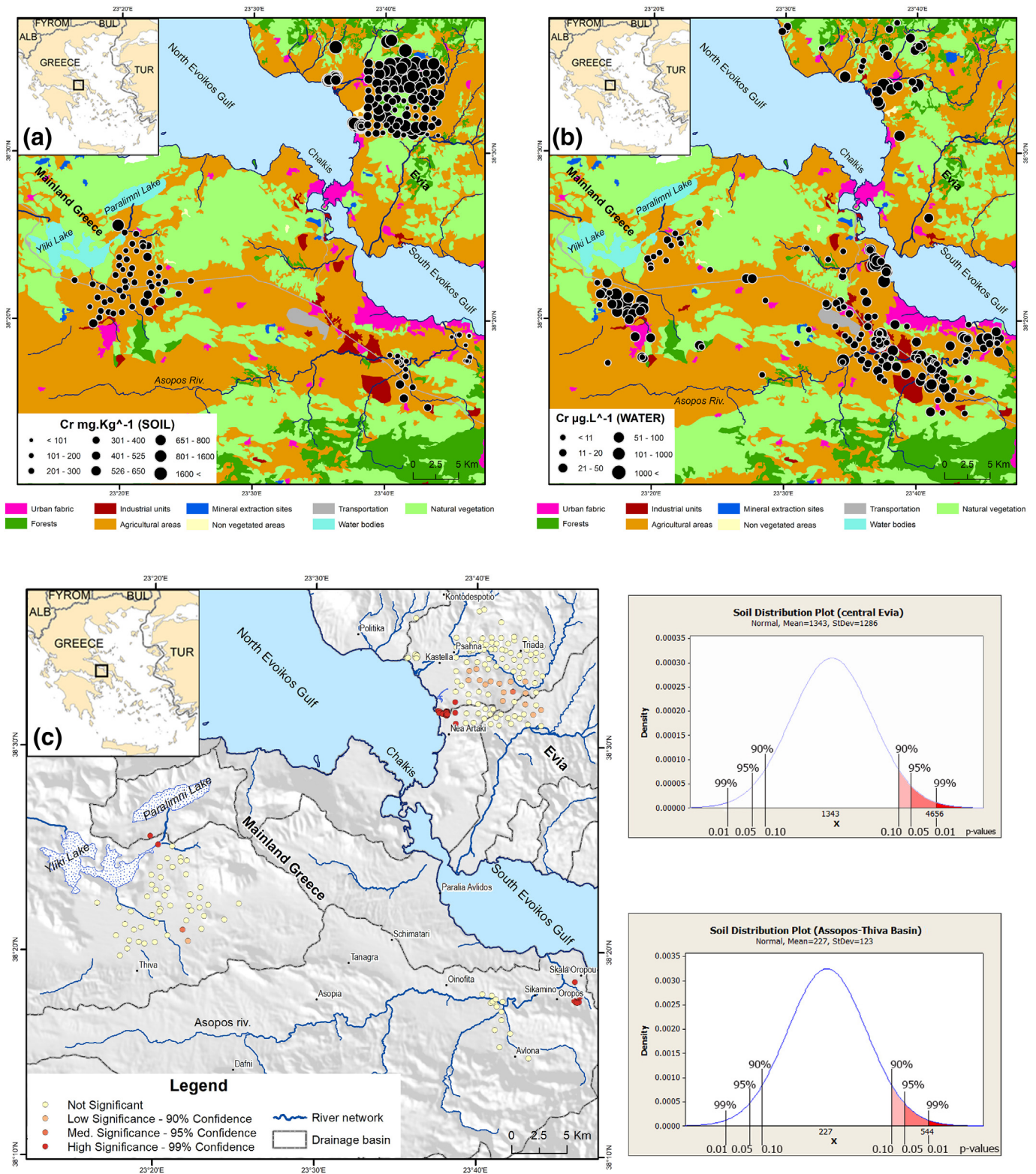

Fig. 5. A combination of Cr spatial distribution with land use maps (a, b) and hotspot analysis in soil (c) and groundwater (d) of C. Evia and Assopos-Thiva Basins. The geostatistical processing and Hot Spot Analysis between mainland Greece and Evia data points had been run independently. The plots in 5c and 5d present the standard normal distributions associated with p-values.
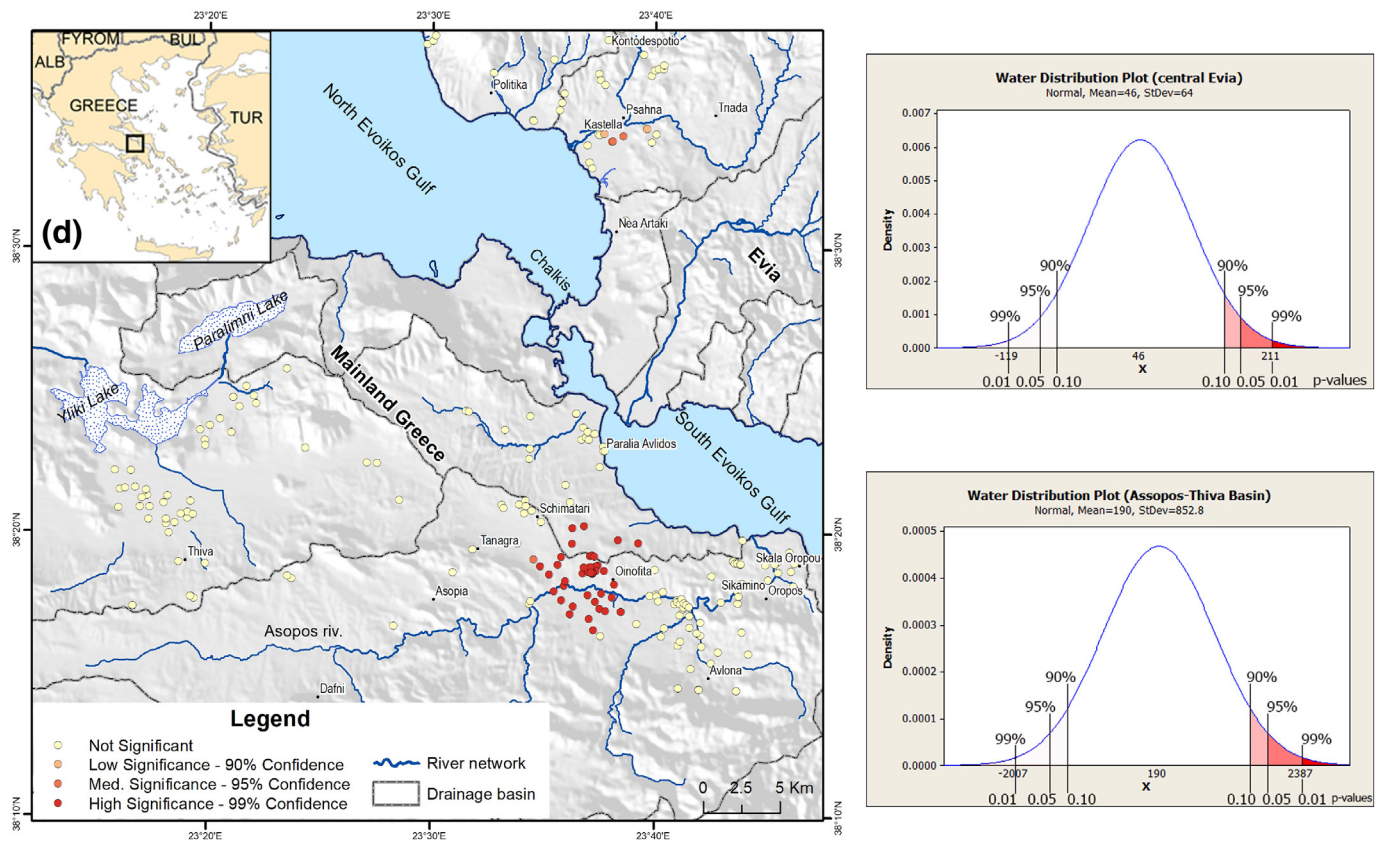
Fig. 5 (*continued*).

industrial sites in the Czech Republic, Central Europe, that have been contaminated since late 1940s, have indicated mean $\delta^{53}Cr$ values in Cr plating baths ranging from 0.0‰ at Zlate Hory (ZH) to 0.5‰ at Loucna and Desnou (LD). At all four sites, groundwater Cr was isotopically heavier, compared to the contamination source, reflecting natural *in-situ* Cr(VI) reduction to insoluble Cr(III) (Novak et al., 2014, 2017). These researchers have also applied the Rayleigh model and concluded that 30% to 60% of Cr(VI) has been removed from the groundwater by reduction. The decreasing trend of the Cr(VI) concentrations in wells from C. Evia (Fig. 4), suggests that processes in the aquifers may facilitate natural attenuation of the Cr(VI) (e.g. Ellis et al., 2002; Izbicki et al., 2008; Farkas et al., 2013). Even though the reason for variation of the Cr(VI) concentrations in heavy contaminated wells throughout the area of Oinofita (Assopos-Thiva Basin) remains unclear (LIFE10 ENV/GR/000601, 2015), and assuming that further contamination does not continue, natural attenuation could reduce the concentration of Cr(VI) in a relatively short period of time.

4.4. Implications for land use and water management

Land use models, which represent the spatial distribution of land type, can be useful tools to apply, since they provide a range of potential scenarios to determine future agricultural land uses or cropping systems in a region (Fresco, 1990). The quality of soils, water, and plant/crop (food chain) varies continuously spatially and temporally, and their management is a topic of much discussion, aiming to define evidence based on environmental policies for sustainable management, and clarify knowledge needs for further research (Key et al., 2016; Keesstra et al., 2016). The compilation of current knowledge of the environmental impact and pathways of potentially toxic metals (the most frequent soil contaminants) from soil to groundwater and plants, their oxidation stage, and the stability of the host mineral phases (bio-availability and bio-accumulation of metals) will provide the required information for the land use and soil/water management.

It is well known that the transfer of harmful elements from soil and irrigation water to plants/crops depends on the element bio-availability (partial extraction, using dilute solutions of reagents, representing plant uptake), and bio-accumulation (element transfer from soil to plants). They depend both on the in situ physico/chemical conditions, such as pH, redox, temperature, available water (Kabata-Pendlas, 2000).
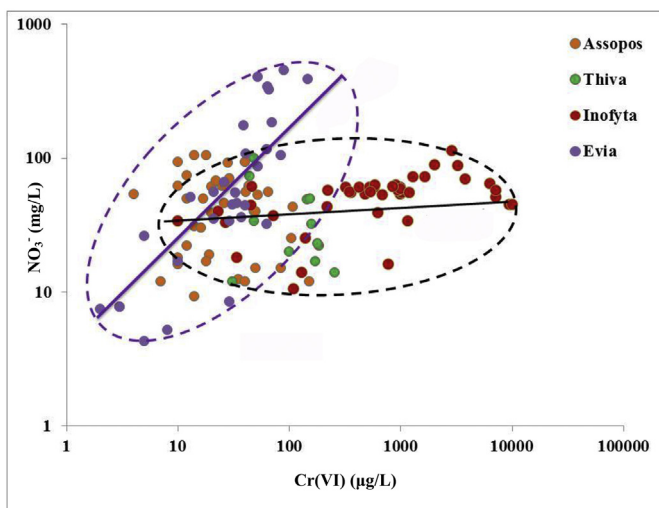

Fig. 6. Plot of Cr(VI) *versus* NO$_3^-$ values in groundwater from C. Evia and Assopos-Thiva Basins.
Data from Giannoulopoulos (2008), Atsarou (2011), LIFE10 ENV/GR/000601 (2015), Remoundaki et al. (2016), Michalakis (2015) and Koilakos (2017).

Management practices applied, should remove the metal contaminants, or determine measures to immobilize them. The ability of soil to immobilize the majority of metals increases with increasing pH, whilst Cr is highly mobile in neutral to alkaline conditions. Detailed investigation on the speciation of metals by X-ray synchrotron radiation microbeams X-ray absorption near-edge structure (XANES) technologies (Zayed et al., 1998; Bluskov et al., 2005; Parsons et al., 2007; Yu et al., 2008) may be of particular importance for the assessment of health risk and phytoremediation. Consideration should be given regarding the role of organic matter that serves as the driving force for the reduction of the harmful Cr(VI) to Cr(III). The addition of organic matter in cultivated soils (Asyminas, 2012) has shown that it plays a significant role in reducing the bioaccumulation of Cr (redox reactions) in crops (lettuce). Laboratory experimental work, implementing the commercial biotic material EDC-M (Electron Donor Compound-Metals), testing contaminated water treatment, has demonstrated the ability of those microorganisms to directly reduce Cr(VI) (Moraki, 2010).

Water samples from the Assopos-Thiva Basin exhibiting high Cr(VI) concentrations, also displayed elevated values of total organic carbon (TOC) (4.1–7.5 mg/L). However, in the same area there are heavily contaminated irrigation wells [>50 μg/L Cr(VI)] presenting TOC values lower than 1 mg/L (Giannoulopoulos, 2008).

Following the international protocols, for the restriction of the transfer of potentially toxic elements to soils and from soils to plants/crops and to groundwater aquifers, is of particular importance in protecting human health and ecosystems. Thus, not only monitoring of the irrigation water in cultivated areas suffering from those environmental issues is required, but further research is needed on the bio-remediation and other remediation ways to restrict the mobility of metals/metalloids without the reduction of agricultural and industrial production. Specific species of plants have been reported to perform reduction of Cr(VI) to Cr(III) in the thin lateral roots with further transport of Cr(III) to the leaves (Han et al., 2004; Babula et al., 2008; Levina et al., 2003). Therefore, only integrated water–soil–plant investigations of metal contamination may provide ways to restrict the risk of human health and ecosystems.

5. Conclusions

A compilation of published data in previous studies combined with the spatial distribution of metals and land use maps for soil and groundwater, in the Mediterranean region (Assopos-Thiva and Central Evia Basins, Greece) indicated a spatial diversity of Cr distribution in soils and groundwater throughout the study area. A means of determining specific areas of agricultural land use with elevated potentially toxic elements contents was provided by combining the spatial distribution of metals in soil and land use maps in a GIS platform. Soil contamination by Cr is attributed to the transfer of weathered material from the surrounding ultramafic rocks and Fe-Ni ores, and that is consistent with the Hot Spot Analysis. The combination of the spatial distribution of Cr in groundwater and land use maps defined the areas of industrial land use with elevated Cr concentrations (Inofita, south Assopos-Thiva Basin) that is also consistent with the Hot Spot Analysis. Salinization of groundwater in the coastal areas studied is characterized by relatively high Na, Mg, B, Li, and As concentrations. The relatively low NO_3^- and extremely high Cr(VI) values (over 10,000 μg/L), and the different trends defined in groundwater from the industrial areas compared to that of highly cultivated land, may provide evidence for a discrimination of the contamination source. Combining land use maps with available chemical data can provide the required information to help land managers to make decisions.

Further research is required on the remediation methods and the restriction factors for the transfer of metals from soils to plants/crops and groundwater aquifers, without the reduction of agricultural and industrial production.

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