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Spatial and temporal assessment of cadmium and chromium contamination in soils in the Karditsa region (Central Greece)

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Abstract

In this work, we aimed at monitoring Cd and Cr levels in surface soils in the Karditsa region (Central Greece). Soil samples were obtained throughout 3 years (2010 to 2012) and analyzed for extractable (DTPA) and for "pseudo"-total concentrations (aqua regia) of Cd and Cr. The temporal variability, recorded twice per year, was also assessed. Significant spatial variability was recorded and illustrated by the respective thematic maps created using geostatistics, with the use of ordinary kriging. We found a possible geochemical connection and interactions between the two studied metals that indicated common lithogenic origin, while Cd was found further enriched due to likely applied phosphate fertilizers over long periods of time. We conclude that although the mapping of soil properties and metal contents is a useful tool when initially visiting an area, further in-depth studies should be conducted; such studies should address issues related to bioavailability of soil pools that may be linked to plant concentrations and possible risks of metals being transferred to plants or even humans.

Introduction

Heavy metals can be essential or beneficial to plants under certain conditions but toxic when available beyond specific thresholds (Khanam et al. 2020). Heavy metal soil contamination, especially of urban and peri-urban areas, has received increasing interest; the reason is their toxicity, persistence, and non-degradability (Chen et al. 2016; Saxena et al. 2019).

Thus, there have been numerous monitoring works recording contamination cases in many countries (Duan et al. 2016; Yoon et al. 2019). Heavy metal fate may vary from case to case: metals may find their way from agricultural soils to growing plants and from there to humans ("soil-to-plant-to-human" pathway), thus through the food chain metals may be affecting human health (Antoniadis et al. 2019b). Alternatively, humans may directly orally ingest, inhale, or even have a skin contact with aerial dust deriving from contaminated soil ("soil-to-human" pathway). In any of these cases, heavy metals may threaten human health.

Metals, once found in soils, may have variable geochemical fractionation profile, depending on metal aging and soil properties (Antoniadis et al. 2017a). As for aging, it has been recognized that metals deposited to soils slowly over long periods of time tend to be less bioavailable; this is due to the fact that metals move towards inaccessible residual soil pools over time (such as occluded into Fe and Al oxides, or into sparingly exchangeable interlayer niches of phyllosilicate clay minerals). As for soil properties, they dramatically affect metal availability. Indeed, there have been reports of soils which have been found to annihilate metal availability to plants: such soils are typically with higher pH (metal cations become less soluble), higher content in $CaCO_3$ (metal cations are readily

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Highlights
- Cd was found elevated, due to the intense agricultural activities.
- Cr levels were low, indicating its lithogenic derivation.
- Cd and Cr were co-related ($r = 0.746$); thus, a portion of Cd is lithogenic.
- Metal thematic maps are useful for identifying contamination hot-spots.

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bound by it), higher content of clay minerals of active nature (e.g., 2:1 clay minerals sorb electrostatically cations due to their negative charge), and higher amorphous Fe and Al oxide contents. In general, metal mobility is expected to be limited by ion-exchange reactions between metal ions and soil colloids (Jayasiri et al. 2014). Indices for potential ecological risk and geoaccumulation have been used to evaluate the environmental effects and intensity of heavy metal pollution over time (Chen et al. 2016).

The natural concentration of heavy metals in arable soils depends primarily on the geological parent material composition. Native concentrations of heavy metals are relatively high in shales and clays and usually lower in sands and limestones (Martin et al. 2006). Metals can also originate from various anthropogenic sources of agricultural origin, such as application of inorganic fertilizers, manures, pesticides, and sewage effluent irrigation. They may also derive from aerial deposition caused by industrial activities (Jayasire et al. 2014). Metal aerial deposition is strongly spatially concentrated: several studies have shown that deposited metals decrease with increasing distance from the contamination source (Morton-Bermea et al. 2002). Source identification and pathway clarification are essential towards sound management practices concerning metal remediation (Qin et al. 2012). Two major goals of such evaluation should be to distinguish natural from human-derived levels and to address the associated ecological and human health potential risks (Ravankhah et al. 2016).

The spatial distribution and temporal variation of pollutants in soils can be determined by geostatistical methods based on geographically scattered sampling at different times. Although there have been a number of works addressing the natural background of heavy metal levels and the effect of anthropogenic activities (Alyazichi et al. 2015; Howard et al. 2019), the use of geostatistics in spatial and temporal metal variability is yet to be further elucidated. Multivariate statistical analysis is a useful technique for identifying common patterns in data distribution (Shan et al. 2013). Geostatistics reduces datasets and makes them easier to be interpreted (Hamzeh et al. 2011). We used it in this work with geographical information system (GIS) techniques, which is very useful when aiming at identifying non-point source contamination (Shan et al. 2013; Chen et al. 2016). The resultant visualization may then help in further assessing contamination sources as related to certain spatially located anthropogenic activities (Zhou et al. 2016). To this goal, we used kriging, one of the most frequently applied methods for interpolating missed data between two given measured points (Ravankhah et al. 2016).

In Greece, the heavy metal status in some regions has been monitored. In Thessaly, Central Greece, a number of scientific reports have been conducted in order to monitor the potential soil contamination, as well as the levels of heavy metal content in vegetables (Mitsios et al. 2005; Golia et al. 2008, 2009a, 2009b; Skordas et al. 2013; Golia et al. 2015;

Antoniadis et al. 2017b, 2019a). The Karditsa region is one of the four prefectures in Thessaly, but it has never been studied before. It includes areas of a productive agricultural plain and a town that has been enormously enlarged and industrialized during the last decades. Major units in the Industrial Park of Karditsa concern food processing technologies (mostly milk/cheese- and cured meat-based products), paint/pigment products and similar. Of the heavy metals, Cd and Cr are among the most frequently studied and monitored (Antoniadis et al. 2017a). Cadmium is often found in elevated concentrations in non-industrial areas, such as that in Karditsa. This is due to rock phosphate additions in intense agricultural practices, such as those typically employed in the study area; this material is known for its Cd content as impurities. Cadmium may be of elevated mobility even when deposited slowly over long periods of time (Matin et al. 2020). As for Cr, its residual form is most probably found in its trivalent species, an inert and immobile metal in the form of Cr^{3+} and strongly bound onto soil colloids. However, it has been reported in elevated concentrations in the area of Thessaly (Molla et al. 2012), and thus, the possibility of its high contents in Karditsa should be evaluated and associated risks assessed.

The aims of this work were to (a) monitor heavy metal levels, focusing on Cd and Cr, in the Karditsa area, over a 3-year period, (b) determine the most important soil properties controlling Cd and Cr concentrations in soils, and (c) create thematic maps of Cd and Cr concentrations in the study area. We consider this approach as an initial step for examining this vast and previously un-examined area, which provides much of the agricultural produce in Greece. We see this area as a pilot of other similar areas around the globe: such areas have been under non-severe non-industrial anthropogenic activities, but may, nonetheless, be proved significant in metal enrichment entirely due to agricultural practices.

Materials and methods

Sampling and pretreatment

A 3-year survey (2010 to 2012) was conducted in the Karditsa Prefecture, which is situated in Thessaly, Central Greece, in order to determine heavy metal concentrations in soil. The study area covers 12,500 ha. It contains the municipalities of (a) Karditsa (consisting of 7 villages apart from the town, with a total population of 37,768 according to the 2011 consensus); (b) Palamas (9 villages apart from the town, population of 10,050); and (c) Sofades (14 villages apart from the town, population of 12,215). The average elevation of the study area is 105 m above sea level. Also, a detailed geological map is presented in the Supplementary Material (Fig. 1; European Soil Database (ESDB); Panagos 2006). In the study area, there are three main land uses: (a) residential: the coverage of this

land use is exhibited on the maps shown in this work as identical to the abovementioned towns and to various villages indicated on the maps; (b) industrial: this land use is rather restricted to the outskirts of the main town of the study, Karditsa; (c) agriculture: this is the main activity of the study area, covering virtually the whole study area except for the residential areas. The area is cultivated mostly with cotton, vegetables, grains, and alfalfa. The town of Karditsa, capital of the prefecture, is situated almost in the middle of the study area. Each year, 89 topsoil samples (0–30 cm) represented mostly farmland areas, which is the predominant land use in the area. On each sample site, five replicate subsamples were obtained, hand-mixed to produce one composite sample per site, and typical soil processing protocol was followed: samples were air-dried, ground with pestle and mortal, and sieved through a sieve of 2 mm into plastic bags. Soil samples were collected two times per year, in October (autumn, series thereafter named A) and in March (spring, B).

Physical and chemical analyses

The physicochemical parameters of the soil samples were measured (Page et al. 1982) as follows: particle size distribution (Bouyoucos hydrometer), pH and electrical conductivity (EC) (1:1 H_2O), organic carbon (wet oxidation by Walkley and Black), and $CaCO_3$ (Bernard calcimeter). Also, samples were determined for extractable Cd and Cr with DTPA (1:2 diethylene-triamine-pentaacetic acid pH 7.3; Lindsay and Norvell 1978). "Pseudo-total" concentration of metals was determined with aqua regia (HCl:HNO_3 3:1 digested at 180 °C for 2 h, ISO/DIS 11466/1994; Golia et al. 2007). All reagents were of analytical grade (Merck, Germany).

The concentrations of the metals studied were determined by atomic absorption spectrophotometry (AAS) using flame (F-AAS) or the graphite furnace (GF) technique (Lajunen 1992). Validation of the analytical recovery was checked by the Standard Reference soil material 2710 (National Institute
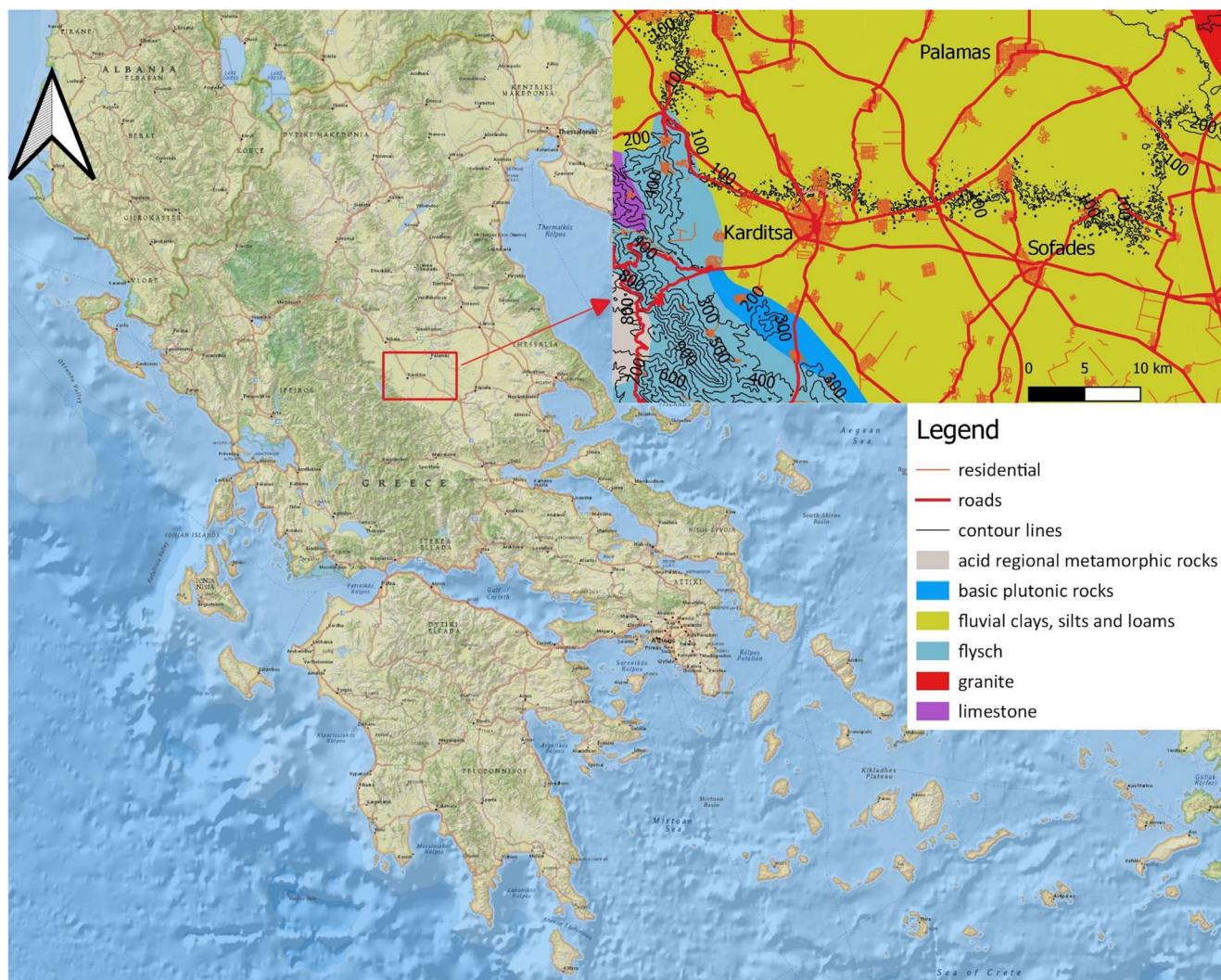

Fig. 1 Map of the study area

of Standards and Technology, USA; Montana soil). Recovery values were calculated as the ratio of the NIST results to those of the aqua regia of our samples and were 94% for Cd and 103% for Cr. Limits of detection based on three times the standard deviation of the blank ($n = 10$) were 0.29 $\mu g\ L^{-1}$ (Cd) and 0.36 $mg\ L^{-1}$ (Cr).

Statistical procedures

The mean, maximum, minimum values, standard deviation (SD), and coefficients of variation (CV) were calculated. The one-sample Kolmogorov–Smirnov test confirmed the normal distribution of all data when log-transformed. The comparison of Cd and Cr contents was carried out using the t test. Each value reported here was the mean of two replicates. The statistical package used was SPSS for Windows. For the creation of the reference and elevation maps, the corresponding topographic diagrams (based on the Geographical Army Service maps at a scale of 1:5000) were digitized, projected, transformed, and corrected with the use of ARC/INFO v. 3.5.2. (Golia et al. 2009a, 2009b, 2015). The projection used was the Lambert azimuthal equal area. Five layers were digitized: the elevation (hypsometric points), the inhabited areas, the road network, the drainage network, and the layer of the sampling points.

The analysis of data of pH and organic matter, as well as that of the extractable and pseudo-total Cd and Cr, was stored in the geodatabase constructed for the study area. The archives of the geodatabase were translated with Workspace Translator. Map layers were joined with ArcTools and ArcMap, while geostatistical analysis was performed with Geostatistical Analyst and Spatial Analyst (ArcGIS, v. 9.2), as per Burrough and McDonnell (2000) and Golia et al. (2015). Kriging interpolation had the following characteristics: (a) the absolute value of the average mean standard error (MSE) should be close to 0; (b) there should be a minimal root mean square prediction error (RMSE), which should be close to the mean standard error (AME); and (c) the standard root mean square (RMSS) should be close to 1 (as further explained by Golia et al. 2009a, Alyazichi et al. 2015, and Musilova et al. 2016).

Results and discussion

Soil properties

Soil pH values ranged from 4.1 to 8.3 and according to MAFF classification (MAFF 1988) were acid to alkaline (Table 1). Electrical conductivity ranged between 156 and 3145 $\mu S\ cm^{-1}$, with the high values measured in the urban, as well as in some agricultural soils. Clay ranged between 15 and 41%, while CaCO$_3$ was non-existent in the acid soils and had a

maximum of 18.6% and a mean value of 11.9%. This indicates that the soil properties varied considerably, a desirable feature assisting in better correlation and mapping. Measured soil properties were not expected to have any seasonal variations; thus, they were measured only once.

Levels of Cd and Cr in the area studied

The mean (of the 3 years of the study) concentrations of DTPA-extractable and pseudo-total Cr were rather lower than those reported in other agricultural areas (Martin et al. 2006; Micó et al. 2007; Peris et al. 2007; Chen et al. 2016) (Table 2). Both Cd and Cr extracted with DTPA were lower in spring than in autumn. Also, it is apparent that there is an increasing trend in the 3-year period of our study in the DTPA extractability of the two studied metals. However, we recognize that this finding should be further evaluated with other more sensitive extractants concerning likely metal seasonal variations before solid conclusions are drawn.

Although the total concentrations of Cr were lower than the non-legal maximum allowable concentration (MAC) and trigger action value (TAV) as reported by Kabata-Pendias (2011), those of Cd were in almost all cases higher than the European Union threshold limit of 3 $mg\ kg^{-1}$ (CEC 1986). Given the slight increasing trend in the DTPA-extractable concentrations of the studied metals, elevated Cd content may constitute a health issue for the area. Elevated Cd may be related to phosphate fertilizers which have been well known as a source of Cd in agricultural soils (Jayasire et al. 2014; Chen et al. 2016). This is a finding already recognized by previous works performed on similar areas of relatively low industrial activity, where Cd elevation to similar levels as ours has been linked with the likely decades-long use of phosphate fertilizers in the area (e.g., Golia et al. 2017, 2019). Given the fact that the study area has been for several decades under intensive cultivation, such enrichment is not unreasonable, although the magnitude of Cd elevation was rather unexpected. Moreover, the enrichment of Cd is rather unlikely to have occurred due to geological enrichment. On the other hand, Cr was found in low concentrations compared with MAC and TAV (please note that there are no set limits in the EU Directive); this finding indicates that probably all Cr content was of non-anthropogenic origin in the study area but was rather lithogenic.

Correlation analyses

In order to identify common sources and relationships between measured properties and metals, we performed correlation analyses (Table 3). We found that DTPA-extractable concentrations of Cd and Cr were correlated negatively and significantly with soil pH. This is a consequence of the fact that higher concentrations of extractable Cd and Cr were found in

Table 1 Chemical and physical properties of the soils of the study area in the Karditsa region (Central Greece)

	pH (1:1)	Electrical conductivity ($\mu S\ cm^{-1}$)	Organic matter (%)	Clay (%)	CaCO$_3$ (%)
Minimum	4.1	156	0.4	15	0
Maximum	8.3	3145	2.5	41	18.6
Mean	7.2	1745	1.9	22	11.9
CV%	24.4	57.3	28.4	26.6	18.6

acid soils compared with the alkaline, a finding in agreement with the literature (Morton-Bermea et al. 2002; Chen et al. 2016; Musilova et al. 2016; Antoniadis et al. 2017b). This also could have been the case due to the acidifying effect of conventional fertilizers; this effect would further affect the concentrations of extractable Cd and Cr. Soil pH is probably the single most important physicochemical parameter affecting metal mobility, including that of Cd and Cr. In lower (e.g., acidic) pH values, metals are found predominantly as hydrated ionic species which have high solubility. As pH increases, metals tend to be predominantly in their hydrolysis species (e.g., Cd(OH)$^+$) and their retention by electronegative soil colloids increases. Thus, in acidic soils, possible metal transport from soil to plants increases, while in neutral to alkaline soils, metal bioavailability is minimized (Antoniadis et al. 2017a). As rather expected, EC did not generate any significant correlation with either Cd or Cr, and neither did organic matter. On the other hand, clay content generated significant positive relationship with DTPA-Cd, while it had a high (but not significant) relationship with the other extracted and digested concentrations of Cd and Cr. This is an indication that high-clay soils tend to retain higher concentrations of metals, an ability likely to be exhibited in DTPA extractions, as also reported elsewhere (Jafarnejadi et al. 2013). An

interesting finding in this analysis is the fact that Cd and Cr were found to be inter-related: all relationships between Cd and Cr extracted with DTPA and between Cd and Cr digested with aqua regia were positive and significant. This indicates coexistence of the two studied metals (i.e., where the one was found elevated, the other was also elevated), and thus a strong possibility of the metals deposited from the same origin to some extent (Jayasiri et al. 2014). Since Cr is rather lithogenic, we would incline in the possibility that this coexistence (as evidenced by the high r value of 0.746 between aqua regia Cr and Cd) is rather connected to the particular percentage of Cd which is lithogenic.

Geostatistical analysis and thematic maps

In Table SM-1 (Supplementary Material) we show the geostatistical methods, parameters, and models that were used for the creation of the thematic maps. Heavy metal concentrations were interpolated using the multi-scale nested model. The accuracy was measured by RMSE, which assesses the average magnitude of the error (Ravankhah et al. 2016), and was found relatively low (Table SM-1). As for soil pH (Fig. SM-1, map 1), in the west side of the study area, soils with acidic pH values were found. This is due to base-poor felsic

Table 2 Extractable and pseudo-total Cd and Cr concentrations in the soils of the study area of the Karditsa region over the 3 years of monitoring

	Cd DTPA A (autumn)	Cd DTPA B (spring)	Cd (aqua regia)	Cr DTPA A (autumn)	Cr DTPA B (spring)	Cr (aqua regia)
Minimum	0.06	0.02	0.50	0.90	0.40	1.01
Maximum	0.60	0.30	10.0	12.9	5.01	50.07
Mean value (2010)	0.29	0.11	2.9	4.8	1.9	20.14
Mean value (2011)	0.38	0.19	3.1	5.71	2.74	22.91
Mean value (2012)	0.46	0.29	3.8	6.77	3.86	29.88
Overall mean	0.35	0.18	3.2	5.7	2.77	22.9
CV%	22.3	29.5	37.7	33.8	24.6	61.1
EU[a]	N.A.[b]	N.A.[b]	1–3	N.A.[b]	N.A.[b]	N.E.[c]
TAV[d]	N.A.[b]	N.A.[b]	2–20	N.A.[b]	N.A.[b]	50–450
MAC[e]	N.A.[b]	N.A.[b]	1–5	N.A.[b]	N.A.[b]	50–200

[a] Limits according to the European Union Directive CEC 86/278/EEC (CEC, 1986)

[b] Non-applicable

[c] Non-existent

[d] Trigger action value, as reported by Kabata-Pendias (2011, p. 24)

[e] Maximum allowable concentration, as reported by Kabata-Pendias (2011, p. 24)

Table 3 Correlation coefficients of the relationship between soil parameters and extractable and pseudo-total Cd and Cr concentrations

	Cd DTPA A	Cd DTPA B	Cd Aqua regia	Cr DTPA A	Cd DTPA B	Cr Aqua regia
pH	− 0.553*	− 0.778**	− 0.783**	− 0.619*	− 0.749**	− 0.677*
EC	− 0.227	− 0.256	− 0.323	− 0.346	− 0.285	− 0.156
OM	0.377	0.449	0.565*	0.367	0.435	0.554*
Clay	0.567*	0.435	0.559*	0.222	− 0.419	0.456
CaCO$_3$	− 0.519*	− 0.554*	− 0.222	− 0.319	0.355	0.267
Cd $_{DTPA\ A}$	1.000	0.519*	0.588*	0.503*	0.623*	0.522*
Cd $_{DTPA\ B}$		1.000	0.669*	0.766**	0.655*	0.668*
Cd $_{aqua\ regia}$			1.000	0.426	0.554*	0.786**
Cr $_{DTPA\ A}$				1.000	0.677*	0.746**
Cr $_{DTPA\ B}$					1.000	0.758**
Cr $_{aqua\ regia}$						1.000

**Correlation significant at $p < 0.01$ (2-tailed)

*Correlation significant at $p < 0.05$ (2-tailed)

underlying parent materials, and also due to the presence of soils belonging to the order of well-weathered Alfisols. Such soils are indeed often found in Thessaly; these are also known as red Mediterranean soils, identified as Rhodoxeralfs according to Soil Taxonomy, are typically with low base saturation due to extended weathering and leaching, and are developed over long geological periods on stable geomorphic areas so that deposition of materials (e.g., alluviation) and loss of materials (e.g., erosion) may be slower than pedogenesis (Sgouras et al. 2007). On the other hand, in the east side of the study area, soil pH was higher, as a result of alluvial

deposits and parent materials consisting mainly of limestone and marble (typically rich in bases, mainly Ca). Higher contents of organic matter (Fig. SM-1, map 2) were observed in the area situated between the towns of Sofades and Palamas, possibly due to extended application of manures.

High pseudo-total concentrations of Cd were found eastwards in the study area, covering (but not restricted to) the town of Karditsa, and also around the town of Sofades (Fig. 2). As for Cr, it is rather found on the same traces where Cd was observed, only more spatially scattered (Fig. 3). This is an indication of a lithogenic derivation of Cr; as for Cd, although
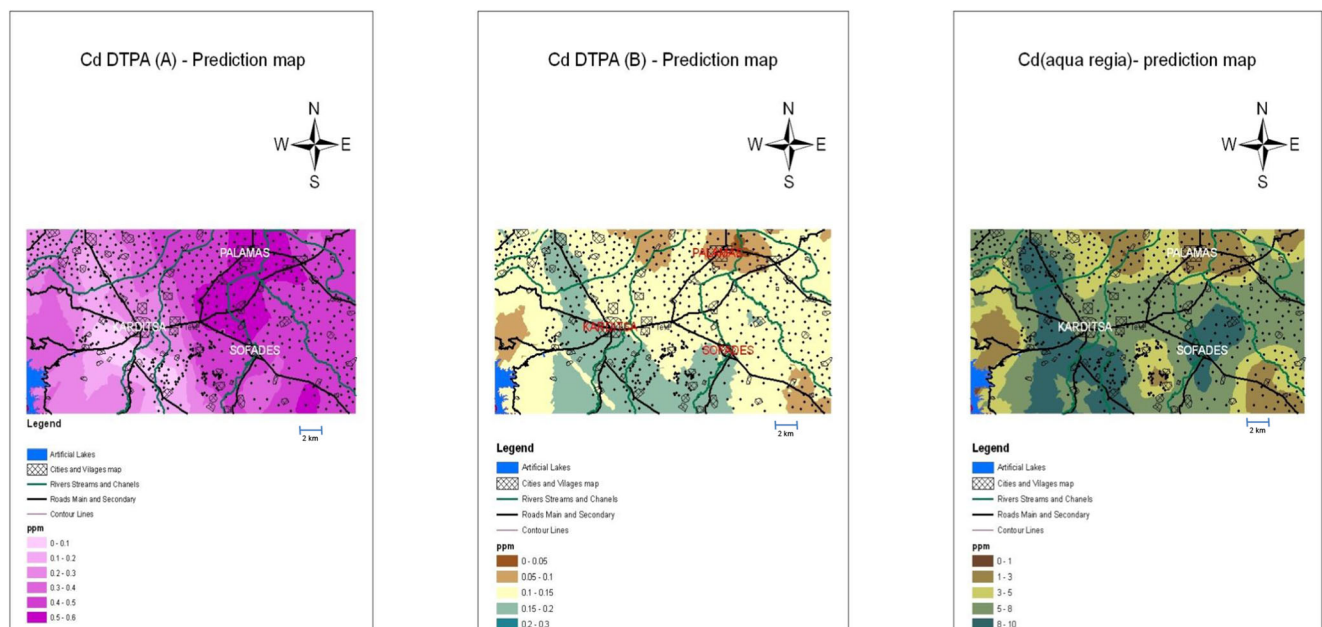

Fig. 2 Spatial variability of DTPA-extractable (measurement A, representing the autumn sampling, and measurement B, representing the spring sampling) and pseudo-total Cd concentrations. Sampling points are shown as dots in the map. Map dimensions are 34 × 17 km^2
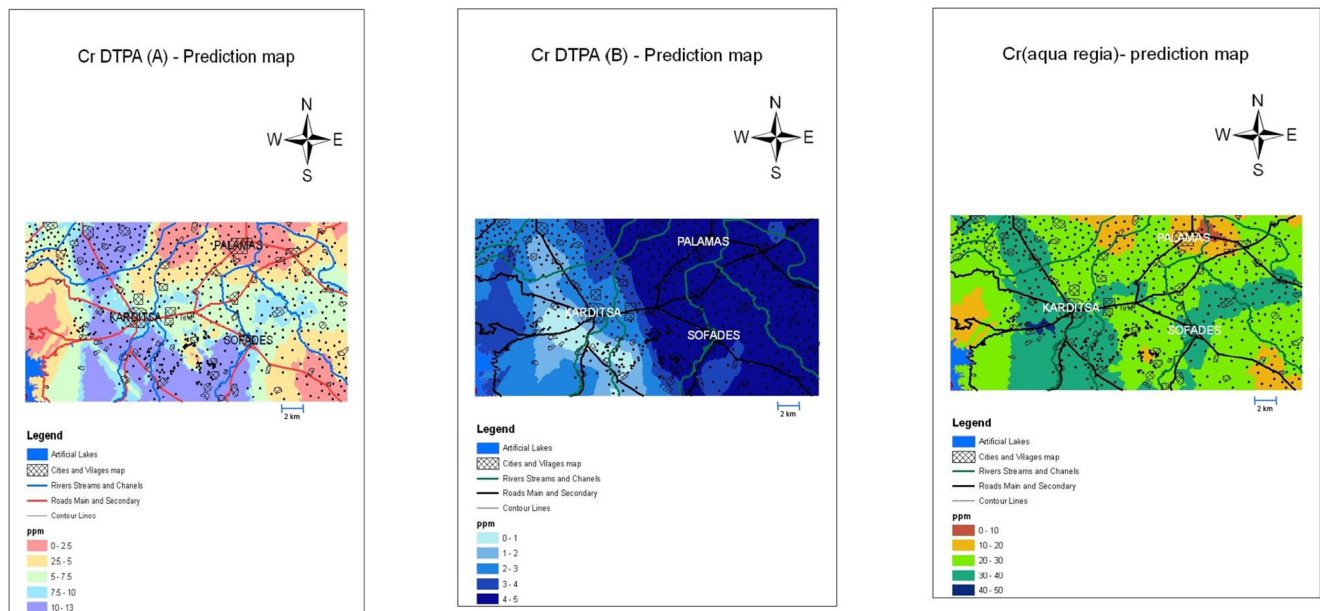
Fig. 3 Spatial variability of DTPA-extractable and pseudo-total Cr concentrations (measurement A, representing the autumn sampling, and measurement B, representing the spring sampling). Sampling points are shown as dots in the map. Map dimensions are 34×17 km^2

also lithogenically enriched in the same areas to a certain extent, it is rather further enriched due to intense cultivation practices around the agricultural area of Karditsa town. Thus, the spatial distribution maps for Cd and Cr showed similar geographical trends of the two metals. As for the DTPA-extractable Cd concentrations, 61% of the study area had high concentrations (> 0.5 mg Cd kg^{-1} soil; Fig. 2), while 19% of the area appeared to have high available Cr concentrations (> 10 mg Cr kg^{-1} soil; Fig. 2, maps 1 and 2) (both related to the Autumn DTPA values).

seasonal variations need to be verified with other more suitable means. Thus, further studies should be targeting metal-enriched areas and should focus on soil geochemical fractionation of metals; also, soil availability pools should be identified, in order to affirm the links between metal concentrations in crops and soil bioavailable levels.

Conclusions

Cadmium was unexpectedly found elevated, probably due to the intense agricultural activities of the study area. On the other hand, Cr pseudo-total levels were low, a finding indicating the probability of an entirely lithogenic derivation. The fact that pseudo-total Cd and Cr generated a positive and significant relationship ($r = 0.746$) shows that more than half of the measured Cd must have been lithogenical in origin, with the remaining being anthropogenic; such anthropogenic levels have likely derived from phosphate fertilizer impurities. This was confirmed by the thematic maps of pseudo-total Cd and Cr spatial distribution, indicating that the two metals were found to be located in approximately the same areas. Although thematic maps of contaminant metals can aid in identifying contamination hot-spot areas, we recognize that further studies are necessary for assessing the possibility of metals being transferred to crops. We also recognize that DTPA used here is a rather non-sensitive extraction and

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