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Monitoring the Variability of Zinc and Copper in Surface Soils from Central Greece

E. E. Golia · St. A. Floras · A. Dimirkou

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Abstract The main purpose of this investigation was the monitoring of Zn and Cu levels in soils of central Greece over three consecutive years (2005 to 2007). Soil samples were analysed for available forms (after extraction with DTPA) and for total concentrations (after digestion with Aqua Regia) of Zn and Cu. A temporal variability, from 2005 to 2007, was observed, as an increasing of 25.5% in available Zn, 25.1% in total Zn, 209% in available Cu and 19.6% in total Cu concentrations were recorded. A spatial variability was also observed and illustrated by the respective thematic maps created using geographic information systems (GIS). Significant correlations among metals concentrations and soil physicochemical parameters were obtained and discussed.

Keywords Central Greece · Zn · Cu · GIS

Among environmental pollutants, metals have been the subject of particular attention because of their long-standing toxicity when exceeding specific thresholds. The environmental pollution of soils directly influences human health since they have excellent ecological transference potential (Kabata-Pendias and Pendias 1992). They are harmful to humans, animals and tend to bio-accumulate in the food chain. Metals in soils can be associated with several reactive materials and may exist in various forms that reflect their solubility and availability to plants (Alloway 1990).

The levels of metals in soils may be affected by soil materials as well as anthropogenic sources. The natural concentration of metals in arable soil depends primarily on the geological parent material composition (Morton-Bermea et al. 2002). Although these metals occur naturally in the earth's crust, they tend to accumulate in agricultural soils because of application of commercial fertilizers, insecticides, manure and sewage sludge that contain heavy metals (Peris et al. 2007). In industrial areas the automobile exhausts, the uncontrolled factory emissions and activities, such as mining and smelting of metal ores have all contributed to elevate levels of metals in the environment. These metallic pollutants in the air eventually precipitate on the soil surface depending on wind flow patterns and increased their concentration in adjacent areas (Tembo et al. 2006). The degree of anthropogenic impact in the agricultural and industrial environment can be evaluated in terms of metal contamination of soils (Martin et al. 2006).

In our days, there is a growing need for optimum crop production in order to cover the nutrition needs of the population. However, there is also the need for sustainable management of soil resources in order to protect them from pollution and degradation. For this scope, precise fertilization tactics have become a necessity. Geographical information systems (GIS) through geostatistics and prediction maps of soil nutrients provides a helpful tool for soil sustainable management (Malkakis et al. 2006). The need for optimal and sustainable soil management pointed out to the use of GIS in order to build geodatabases that can store information about soil physico-chemical properties, nutrients concentration, hydrography, hillshade, etc., and can be updated in time and in space (ESRI 1996; Burrough and McDonnell 2000).

E. E. Golia (✉) · St. A. Floras · A. Dimirkou
Department of Agriculture, Crop Production and Rural Environment, Laboratory of Soil Science, University of Thessaly, Fytokou Road 36 446 Nea Ionia Magnissias, Volos, Greece
e-mail: egol@uth.gr

The objective of this work was to: (a) determine Zn and Cu concentrations in soils in Thessaly area, one of the most important agricultural area in Greece, (b) determine the most important soil factors (chemical and physical) which influence Zn and Cu concentrations in soils, and (c) create thematic maps of Zn and Cu concentration in the area studied.

Materials and Methods

A three years survey (2005 to 2007) was conducted in Thessaly–Almyros region in Central Greece in order to determine heavy metal concentration in soil. The area has a Mediterranean climate, with temperature that ranges from 14 to 24°C and annual rainfall of 200–300 mm. It is lowland, with elevation that ranges from 1 to 200 m and rebounds to the sea to its East and Southeast borders (Pagassiticos Gulf). Many streams and small rivers traverse the whole area of the study. It covers 15,000 ha. The area is cultivated mostly with vegetables, cotton, grains, medic, olive trees, and tobacco in the middle and in the north site, while a relatively new industry for metals reprocessing has been developed in the region studied (near the sea). Two hundred and fifty one surface (0–30 cm) soil samples were collected and the coordinates of the sampling points were detected with a differential global positioning system (DGPS) and marked on the satellite image that is shown in Fig. 1.

Soil properties were measured (Page et al. 1982), such as clay content (%), organic matter (Walkley–Black method), pH (1:1) and electrical conductivity (1:1). Plant available fractions of metals were determined by using diethylene–triamine–pentacetic acid (DTPA) buffered at pH 7.3 (Lindsay and Norvell 1978). Total concentration of metals was determined using the Aqua Regia (HCl–HNO_3, 3:1) extraction method (ISO/DIS 11466 1994) after digestion at 180°C for 2 h. All reagents were of analytical grade (Merck, Germany). The stock solutions of metals (1,000 mg/mL) were prepared from "titrisol" Merck.

Fig. 1 The area studied (prefecture of Magnissia-Central Greece)

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). Deuterium background corrections were used in the analysis of metals with the GF-AAS followed the standard Methods of JAOAC (1984). Certified Reference Material (CRM) (No. 141R, calcareous loam soil) by Community Bureau of Reference (BCR) was also analyzed for the verification of the accuracy of trace element determination in soils. Recovery values were calculated as the ratio of the BCR results to those of the Aqua Regia digestion and ranged from 95% (Zn) to 101% (Cu). The detection limits based on three times the standard deviation of the blank ($n = 10$), were found between 0.27 μg L^{-1} and 0.3 mg L^{-1} for Zn and Cu (FAAS), respectively.

The comparison of Zn and Cu contents among the three years duration of the study was carried out using the *t*-test. Results from two replicates were averaged prior to statistical analyses, which they obtained using statistic program for social sciences (SPSS®) for Windows.

For the creation of the reference and elevation map the corresponding topographic diagrams (1:5,000, Geographical Army Service) were digitized, projected, transformed and corrected with the use of ARC/INFO v. 3.5.2. GIS program. The projection used is 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 sample points.

The analysis data about the available and total concentration of Zn and Cu were stored in the geodatabase that is constructed for the study area. The archives of the geodatabase were translated with the program workspace translator. The modules ArcTools and ArcMap were used in order to join the map sheets and their corresponding layers, while the extensions geostatistical analyst and spatial analyst (ArcGIS v. 9.2) were used for the geostatistical analysis of the data and the creation of thematic maps of Zn and Cu (Burrough and McDonnell 2000).

Results and Discussion

The soil samples of the region studied were sandy clay loam (33%), silty loam (28%), clay loam (22%), and clay (17%). The soils according to soil taxonomy, they belong to different soil orders, such as: Alfisols (31%), Inceptisols

Table 1 Chemical and physical properties of soil samples

	pH (1:1)	Electrical conductivity (µS cm^{-1})	Organic matter (%)	Clay (%)
Minimum value	5.0	123	0.9	13
Maximum value	8.4	3000	5.0	44
Mean value	6.3	1560	2.4	22
CV (%)	17	54	32	18

(27%), Entisols (22%), and Vertisols (20%) (Soil Survey Staff 1999).

In Table 1 the mean values (of the three years of study) of chemical and physical properties of the soil samples are presented.

Soil electrical conductivity ranged between 123 and 3,000 µS cm^{-1}, with a high value appeared in industrial soil samples. This is probably due to the fact that this region is nearby the coastal zone of the Pagassiticos Gulf. The type of nitrogen fertilizers should be carefully chosen and applied, in order to avoid salination of soils (Mitsios et al. 2003).

The mean (of the three years of the study) concentration of DTPA extractable and total Zn and Cu in soils samples are presented in Table 2. The concentrations were lower than in other reports of agricultural areas (Martin et al. 2006; Micó et al. 2007; Peris et al. 2007).

In Table 2 the temporal variation of Zn and Cu concentrations is also presented. As it is obvious the available as well as the total concentrations of the metals studied appeared to have an increasing trend every year. From 2005 to 2007 an increasing of 25.5% in available Zn, 25.1% in total Zn, 209% in available Cu and 19.6% in total Cu concentrations were recorded. Although the total concentrations of Zn and Cu were lower than the critical limits (Alloway 1990; Kabata-Pendias and Pendias 1992), the continuous increase of them is of a great concern and may lead to pollution problems in the area studied.

In Table 3, the correlation coefficients among soil parameters and available and total Zn and Cu concentrations are presented.

Available concentration of Zn and Cu correlated negatively with soil pH. As a consequence high concentrations of available Zn and Cu were recorded in acid soils, as it is well documented from the literature (Alloway 1990; Kabata-Pendias and Pendias 1992) and found by other researchers (Martin et al. 2006; Malkakis et al. 2006).

In Table 4, the geostatistical methods, parameters and models that had been used for the creation of the thematic maps of the metals studied (Figs. 2–5).

In Figs. 2–5, the mean (2005–2007) available and total metal concentrations of Zn and Cu, are respectively presented. High available as well as total concentration of both Zn and Cu were observed in the east part of the area studied were the industry is activated for almost 10 years. Soil samples with high Zn and Cu concentrations were also

Table 3 Correlation coefficients among soil parameters and available and total Zn and Cu concentrations

	Zn_{DTPA}	$Zn_{Aqua\ Regia}$	Cu_{DTPA}	$Cu_{Aqua\ Regia}$
pH	−0.657[b]	−0.683[a]	−0.559[a]	−0.622[a]
EC	−0.227	−0.223[a]	−0.356	−0.256
OM	0.577[a]	0.565	0.778[b]	0.354
Clay	0.567	0.359[a]	0.522[a]	0.456[a]
Zn_{DTPA}	1.000	0.788[b]	0.503[a]	0.557[a]
$Zn_{Aqua\ Regia}$		1.000	0.426[a]	0.766[b]
Cu_{DTPA}			1.000	0.457[a]

[a] Correlation is significant at the 0.05 level (2-tailed)

[b] Correlation is significant at the 0.01 level (2-tailed)

Table 2 Mean available and total Zn and Cu concentration in soils

	Zn (available)	Zn (total)	Cu (available)	Cu (total)
	mg/kg dry soil			
Minimum value	0.2	7.4	0.09	5.4
Maximum value	11.4	88.2	6.4	70.6
Mean value (2005)	4.7	37.4	1.1	37.1
Mean value (2006)	5.1	43.1	2.2	42.7
Mean value (2007)	5.9	46.8	3.4	44.4
Mean value	5.2	42.4	2.2	41.4
CV %	19.4	39.1	51.8	54.3

Table 4 Geostatistical methods, parameters and models

	Map 1	Map 2	Map 3	Map 4
Geostatistical method	Ordinary kriging	Ordinary kriging	Ordinary kriging	Ordinary kriging
Transformation	None	None	None	None
Model	Spherical	Circular	Spherical	Spherical
Anisotropy	Yes	Yes	Yes	Yes
Nugget	0.2321	0.4498	0.2889	0.2694
MPE[a]	−0.0089	0.0022	−0.0033	−0.0028
RMS[b]	0.5777	0.5698	0.6698	0.3458
RMS SD[c]	1.039	1.008	1.109	1.017
R^2	0.633	0.789	0.556	0.512

[a] Mean prediction error; [b] Root-mean-square; [c] Root-mean-square-standardized

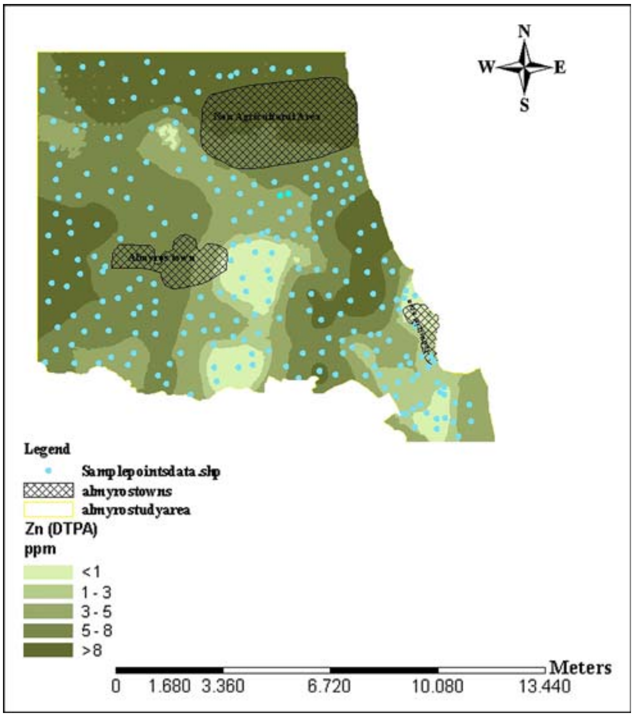

Fig. 2 Spatial variability of available Zn

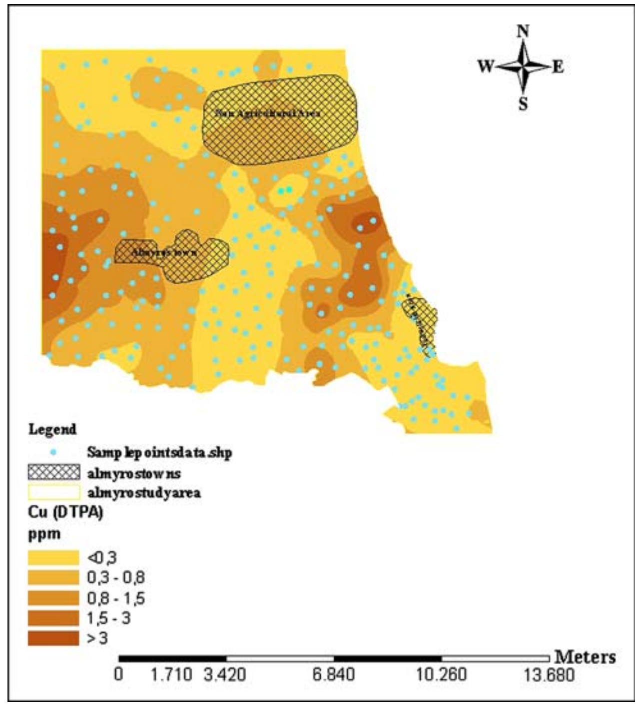

Fig. 4 Spatial variability of available Cu

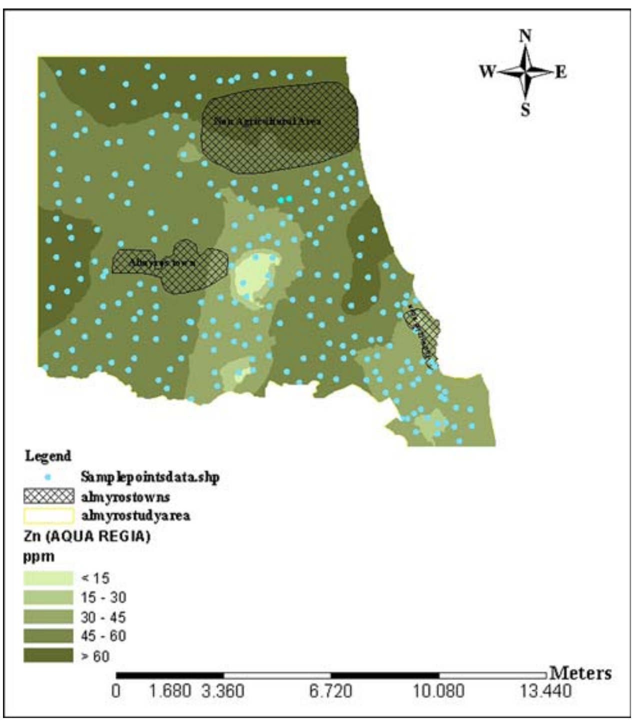

Fig. 3 Spatial variability of total Zn

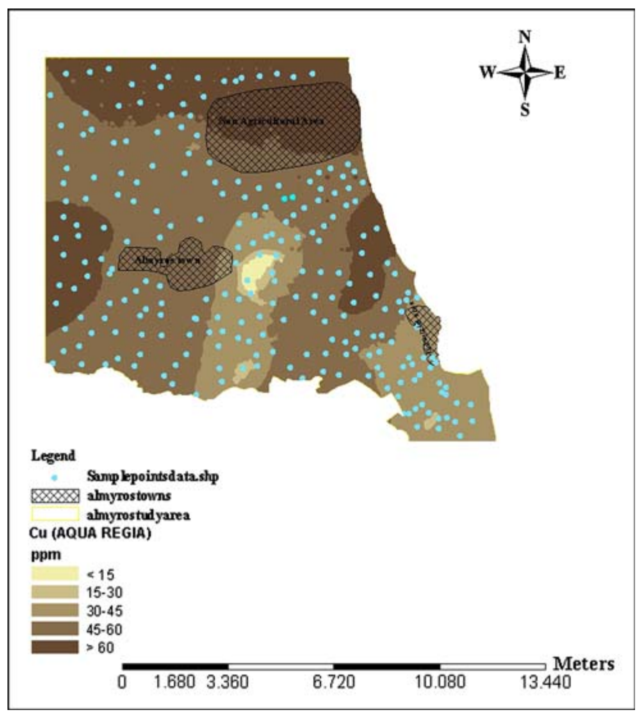

Fig. 5 Spatial variability of total Cu

observed in the west side of the area studied. These soil samples appeared to have also low pH values, as they were collected from the early beginning of the mountain Othrys and they are characterized by erosion of both wind and rainwater (Malkakis et al. 2006).

The available concentrations of Zn and Cu were classified among five classes (Figs. 2 and 4) according to

MAFF classification (MAFF 1988). Fifty-five percentage of the area studied had high concentrations of available Zn (>5 mg Zn kg^{-1} dry soil), while 17% of the area appeared to have high available Cu concentrations (>1.5 mg Cu kg^{-1} dry soil).

Comparing the four maps it is obvious a grate affinity among them. This is also concluded from the high correlation coefficients among available and total concentration of each metal and the concentrations of the two metals studied. High concentrations of available Zn were followed by high total Zn concentration. Also, high total Zn and Cu concentrations were recorded in the same sites of the area studied.

In conclusion, Zn and Cu available and total concentrations were lower than the critical limits (Alloway 1990; Kabata-Pendias and Pendias 1992). On the other hand the continuous increase of the levels of the metals studied requires constant monitoring. Thus, Zn and Cu maps are expected to constitute an important tool for further research in the region studied, because they give the opportunity of continuous renewal of database and verification or even correction of estimation of metals pollution.

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