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# Accumulation of heavy metals in agricultural soils of Mediterranean: Insights from Argolida basin, Peloponnese, Greece

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ABSTRACT

Excessive application of chemical products for promoting crop growth is a significant contributor for elevated concentrations of heavy metals in agricultural soils potentially threatening human health through the food chain. In this study, a series of heavy metals were quantified in 132 agricultural soils of Argolida basin, Peloponnese, Greece, with the aim to characterize their accumulation patterns. Median concentrations of Cu, Pb, Zn, Ni, Co, Mn, As, Cd, Cr and Fe were 65.23, 20.1, 72.75, 120.3, 20.6, 956.5, 7.1, 0.45, 72.3 and 27,100 mg/kg respectively. Statistically significant differences for Cu, Zn, Pb and Cd content were found between agricultural and background soils in the same region. Implementation of principal component analysis and cluster analysis successfully grouped the investigated chemical elements according to their anthropogenic or natural origin. The prolonged application of large amounts of fertilizers and pesticides–fungicides has resulted to Cu, Zn, Cd, Pb and As accumulation in the agricultural fields whereas Ni, Cr, Co and Fe amounts are controlled by parent material influences. Contrary to results commonly reported in the literature that characterize Mn as a geogenic element, this metal was found to exhibit a mixed source in the study agricultural system. Geographical information system techniques were used to illustrate the spatial distribution trends of the investigated elements confirming the clear contribution of agrochemicals to soil chemistry and highlighting the citrus soils around Argos town to have received large anthropogenic inputs. The agricultural area represented by olive groves does not demonstrate significant anthropogenic soil metal enrichment indicating that accumulation phenomena are restricted to the soils cultivated for oranges and mandarins. This study is the first detailed report on metal accumulation in citrus soils from Argolida basin, and results promote the care for the environment by reducing application rates of fertilizers and pesticides–fungicides and monitoring heavy metals levels in receiving soils. Future studies should pay attention to characterize the fractionation and reactivity of metals in citrus soils by utilizing selective chemical extractions with the aim to assess the actual risks for the environment.



## 1. Introduction

Soil is a natural component of the earth serving a variety of vital functions in our society including food production. With rapid industrialization and urbanization that have occurred in most parts of the world during the last decades, the soil compartment is receiving a substantial amount of pollutants from different sources including heavy metals (Wei and Yang, 2010). A vast count of publications has appeared in the scientific literature documenting metal concentrations in soils of various land uses because of the non-biodegradable nature of these chemical substances and the potential adverse effects on human health. Typical human activities like industrial operations, vehicle exhaust fumes, mining and smelting and atmospheric deposition are known to greatly impact the urban and rural soil environs in terms of heavy metal levels (Aelion et al., 2008; Chabukdhara and Nema, 2013; Christoforidis and Stamatis, 2009; Douay et al., 2008; Gowd et al., 2010).

In agricultural soils, the presence of metals is of increasing concern because they have the potential to be accumulated in less soluble forms, transferred into soil solution and subsequently deteriorate the groundwater and crop quality. The food crops constitute an important source of human oral exposure to metals (Harmanescu et al., 2011; Zheng et al., 2013), and as a result careful monitoring of metal levels in agricultural soils is of great importance for protecting its quality and ensuring future sustainability (Wong et al., 2002). The natural concentrations of heavy metals in these soils tend to remain low depending on the geological parent material composition (Shan et al., 2013), although significant geogenic enrichment has also been recently reported (Kelepertzis et al., 2013). On the other hand, anthropogenic inputs in agricultural soils that contribute to an increase of the content of some toxic heavy metals have reported including sewage irrigation (Liu et al., 2005), petrochemical activities (Li et al., 2009) and the excessive usage of agrochemicals and manure (Hani and Pazira, 2011; Lu et al., 2012; Nicholson et al., 2003). Although fertilizers are essential for providing adequate nutrients and ensuring successful harvests, long-term repeated application of fertilizers and metal-containing pesticides and fungicides can gradually add potential harmful

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levels in soils (Jiao et al., 2012). Additionally, because fertilizers tend to be local and ingredient specific, the chemical composition of soils receiving fertilizers inputs is expected to vary according to application rates and source of raw material (Jiao et al., 2012; Nziguheba and Smolders, 2008). Enrichment of soils with Cu, Zn and Cd is the most apparent result characterizing areas that have suffered a long history of intensive agrochemical application (Franco-Uria et al., 2009; Maas et al., 2010; Peris et al., 2008).

China is a country where the heavy metal status of agricultural soils has been extensively investigated during the last decade because of the emerging contamination problems accompanying the rapid urban and peri-urban growth and the establishment of new industrial operations (e.g. Cai et al., 2012; Chen et al., 2008; Huang et al., 2007; Lu et al., 2012; Luo et al., 2012; Niu et al., 2013; Sun et al., 2013). In the Mediterranean area, the majority of the investigations have focused on Spanish agricultural soils (Franco-Uria et al., 2009; Micó et al., 2006; Peris et al., 2008; Rodríguez Martín et al., 2006, 2013) whereas geochemical data also exist for Italy (Abollino et al., 2002; Facchinelli et al., 2001) and Zagreb (Romic and Romic, 2003). In Greece, there is an ongoing body of knowledge regarding the agricultural fields in the central part of the country (Antibachi et al., 2012; Golia et al., 2007; Skordas and Kelepertsis, 2005; Skordas et al., 2013). However, at present, there are no data about the accumulation of metals in agricultural soils of Peloponnese and in particular of the Argolida basin which exhibits a history of agriculture for more than 50 years. In addition, most studies have conducted at a large scale which may conceal or neglect regional scale information for metal accumulation. For instance, Nanos and Rodríguez Martín, 2012 concluded that anthropogenic heavy metal enrichment in agricultural soils from the Duero river basin (Spain) is masked when considering large spatial scales. Therefore, this study was designed to characterize the accumulation and sources of 10 metals (Cu, Pb, Zn, Ni, Co, Mn, Cd, Cr, As and Fe) in a substantial number of soil-survey plots within the agricultural system of Argolida basin covering an area of approximately 300 $km^2$. Chemical results for P and K are also included to assist in the source apportionment of metals. Multivariate statistical methods combined with Geographic Information System (GIS) techniques were implemented to identify contamination sources and delineate the areas at hazard of contamination that need a more detailed investigation. Results will be used to provide baseline information for the soil quality status in Mediterranean agricultural soils and support decision makings for ensuring food crop quality and protecting human health.

## 2. Materials and methods

### 2.1. Study area and sampling procedure

The study area is located in the south part of Greece (Fig. 1) surrounding the Argos (~22,000 inhabitants), Nafplio (~15,000 inhabitants) and Ligourio (~3000 inhabitants) residential areas. The region has been traditionally associated with agricultural activities favoring mainly the production of orange, mandarin and olive trees. At places, some vegetables like artichokes and tomatoes and fruits like peaches and apricots are cultivated. This area represents one of the major suppliers of Greek population with oranges. The geology of the area is dominated by Quaternary alluvial deposits whereas the surrounding mountains are characterized by the occurrence of carbonate rocks and flysch consisting of marls, sandstones and carcareous shales. The flysch also comprises at places serpentinitic rocks.

Soil samples were collected in March and April 2013 from the upper 20 cm of soil depth. For logistical reasons, the sampling was performed near roads following a random strategy with the aim to cover the whole basin. A total of 132 agricultural soils were recovered by collecting material 1 m apart from the vertices of a triangle to form a composite sample. The sampling points are shown in Fig. 1. Following recommendations by Roca-Perez et al. (2010), 8 reference non-agricultural soils developed in the close vicinity of exposed rock outcrops were collected and were considered as unaffected soils, or at least minimally affected by anthropogenic activities. The soil samples were stored in polyethylene bags for transportation and storage, air-dried at a constant temperature of 40 °C for three days and then sieved through a 2-mm screen. Representative portions of each soil sample were further sieved through a plastic 100-μm sieve in order to focus on metal fractions that are potentially most environmentally reactive (Huang et al., 2007; Kelepertzis et al., 2013).

### 2.2. Chemical determinations

Geochemical analyses were provided by the accredited Acme Analytical Laboratories of Canada. More specifically, a 0.5 g aliquot of each soil was digested by hot (95 °C) aqua regia ($HNO_3$–HCl–$H_2O$) following the common analytical decomposition method applied to most investigations carried out in European agricultural soils (e.g. Facchinelli et al., 2001; Micó et al., 2006; Rodríguez Martín et al., 2013); this allowed the chemical results from the present study to be straightly comparative with findings from the other Mediterranean areas. The applied acid digestion can be considered as almost total for the majority of determined elements except for some metals like Fe and Cr due to their incorporation in crystal structure of insoluble recalcitrant minerals like some silicates or spinels if present in the serpentinitic small bodies (Kelepertzis et al., 2013).

Taken into account the environmental purposes of the present study, extractable concentrations of Cu, Pb, Zn, Ni, Co, Mn, Fe, As, Cd, P, Cr and K are presented herein. Geochemical solutions were analyzed by inductively coupled plasma-mass spectrometry with notably very low detection limits. In particular, limits of detection were 0.01 mg $L^{-1}$ for Cd, Pb and Cu, 0.1 mg $L^{-1}$ for As, Co, Zn and Ni, 0.5 mg $L^{-1}$ for Cr, 0.01% for Fe and K, 0.001% for P and 1 mg $L^{-1}$ for Mn. Replicates, reagent blanks and in-house reference materials provided by the ACME Analytical Laboratories were analyzed as part of the quality control procedures validating the good precision and accuracy of analytical results. Recoveries between 90 and 110% were obtained for the considered elements whereas the relative percent difference (RPD) calculated for each pairs of duplicates revealed RPD values lower than 20% in all cases.

### 2.3. Statistical analyses and spatial distribution maps

Statistical analysis was carried out in SPSS 20.0 software. Basic statistical parameters for raw soil data were established, and the Kolmogorov–Smirnov test was used for data normality assessment. A $p$ value higher than 0.05 was used to agree with the hypothesis of the data set belonging to a normal distribution. Box-and-whisker plots were also generated for displaying the data distribution. For the boxplots, the length of the box indicates the interquartile range whereas the horizontal line within each box represents the median value. Outliers are values that are more than 1.5 times the interquartile range. To compare metal concentrations between the reference and the agricultural soils, parametric *t-test* analysis of variance was applied with a $p$ value of $<0.05$ showing a significant difference between the compared groups.

Principal component analysis (PCA) and cluster analysis (CA) were employed to the data set with the aim to identify associations and common origin among metals (Lu et al., 2012; Zhang, 2006). PCA was performed with Varimax rotation which facilitates the interpretation of the output results by minimizing the number of variables with a high loading on each component. Results from PCA were interpreted according to the hypothetical sources of chemical elements (Peris et al., 2008; Yuan et al., 2013). Hierarchical CA was developed according to the Ward method (Cai et al., 2012; Chen et al., 2012; Franco-Uria et al., 2009; Micó et al., 2006; Xia et al., 2011), and the results are reported in the form of dendrogram providing a visual summary of the clustering processes. Squared Euclidean distance was applied for measuring the distance between clusters of similar elemental contents. High internal (within cluster)

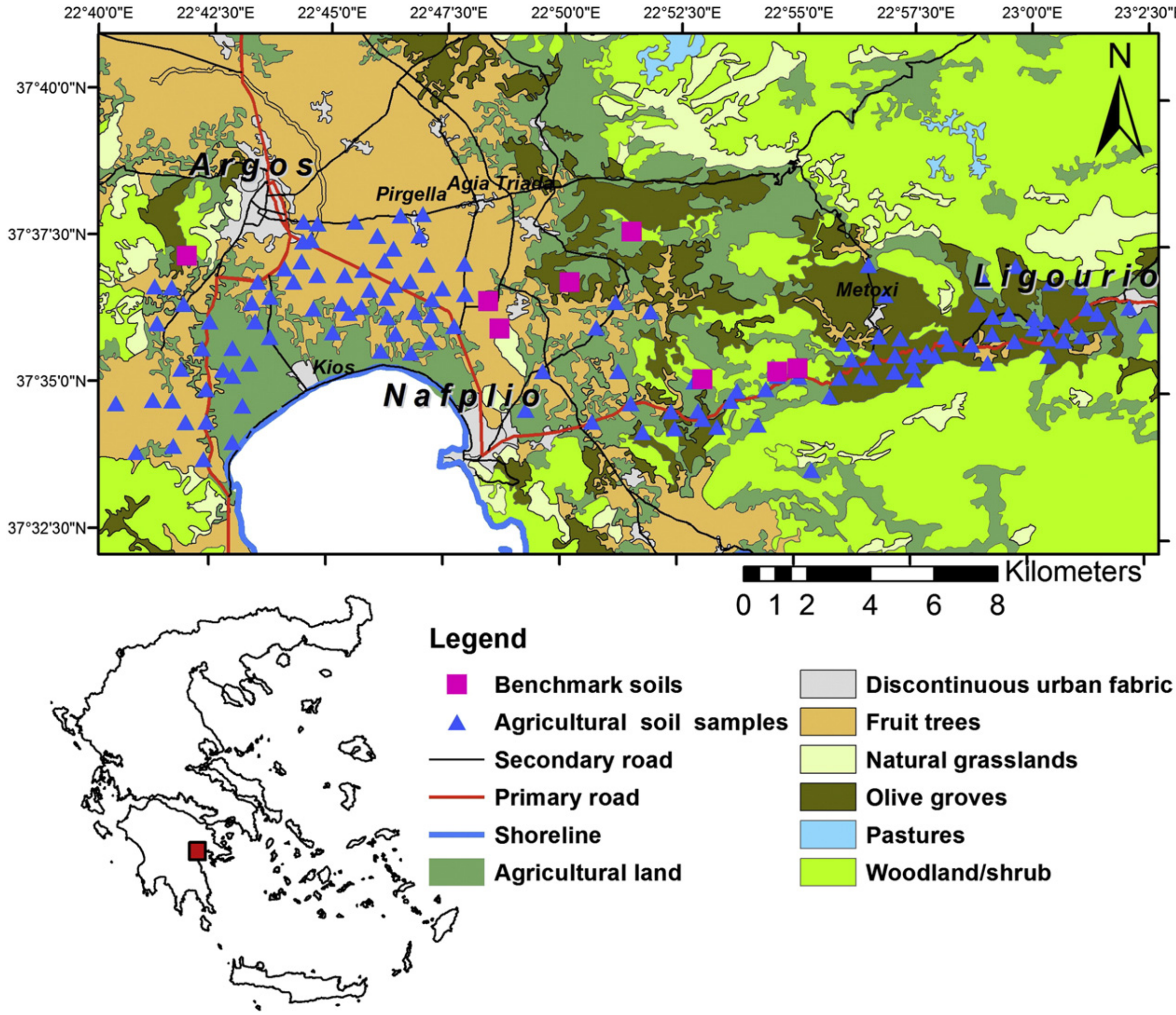


**Fig. 1.** Location map of the study area showing the land use and the sampling sites for both the agricultural and benchmark soils.

homogeneity and high external (between clusters) heterogeneity assist in the interpretation of the output results. Because multivariate analysis is sensitive to outliers and non-normality of geochemical data sets (Chen et al., 2008; Hani and Pazira, 2011; Niu et al., 2013), elemental concentrations were normalized prior to implementation of PCA and CA.

The first step in spatial analysis was the integration of the georeferenced sampling points and the land use of the area according to the Corine classification (EEA, 1994) using ArcMap v.10.0 (ArcGIS). The geochemical maps showing the overall spatial distribution patterns of elemental concentrations were generated by using the Geostatistical

**Table 1**
Statistical summary of chemical elements in soils ($n = 132$) from Argolida basin (in mg/kg except Fe, P and K in %).

| | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | Cr | Fe | P | K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 74.68 | 19.74 | 74.88 | 146.8 | 21.99 | 1020.5 | 6.95 | 0.54 | 83.12 | 2.65 | 0.127 | 0.313 |
| SD | 63.87 | 7.44 | 32.8 | 120.3 | 11.54 | 544 | 2.317 | 0.69 | 48.25 | 0.58 | 0.15 | 0.13 |
| Q1 | 39.19 | 14.3 | 54.13 | 90.6 | 13.98 | 558.8 | 5.1 | 0.22 | 55.78 | 2.26 | 0.65 | 0.22 |
| Median | 65.23 | 20.1 | 72.75 | 120.3 | 20.6 | 956.5 | 7.1 | 0.45 | 72.3 | 2.71 | 0.09 | 0.3 |
| Q3 | 96.97 | 23.89 | 87 | 162.8 | 27.88 | 1404.3 | 8.4 | 0.61 | 93.75 | 3.12 | 0.14 | 0.39 |
| Minimum | 11.89 | 3.17 | 23 | 43.8 | 5.9 | 267 | 2.7 | 0.07 | 28.1 | 1.28 | 0.018 | 0.06 |
| Maximum | 653.14 | 48.49 | 288.5 | 1258.1 | 113.1 | 3495 | 12.8 | 6.1 | 353.6 | 4.05 | 1.515 | 0.74 |
| Skewness | 6.01 | 0.51 | 2.47 | 6.41 | 3.87 | 1.21 | 0.3 | 5.78 | 3.03 | −0.38 | 6.5 | 0.64 |
| Kurtosis | 51.7 | 51.07 | 13.17 | 55.87 | 28.67 | 2.88 | −0.33 | 40.3 | 12.23 | −0.38 | 56 | 0.44 |
| K–S test | 0.000 | 0.200 | 0.000 | 0.000 | 0.000 | 0.002 | 0.200 | 0.000 | 0.000 | 0.200 | 0.000 | 0.0140 |
| CCME, 2007; [a] | 63 | 70 | 200 | 50 | 40 | | 12 | 1.4 | 64 | | | |
| Dutch target value[b] | 36 | 85 | 140 | 35 | 20 | | 29 | 0.8 | 100 | | | |
| Dutch intervention value[b] | 190 | 530 | 720 | 210 | 240 | | 55 | 12 | 380 | | | |

*SD* Standard deviation, $Q1$ = First quartile, $Q3$ Third quartile.
[a] Canadian soil quality guidelines for the Protection of Environment and Human Health, 2007.
[b] VROM, 2000.

Analyst tool for ArcMap (ArcGIS) and the Inverse Distance Weighted interpolation method.

## 3. Results and discussion

### 3.1. Metal concentrations in agricultural soils

The descriptive statistics of the heavy metal concentrations in agricultural soils of Argolida basin are listed in Table 1. The median values of elemental contents in soils follow a decreasing order as: Fe > K > Mn > P > Ni > Zn ~ Cr > Cu > Co ~ Pb > As > Cd. High values of standard deviation are observed for metals like Cu, Ni, Mn, Zn and Cr reflective of the large geochemical variability characterizing these soils. Application of the K–S test showed that concentrations of Cu, Zn, Ni, Co, Mn, Cd, Cr and P are not normally distributed; Pb, As, Fe and K followed a normal distribution. The skewness values which are a measure of the degree of asymmetry of a distribution in relation to a normal distribution also confirmed the above. Moreover, the kurtoses of most metals (Cu, Zn, Ni, Co, Cd, Cr and P) were very sharp because the majority of the samples were clustered at the relatively lower values. These statistical features imply that the median values are more representative of metal concentrations than arithmetic means. After log-transformation, the distributions of Ni and Mn were still not normal ($p$ values of K–S test 0.005 and 0.001); $n$-score transformation was performed to guarantee the normal distribution of all elemental concentrations (Kaitantzian et al., 2013). Generated box-and-whisker plots (Fig. 2) for representative metals indicate the presence of several outliers in the data set corresponding to the most contaminated samples; however, as it will be shown later, the existence of outliers did not necessarily imply human influence on soil quality as commonly reported (Micó et al., 2006).

Median levels of Cu, Pb, Zn, As, Mn and Cd in agricultural soils were higher than corresponding values determined for the reference soils (Table 2). The $t$-test confirmed statistical differences between concentrations of Cu ($p = 0.000$), Pb ($p = 0.044$), Zn ($p = 0.001$) and Cd ($p = 0.013$) suggesting a primary anthropogenic input in the agricultural soils. On the contrary, no statistically significant differences were observed for Ni ($p = 0.292$), Co ($p = 0.393$), Mn ($p = 0.062$), Fe ($p = 0.533$), As ($p = 0.230$) and Cr ($p = 0.182$) between the agricultural and the unaffected (or minimally affected) soils. In comparison with the Dutch guideline values (Table 1) that have been applied to a great number of soil investigations for evaluating metal contamination (e.g. Chabukdhara and Nema, 2013; Man et al., 2010), concentrations of Pb, As and Zn are always lower than the target limits of 85 mg/kg, 29 mg/kg and 140 mg/kg respectively with the only exception for Zn in 4 soil samples. In fact, As and Pb medians are identical to the recently published median levels of these metals for agricultural soils in the European continent which are 16 mg/kg and 5.7 mg/kg respectively (Reimann et al., 2013; Tarvainen et al., 2013). Copper, Ni, Cr, Cd and Co levels are commonly higher than the target limits and lower than the intervention values. Only Ni is present in concentrations well above the intervention limit of 210 mg/kg in a notable number of soils. Loadings of Cu, Ni and Cr are also higher than the Canadian quality guidelines for agricultural soils (63 mg/kg, 50 mg/kg and 64 mg/kg respectively) (Table 1). In addition, Cd levels in 4 sites exceed the corresponding value of 1.4 mg/kg recommended by the Canadian soil contamination guidelines.

**Table 2**
Mean, median, minimum and maximum values for the benchmark soils ($n = 8$).

| | Mean | Median | Minimum | Maximum |
|---|---|---|---|---|
| Cu | 28.64 | 24.71 | 17.24 | 42.81 |
| Pb | 13.96 | 13.31 | 8.26 | 24.08 |
| Zn | 45.26 | 43.15 | 32.7 | 63.6 |
| Ni | 253.7 | 175.9 | 57.7 | 820 |
| Co | 25.05 | 19.55 | 13 | 46.8 |
| Mn | 665 | 627 | 313 | 1025 |
| As | 5.89 | 4.95 | 3.9 | 8.9 |
| Cd | 0.26 | 0.235 | 0.14 | 0.27 |
| Cr | 138.4 | 101.8 | 43.1 | 275.4 |
| Fe | 2.90 | 2.56 | 2.05 | 4.7 |
| P | 0.039 | 0.038 | 0.018 | 0.073 |
| K | 0.239 | 0.26 | 0.12 | 0.43 |

The metal concentrations obtained in this study are compared with data reported for other areas in Mediterranean and China (Acosta et al., 2011; Antibachi et al., 2012; Cai et al., 2012; Facchinelli et al., 2001; Huang et al., 2007; Lu et al., 2012; Micó et al., 2006; Nanos and Rodríguez Martín, 2012; Peris et al., 2008; Rodríguez Martín et al., 2006, 2013; Romic and Romic, 2003; Sun et al., 2013) in Table 4. Lead loadings in Argolida agricultural soils are within the lowest found in the literature, whereas the mean concentration of Zn is similar to those obtained in Zagreb and Castellón province and lower than in Jiangsu province. Arsenic is a metal that has not been determined in lots of investigations; however, the As levels are quite identical to concentrations measured in Shunyi and Huizhou, both located in China. Observing Table 4, a significant enrichment of Cu, Ni, Cr, Co and

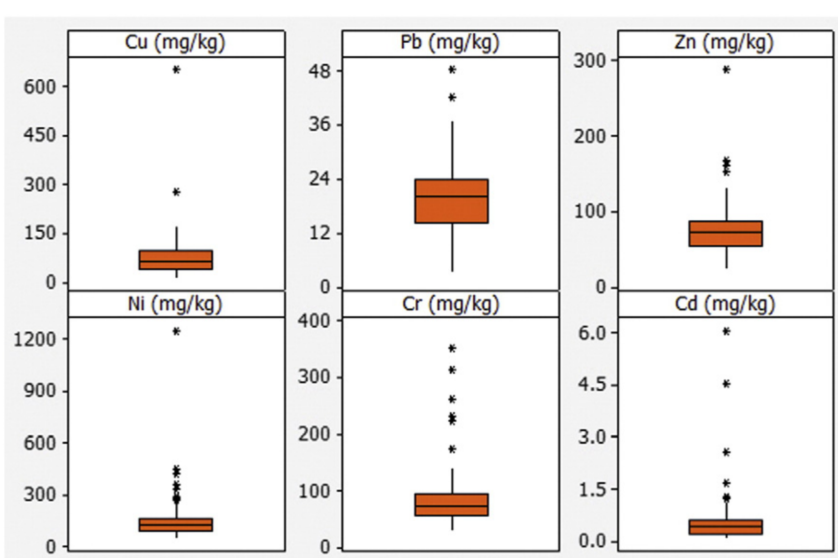


**Fig. 2.** Box-and-whisker plots illustrating the presence of outliers for representative metals.

Mn in agricultural soils of Argolida is revealed since the mean concentrations of these metals are substantially higher than values determined in other areas. Only, agricultural soils in Thiva (central Greece) display higher Ni, Cr and Co mean values that have been ascribed to local parent materials enriched with these specific metals. The mean content of Cd is also among the highest found in the literature with only agricultural soils in Zagreb exhibiting a slightly higher mean concentration.

### 3.2. Multivariate analysis

Since the agricultural soils of Argolida basin were found to be enriched in some metals compared to benchmark soils and agricultural soils around the world, multivariate analysis was conducted to identify the natural or anthropogenic sources of enrichment (Franco-Uria et al., 2009; Kaitantzian et al., 2013). The results of PCA for elemental concentrations in agricultural soils are shown in Table 4. Two principal components with eigenvalues higher than 1 (before and after rotation) were extracted. The PCA method resulted in a reduction of the initial dimension of the data set to two components explaining a 74.8% of the data variation. The graphic representation of these components is shown in Fig. 3 depicting the association between the elements. The rotated component matrix demonstrated that Cu, Pb, Zn, As, Cd, P and K were involved in the first component (PC1) whereas the second component (PC2) included Ni, Co, Fe and Cr. Manganese was the only metal that did not demonstrate a clear association with either the first or the second component, but higher loading plots were observed for PC1 (0.65) compared to PC2 (0.59). Additionally, CA was performed for confirming results obtained by PCA and provided grouping of variables (Chen et al., 2008; Facchinelli et al., 2001). The results of CA are illustrated in Fig. 4 as a dendrogram that enabled the identification of two major groups of elements describing the geochemical complexity of the study area. Group I comprised Ni, Cr, Co, Fe and Mn and was clearly distinguished from Group II that consisted of Pb, As, Zn, P, Cd, K and Cu.

#### 3.2.1. Anthropogenic influence

PC1 explained 43% of the total variance and can be considered to be an anthropogenic component related to the agricultural activities taking place in the area for a long period of time in agreement with the clustering of variables in Group II. Copper, Pb, Zn and Cd were also found to be present in greater amounts in the agricultural soils than the reference soils confirming the interpretation of their anthropogenic origin. In addition, inclusion of P and K in both PC1 and Group II of CA points out that the widespread use of phosphorous and potash fertilizers is the main source of anthropogenic influences in the investigated soil system. A clear subgroup of Cu, K, Cd, P and Zn is evident inspecting the dendrogram produced by CA (Fig. 4) followed by Pb and As that form another subgroup.

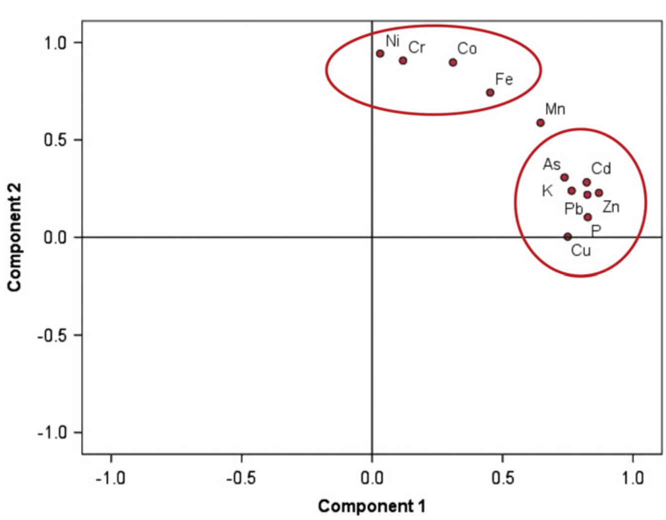


**Fig. 3.** Loading plots of the two components influencing geochemical variation of soils from Argolida basin.

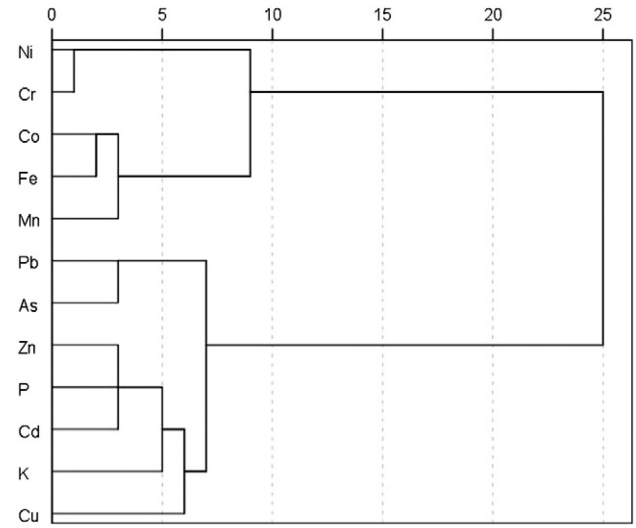


**Fig. 4.** Results of hierarchical cluster analysis for the investigated elements in the form of dendrogram.

Copper is usually considered as a marker element of agricultural activities and is specifically related to application of commercial fertilizers (Acosta et al., 2011). Furthermore, long-term direct usage of Cu-based pesticides and fungicides on agricultural crops contributes to an increased accumulation of Cu in these kinds of soils (Epstein and Bassein, 2001; Sun et al., 2013). Previous investigation concerning Cu content in agricultural soils related to various cropping systems in different regions of Greece has revealed some Cu accumulation due to the traditional use of Cu-based fungicides for controlling fungal diseases (Vavoulidou et al., 2005). The long agricultural history combined with the excess use of fertilizers and pesticides has resulted into extensive Cu accumulation in agricultural soils from Argolida.

Cadmium is a toxic metal that exhibited higher geochemical values in the agricultural soils compared to the reference samples (maximum 6.1 mg/kg). The main source of Cd is the use of phosphate fertilizers with a large number of studies documenting an increase in Cd accumulation in agricultural soils under intense application of P fertilizer with high Cd content (e.g. Atafar et al., 2010; Cai et al., 2012; Peris et al., 2008). Phosphate rocks are the primary stock materials for manufacturing the fertilizers, and these rocks may contain significant Cd levels (Jiao et al., 2012). Zinc is a metal that has been proposed to exhibit a mixed source from both lithogenic and human sources in agricultural soils (Micó et al., 2006; Sun et al., 2013); nevertheless, in Argolida, most Zn variability is controlled by the application of mineral fertilizers. Animal manure has also been suggested to contribute to Zn as well as Cu levels in agricultural soils; for instance, it has reported that livestock manure contributes to 37–40% of total Zn inputs in agricultural soils in England and Wales (Nicholson et al., 2003). In addition, McBride and Spiers (2001) reported high Zn and Cu concentrations in manure due to the Zn and Cu-enriched feed additives used to promote animal growth. However, the association of Zn with Cd as revealed by the CA (Fig. 4) points out that the application of phosphate fertilizers is the important source for Zn in the study agricultural system.

High loading factors on PC1 for Pb and As suggest that levels of these toxic metals can be primarily attributed to anthropogenic influences. Atmospheric industrial fallout and emissions by vehicular exhausts are the major sources of contamination of Pb in agricultural croplands (Facchinelli et al., 2001; Franco-Uria et al., 2009). Increased Pb and As levels in cultivated soils have also been ascribed to mineral fertilizer application (Atafar et al., 2010; Nicholson et al., 2003) with the P fertilizers being regarded as the main contributor to their accumulation in the receiving soils (Nziguheba and Smolders, 2008). However in Argolida soil system, the differentiation of these metals from Cu, Zn and Cd as revealed by CA may be explained either by a slight enrichment of Pb and As in compound fertilizers applied in the soils as informed by local farmers or by their geochemical tendency to be adsorbed by iron-, manganese-, and aluminum-hydroxides after accumulating in the soils (Jiao et al., 2012). Nonetheless, it must be emphasized that the measured concentrations are generally low, especially for As, and can be considered as normal values for agricultural soils (Table 3).

#### 3.2.2. Natural influence

The second principal component (PC2) accounting for 31.3% of the total variability can be presumed to represent a lithogenic component as may also be inferred by the clustering of Ni, Cr, Co and Fe in group I of CA. The study area is mostly sited in an alluvial plain that has been supplied by parent materials from the surrounding mountains via weathering and pedogenic processes. The concentrations of these elements are not statistically different from the values determined in the benchmark soils suggesting their natural source. Such an interpretation is in line with repeated findings by various authors who demonstrated that loading's variability of Ni, Cr, Co and Fe in agricultural soils is controlled by bedrock influence (Micó et al., 2006; Nanos and Rodríguez Martín, 2012; Niu et al., 2013), whereas anthropogenic inputs of these metals in fertilizers are lower than concentrations already present in the soil (Sun et al., 2013). The obvious enrichment of Ni, Cr and Co in agricultural soils of Argolida in relation to other areas (Table 4) is ascribed to the presence of small serpentinitic bodies in the geological formations outcropping in the area in accordance to Facchinelli et al. (2001) who related Ni, Cr and Co amounts in agricultural fields from Piemonte (Italy) to occurrence of ultramafic rocks.

A peculiar behavior was revealed in the present study for Mn. Although it was included with slightly higher loadings on PC1, CA indicated that this metal is associated with the naturally derived elements. In fact, whenever quantified Mn has been proposed to be a lithogenic element in all studies investigating this metal in agricultural soils (Antibachi et al., 2012; Micó et al., 2006; Peris et al., 2008; Romic and Romic, 2003). However, the high loadings of this element observed in PC1 suggest that this metal probably has a mixed source, by both natural and anthropogenic sources. For example, Mn concentrations up to 205 mg/kg have been measured in pesticides applied to plots in Valencia (Gimeno-García et al., 1996) pointing out that the application of pesticides might have a major impact on the distribution of Mn in Argolida soils; on the other hand, Mn is known to exhibit large amounts in parent ultramafic rocks resulting to a geogenic enrichment in soils derived from the metal-rich bedrock (Kelepertzis et al., 2013).

**Table 4**
Matrix of principal component analysis for normalized elemental concentrations of agricultural soils in Argolida basin (significant loading factors are marked in bold).

| Element | Rotated component matrix | |
|---|---|---|
| | PC1 | PC2 |
| Cu | **0.749** | 0.003 |
| Pb | **0.825** | 0.218 |
| Zn | **0.869** | 0.228 |
| Ni | 0.031 | **0.944** |
| Co | 0.310 | **0.898** |
| Mn | 0.645 | 0.588 |
| Fe | 0.452 | **0.743** |
| As | **0.737** | 0.307 |
| Cd | **0.822** | 0.282 |
| P | **0.827** | 0.103 |
| Cr | 0.118 | **0.907** |
| K | **0.765** | 0.239 |
| Eigenvalue | 5.218 | 3.759 |
| % variance explained | 43.479 | 31.326 |
| Cumulative % variance | 43.479 | 74.806 |

### 3.3. Elemental spatial distribution patterns

The spatial distribution maps of the investigated metals in Argolida are shown in Figs. 5 and 6 and were used to identify metal-enriched areas. Class intervals were defined by quantiles of the original data set, and elemental concentrations were plotted as growing dots over the interpolated surfaces for better visual inspection of the spatial trends. The spatial patterns for Cu, Zn, Cd and Pb (Fig. 5) and As (not shown) were similar with the highest concentrations occurring in the west part of the area and coinciding with the area intensively cultivated for oranges and mandarins (Fig. 1). Some other hotspots, especially in the distribution map of Cu, are also located in the eastern direction and particularly in the orange trees surrounding Ligourio village indicating that the long-term application of Cu-based fungicides and pesticides and subsequent wash-off from the treated plants have resulted into extensive Cu accumulation in citrus soils from Argolida. The spatial trends for Cu, Zn, Cd and Pb reveal that the explanation for the high geochemical variability related to the anthropogenically introduced elements is most likely attributed to the land use. Soils cultivated for olive production do not show an enrichment with these elements. Spatial analysis enforces the interpretation of results by multivariate analysis demonstrating that the application of large quantities of agrochemicals during the last 50 years has contributed to metal accumulation in agricultural fields around Argos town.

Nickel, Cr and Co show similar distribution patterns at a regional scale. These metals do not follow any specific trend, and elevated levels of concentrations are observed in the east, central as well as the west

**Table 3**
Literature data on mean concentrations (mg/kg) of the common metals determined in agricultural soils of various areas around the world.

| Location | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | Cr | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Almería (Spain) | 25.7 | 25.6 | 65.7 | 26.9 | | | | 0.4 | 29.6 | Rodríguez Martín et al. (2013) |
| Alicante (Spain) | 22.5 | 22.8 | 52.8 | 20.9 | 7.1 | 295 | | 0.34 | 26.5 | Micó et al. (2006) |
| Murcia (Spain), medians | 11 | 48.9 | 18.4 | 13.5 | | 152 | | 0.22 | 17.6 | Acosta et al. (2011) |
| Ebro basin (Spain) | 17.33 | 17.54 | 57.53 | 20.5 | | | | 0.42 | 20.27 | Rodríguez Martín et al. (2006) |
| Castellón (Spain) | 36.6 | 55.8 | 78.5 | 19.3 | 7.7 | 385 | | 0.33 | 33.3 | Peris et al. (2008) |
| Piemonte (Italy) | 58.3 | 16.1 | 62.68 | 83.2 | 19 | | | | 46.16 | Facchinelli et al. (2001) |
| Duero basin (Spain) | 11.01 | 14.06 | 42.42 | 15.08 | | | | 0.159 | 20.53 | Nanos and Rodríguez Martín (2012) |
| Zagreb (Croatia) | 20.8 | 25.9 | 77.9 | 49.5 | | 613 | | 0.66 | | Romic and Romic (2003) |
| Shunyi (China) | 22.4 | 20.4 | 69.8 | | | | 7.85 | 0.136 | | Lu et al. (2012) |
| Dehui (China) | 18.9 | 35.4 | 58.9 | 20.8 | | | | | 49.7 | Sun et al. (2013) |
| Huizhou (China) | 16.74 | 44.66 | 57.21 | 14.89 | | | 10.19 | 0.10 | 27.61 | Cai et al. (2012) |
| Jiangsu (China) | 33.9 | 35.7 | 98.1 | 38.5 | | | 10.2 | 0.3 | 77.2 | Huang et al. (2007) |
| Thiva (Greece) | 32 | 24 | 67 | 1591 | 54 | 1010 | | | 277 | Antibachi et al. (2012) |
| Argolida basin (Greece) | 74.68 | 19.74 | 74.88 | 146.8 | 21.99 | 1020.5 | 6.95 | 0.54 | 83.12 | This study |

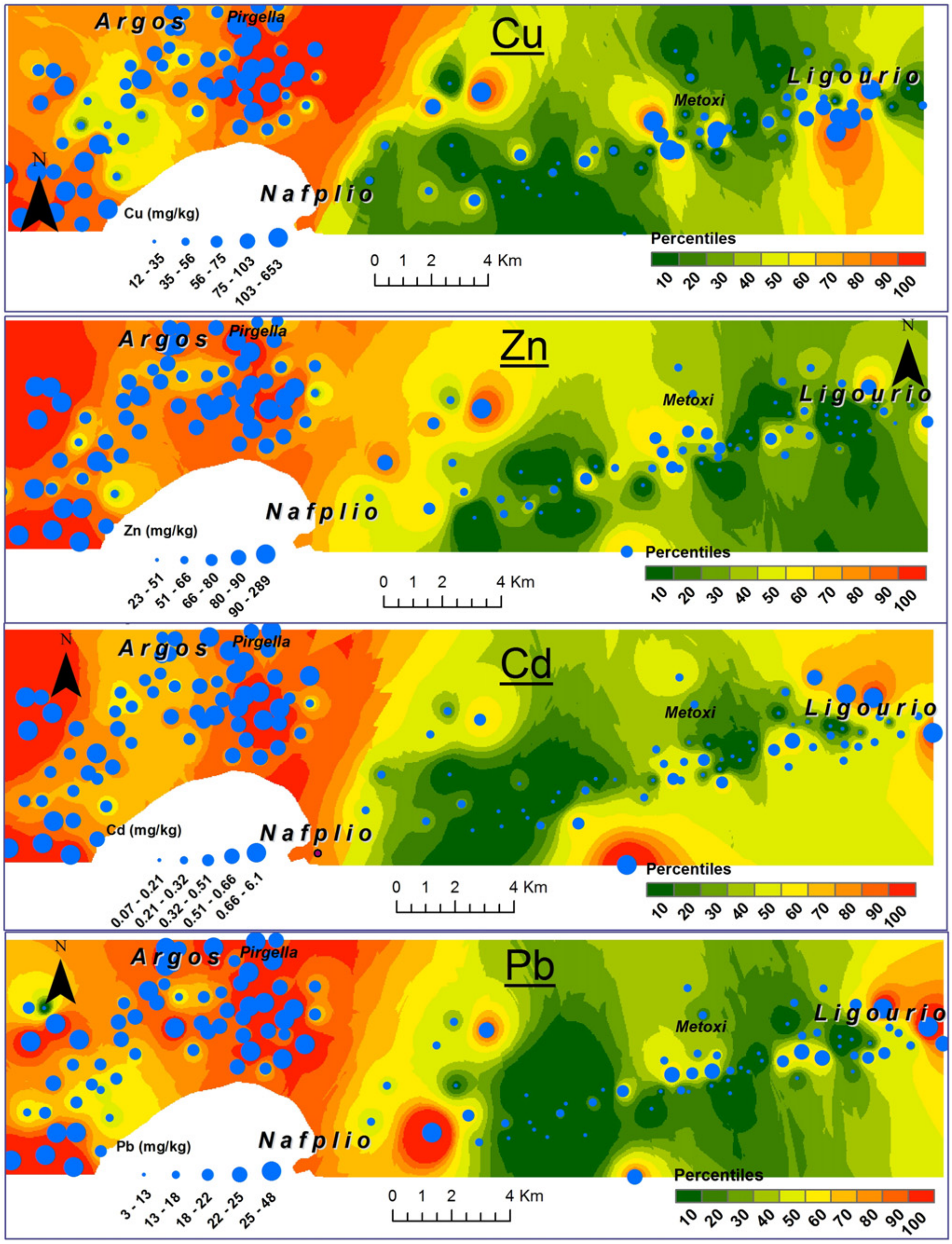


**Fig. 5.** Spatial distribution maps of Cu, Zn, Cd and Pb in agricultural soils from Argolida basin.

part of the basin. The variability of geochemical values of Ni, Cr and Co is indicative of the parent bedrock influence due to the presence of ultramafic materials composed of small serpentinitic bodies. This interpretation is in agreement with the elevated geochemical background of these elements observed over the whole country in the FOREGS Geochemical Atlas of Europe (Salminen et al., 2005) and the findings by numerous soil geochemical investigations that have been conducted in various areas from Greece (e.g. Antibachi et al., 2012; Kanellopoulos and Argyraki, 2013; Skordas and Kelepertsis, 2005). The large geochemical variability of Ni, Cr, Co and Mn can be explained by the abundance of the various mineral phases that host Ni and Cr within the soils and are capable to release their Ni and Cr content when attacked by the aqua regia mixture (Kelepertzis et al., 2013). Nevertheless, the spatial trends of Mn, a metal that is commonly associated with Ni, Cr and Co in these kinds of soils (Kaitantzian et al., 2013; Kelepertzis, 2014), are different and resemble that of the anthropogenic Cu, Zn, Cd and Pb. The highest Mn concentrations are plotted in the agricultural fields surrounding Argos town indicating its association with the intensive application of agrochemical products in the citrus soils and supporting its origin by both natural and anthropogenic sources.

## 4. Conclusions

This study was scheduled to delineate the accumulation and identify the sources of heavy metals in agricultural soils of Argolida, a representative agricultural area of the Mediterranean. Results highlight a clear impact of anthropogenic agents on abundances of specific metals (Cu, Zn, Cd, Pb, As) in agricultural soils due to many years of uncontrolled application rates of fertilizers and pesticides–fungicides. The inclusion of P and K levels allowed the confirmation of the anthropogenic origin for these metals. Although Ni, Cr and Co were present in large amounts in the studied soils compared to international guidelines and agricultural soils in China and Europe, multivariate analysis and comparison with benchmark

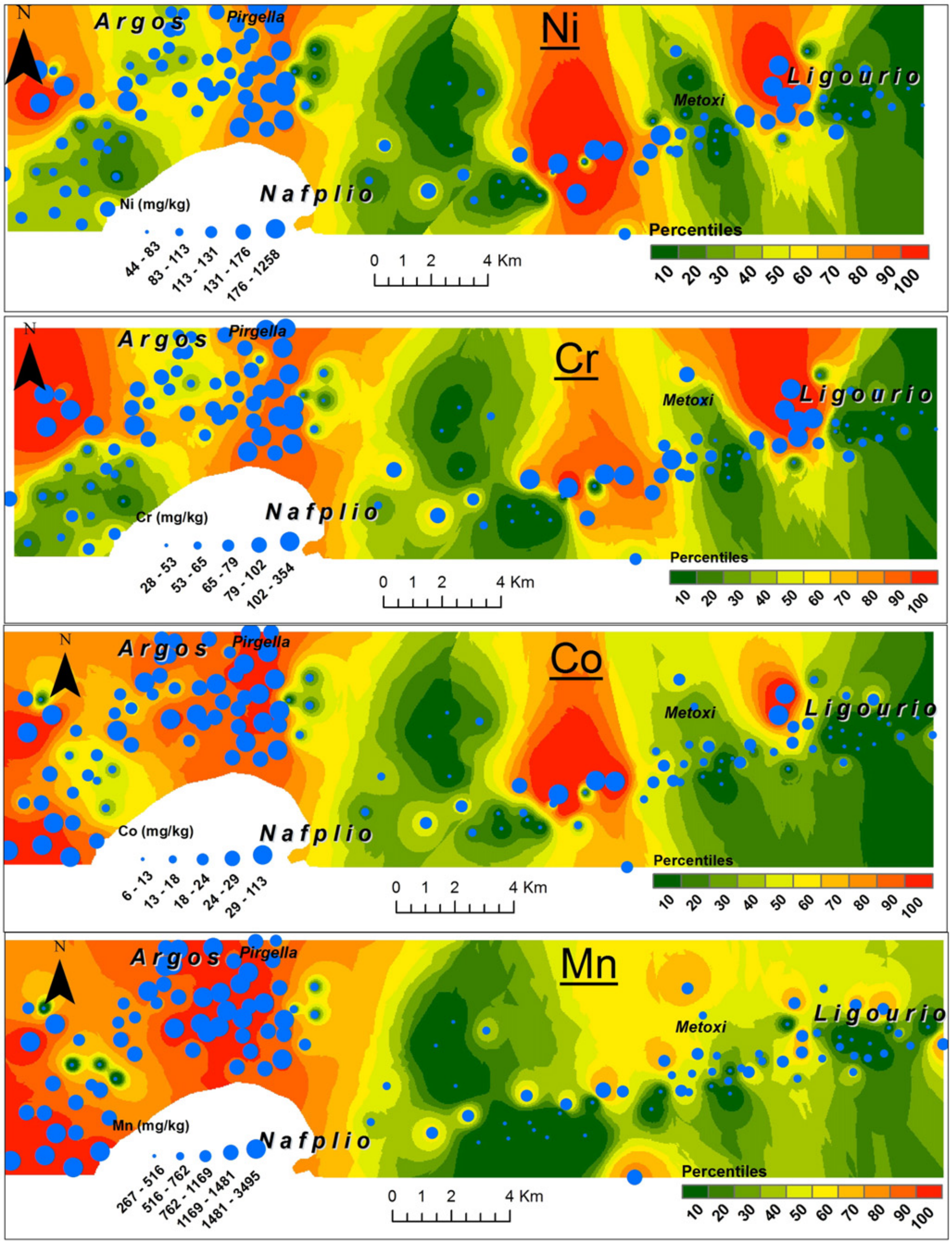


**Fig. 6.** Spatial distribution maps of Ni, Cr, Co and Mn in agricultural soils from Argolida basin.

soils indicated that geological parent materials govern their loadings. The only metal that was evaluated to exhibit a mixed source was Mn with both the application of agrochemicals and the small serpentinitic bodies controlling its accumulation patterns. The spatial distribution trends reveal that the high concentrations of Cu, Zn, Pb Cd and Mn are associated with the citrus soils cultivated for the production of oranges and mandarins. Elevated levels of concentrations of the naturally derived Ni, Cr and Co do not follow a specific pattern and are attributed to local abundance of mineral phases that host these metals. Results of this study provide land-managers with invaluable geochemical data for the current qualitative status of the studied agricultural soils that should be taken into consideration for monitoring heavy metals levels and reducing application rates of agrochemicals. Further investigations should pay attention to characterize the geochemical reactivity of both anthropogenic and geogenic metals in citrus soils by utilizing selective extraction procedures.

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