Insights into the chemical partitioning of trace metals in roadside and off-road agricultural soils along two major highways in Attica's region, Greece

Fotini Botsou [a], Ali Sungur [b], Efstratios Kelepertzis [c,*], Mustafa Soylak [d]

[a] Department of Chemistry, University of Athens, Panepistimiopolis, Zographou, 157 84 Athens, Greece
[b] Çanakkale Onsekiz Mart University, Faculty of Agriculture, Department of Soil Science and Plant Nutrition, 17000 Çanakkale, Turkey
[c] Department of Geology and Geoenvironment, University of Athens, Panepistimiopolis, Zographou, 157 84 Athens, Greece
[d] Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri, Turkey

ABSTRACT

We report in this study the magnetic properties and partitioning patterns of selected trace metals (Pb, Zn, Cu, Cd, Ni) in roadside and off-road (> 200 m distance from the road edge) agricultural soils collected along two major highways in Greece. Sequential extractions revealed that the examined trace metals for the entire data set were predominantly found in the residual fraction, averaging 37% for Cd up to 80% for Cu. Due to the strong influence of lithogenic factors, trace metal pseudototal contents of the roadside soils did not differ significantly to those of the off-road soils. Magnetic susceptibility and frequency dependent magnetic susceptibility determinations showed a magnetic enhancement of soils; however, it was primarily related to geogenic factors and not to traffic-derived magnetic particles. These results highlight that in areas characterized by strong geogenic backgrounds, neither pseudototal trace metal contents nor magnetic properties determinations effectively capture traffic-related contamination of topsoils. The vehicular emission signal was traced by the increased acid-soluble and reducible trace metal contents of the roadside soils compared to their off-road counterparts. In the case of Cu and Zn, changes in the partitioning patterns were also observed between the roadside and off-road soils. Environmental risks associated with agricultural lands extending at the margins of the studied highways may arise from the elevated Ni contents (both pseudototal and potentially mobile), and future studies should investigate Ni levels in the edible parts of plants grown on these agricultural soils.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Roadside soils are enriched in several classes of organic and inorganic contaminants, including trace metals (Sutherland and Tolosa, 2000). The sources of trace metals in these soils are related to road surfaces, vehicular traffic, as well as road traffic control and maintenance operations. In detail, these include: road surface wear, road paint degradation, vehicle wear of tires, body and brake linings, lubricating oils, corrosion of galvanized surfaces of crash barriers and road signs, as well as particulate emissions (Sutherland and Tolosa, 2000; Thorpe and Harrison, 2008; Werkenthin et al., 2014). Trace metals could be easily transported to the roadside environment through re-suspension and aeolian transport, surface runoff and spray water, and road drainage systems, leading to adverse effects on terrestrial and aquatic systems. There

is a general concession that these metals decrease in concentration with distance from the roadway (Werkenthin et al., 2014). The chemical form in which the metals in roadside soils occur, however, has not been investigated so far and consequently there is a gap of knowledge for their mobilization.

Large scale urbanization and outward growth of cities has resulted in the expansion of transport systems, assuring the continued need for transportation of people, natural resources and products. The heavy traffic and the fast movement of vehicles can produce a large amount of road-deposited particles contaminated with trace metals that are eventually incorporated in the roadside soil (Christoforidis and Stamatis, 2009; Huber et al., 2016; Nazzal et al., 2013). Agricultural lands extending at the margins of highways are not uncommon in modern sprawling cities (e.g. Morse et al., 2016; Ward, 1990). Trace metal contamination of agricultural soils is of great environmental concern because of the possible long-term phytotoxic effects and food chain contamination. Therefore, assessing the availability of trace metals relevant to plant uptake is essential for evaluating agricultural implications

and managing human health risks (Chen et al., 2016; Kelepertzis et al., 2015). Furthermore, health risks may arise to urban and suburban populations through respiration and inadvertent ingestion of contaminated dusts re-suspended by wind, or, street sweeping operations. The degradation of groundwater quality is another issue of concern when road runoff water percolates through the roadside soils, resulting to the dispersion and mobilization of contaminated soil particles (Huber et al., 2016; Werkenthin et al., 2014).

The potential mobility and ecotoxicity of trace metals are determined by their specific binding form and coupled reactivity, rather than by their total concentrations (Peijnenburg et al., 2007). This is particularly valid for anthropogenic metals, because large amounts of them are associated with less stable geochemical phases, with severe consequences regarding their availability to plant uptake and migration into groundwater aquifers. Furthermore, metal release-retention processes are largely controlled by the soil properties. Changes of the physical biogeochemical soil conditions, including leaching and ion exchange processes, changes of soil pH and redox potential, soil organic matter decomposition and microbial activity may have a profound effect on trace metals mobility, thus their bioavailability.

Sequential extractions, despite their limitations and experimental uncertainties reviewed by many authors (e.g. Bacon and Davidson, 2008; Tack and Verloo, 1995), are considered a powerful tool in assessing the strength of trace metals association with the solid phase and predicting their behavior and fate under changing environmental conditions. These methods are based on the rational use of a series of successive chemical treatments, each being more drastic, or of different nature from the other (Gleyzes et al., 2002). In general, the strength of the treatment increases through the steps of the procedure. Hence, the trace metals extracted early in the procedure are those most weakly bound to the solid phase, consequently, those with the greatest potential of mobility than those released later (Bacon and Davidson, 2008). Extraction steps also intend to simulate the modifications of environmental conditions that could affect metal-binding in the solid surfaces, such as acidification, reduction and oxidation (Bacon and Davidson, 2008; Gleyzes et al., 2002). Sequential extraction techniques have been applied in various environmental sampling media, such as in agricultural soil (examples given by Abollino et al., 2002; Sungur et al., 2015; Yang et al., 2013), mining soils (e.g. Li and Thornton, 2001), as well as roadside and industrially contaminated street dusts (Yildirim and Tokalioğlu, 2016).

Magnetic techniques have been successfully applied in urban environments to detect and spatially outline automobile-related, trace metal contamination of soils (e.g. Golden et al., 2015; Lu et al., 2011; Yang et al., 2010). The relationship between magnetic signals and trace metals contents is governed by two major principles: i) magnetic minerals and trace metals derive from a common process (e.g. combustion), and ii) magnetic minerals serve as the substrates for trace metals (deriving probably from a different source), through adsorption, complexation, and co-precipitation processes (Lu et al., 2011; Scoullos et al., 2014). The sources of magnetic minerals in road surfaces were investigated by Beckwith et al. (1986) and included corrosion of surface constructional materials, exhaust particulates, and corroded bodywork, with vehicular rust particulates (wheel hub particulates and corroded paintwork) contributing significantly to the overall magnetic signal.

Although traffic-related trace metal contamination of roadside soils is recognized as a major environmental problem and several studies have been conducted along European main roads and highways (e.g. Kluge and Wessolek, 2012; Pagotto et al., 2001; Ward et al., 1977; Ward, 1990), there are only few studies of roadside soils that included sequential extraction determinations

(Bäckström et al., 2004; Harrison et al., 1981; Norrström and Jacks, 1998). More importantly, peer-reviewed research on the speciation of trace metals associated to farming on marginal land adjacent to highways is limited (Bacon and Hewitt, 2005). From a human health risk perspective, a question is if there are differences in the chemical partitioning of metals between agricultural soils near to major highways, and agricultural soils away from the highways. The present study, by combining chemical analyses and magnetic techniques, was initiated to examine traffic-related pollution at the marginal agricultural soils along two major highways of the Metropolitan city of Athens in Greece. The specific objectives of the study are: (a) to investigate the potential of magnetic susceptibility measurements for detecting the roadside trace metal contamination in the studied agricultural soils, (b) to compare the levels and partitioning of trace metals into the major fractions of soil components at distances 0–10 m and > 200 m off the highways, c) to evaluate the potential risks arising from the agricultural activities of the roadside soils.

2. Materials and methods

2.1. Sampling and samples pre-treatment

Samples were collected from roadside and off-road agricultural soils located in ten sites in the vicinity of two major highways in Greece (Fig. 1). Five sites were selected from the National Road Athens-Lamia, which is the oldest and most important highway in Greece (this highway connects the country's largest cities, Athens and Thessaloniki). Another five sites were selected from the Attiki Odos highway, which forms part of the urban highway network of Athens metropolitan area, leading to the Athens International Airport. In both highways, the majority of cultivated plants were primarily vines, followed by olive trees, clover, vegetables and walnut trees. The Attiki Odos along with the Athens International Airport to which it connects opened in 2001. Anthropogenic enrichment for Pb (median value of 67 mg/kg) in agricultural soils surrounding the Athens International Airport was identified in the study of Kaitantzian et al. (2013). In each site, two soil samples were collected, the first at the closest vicinity to the road, at distances ranging from 2 to 10 m, (denoted as sample A), and the second one at a distance of approximately 200–400 m from point A at the perpendicular direction, which is denoted as sample B.

Soil sampling was conducted by using a plastic spade at a depth of 0–10 cm. At each site, three sub-samples were collected within an area of 4 m^2 and mixed to obtain a single composite sample of 1–1.5 kg. A total of 20 samples were collected and stored in plastic bags for transportation to the laboratory. Thereafter, the soil samples were air-dried 3 days and then gently disaggregated and sieved through a 2 mm sieve in order to remove granules, plant debris and litter. These sieved soil samples were used for the determination of soil pH, electrical conductivity and magnetic susceptibility, as well as texture analyses. All other analyses were conducted in representative sub-samples that were finely ground in a mortar and sieved to pass through a 0.5 mm sieve.

2.2. Reagents and apparatus

Reagents of analytical purity (Merck, Germany) and Deionized Distilled Water (DDW; 18.2 MΩ/cm resistivity) were used in the analytical procedures. Plastic and glassware were soaked in 1:1 (v/v) HNO$_3$: DDW for 24 h, then rinsed with 1% (v/v) HNO$_3$ and dried in an oven at 40 °C before use. Precautions were taken during all stages of analytical procedures in order to avoid contamination.
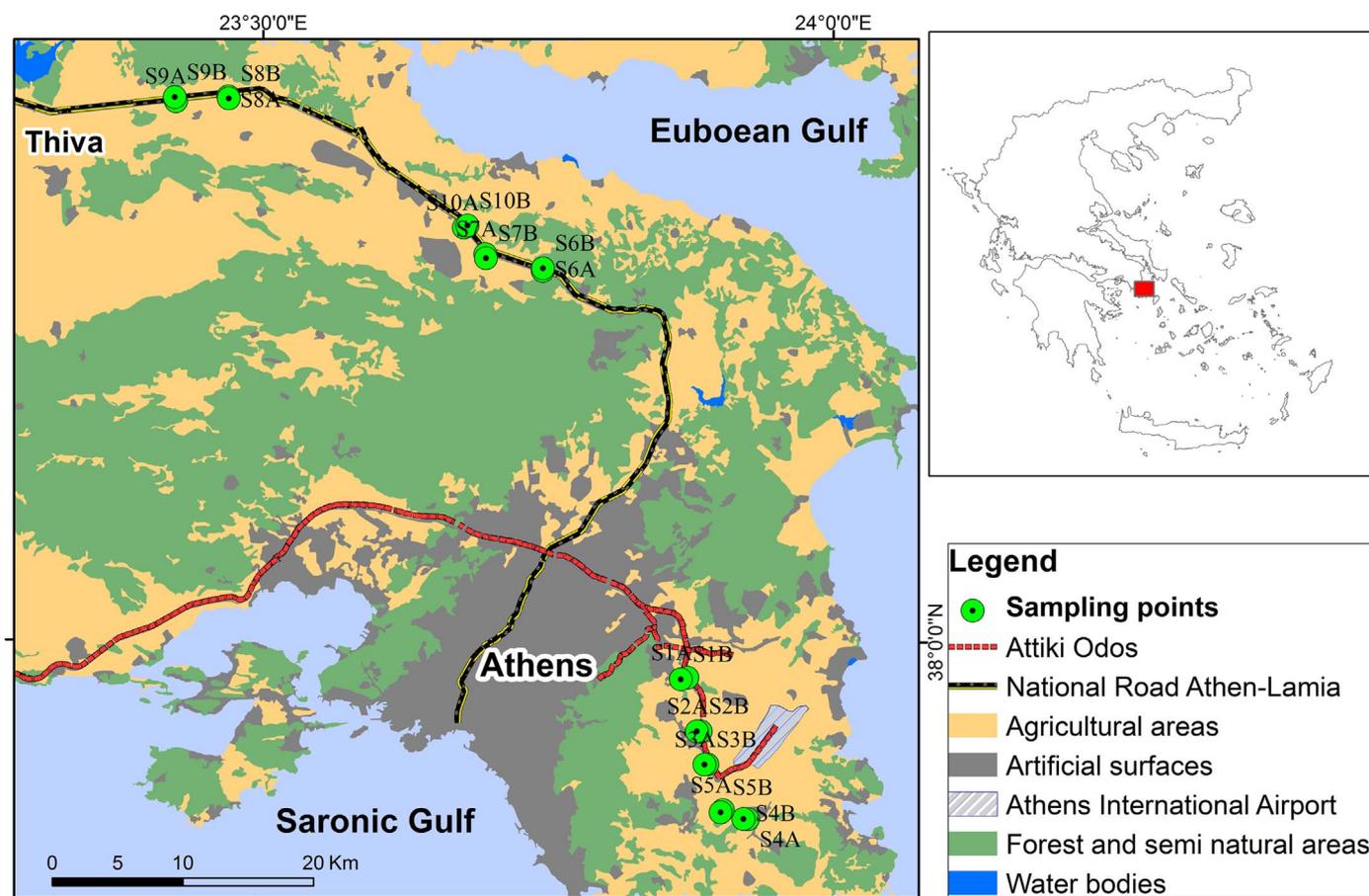
Fig. 1. Location map of the study area showing the land use according to the CORINE Land Cover (CLC) database (Heymann et al., 1994) and the sampling points (the code A corresponds to the roadside soils and the code B to the off-road soils).

In laboratory analyses, a Heidalph Model UNIMAX 2010 shaker, a Nüve Model NF 800 centrifuge and an inoLab Model WTW pH meter were used. Trace metals contents of soil samples were analyzed by an Analytic Jena Model novAA-350 flame atomic absorption spectrometer (FAAS), equipped with a hollow cathode lamp in an air-acetylene flame. Calibration standards were prepared by appropriate dilutions of single-element stock solutions (SCP SCIENCE, 1000 μg/mL, AA Standard).

2.3. Physicochemical and magnetic parameters of the soils

The soil pH and electrical conductivity (EC) were measured in 1:2.5 soil: water suspesions with a combination glass electrode and a conductivity meter, respectively. The soil texture was determined by the hydrometer method according to the principles specified in Bouyoucos (1962). Soil organic matter (SOM) content was determined by the dichromate oxidation procedure (Nelson and Sommers, 1982). Soil calcium carbonate ($CaCO_3$) contents were determined with a calcimeter by measuring the CO_2 volume after acidification of the soil sample (Nelson, 1982). Magnetic susceptibility was measured on 10 mL samples at low (0.47 kHz) and high (4.7 kHz) frequencies using a Bartington dual frequency MSB sensor. The results were expressed on a mass specific basis (χ 10^{-6} m^3 kg^{-1}), and as a percentage frequency dependent susceptibility ($\chi_{fd\%}$). Magnetic susceptibility (χ) is used as a proxy for the magnetic minerals concentration and is often equated to the concentration of ferrimagnetic minerals, such as magnetite. Frequency dependent susceptibility ($\chi_{fd\%}$) indicates the presence of ultrafine grains lying in the stable single domain/superparamagnetic boundary (Dearing et al., 1996; Thompson and Oldfield, 1986). Further details on magnetic measurements are given elsewhere (Scoullos et al., 2014).

2.4. Trace metal extraction, analysis and quality control

The pseudo-total trace metal contents of soil samples were determined by using the *aqua regia* digestion procedure. One gram of each sample was weighed into 100 mL beaker, 12 mL *aqua regia* (mixture of HNO_3:HCl in a ratio of 1:3) was added to the beaker and the sample was then evaporated close to dryness through gradually increasing the temperature. Then, 12 mL of *aqua regia* were added to the beakers and the evaporation process was repeated. The digests were filtered through a 0.45 μm filter and the final volume was adjusted to 15 mL. Certified reference material (NIM-GBW07425, soil) was used to test the accuracy of the wet digestion procedure and the obtained results are presented in Table 1. The recoveries of trace metals were found to be satisfactory, ranging between 92% and 106%.

Soil samples were subjected to the modified BCR (former European Community Bureau of Reference, now Standard Measurement and Testing) sequential extraction procedure in order to partition trace elements contents into four fractions: the acid soluble (F_1), reducible (F_2), oxidizable (F_3) and residual (F_4) fraction. Details on the BCR sequential extraction method can be found in previous studies (e.g., Rauret et al., 1999; Saracoglu et al., 2009; Sungur et al., 2014a). The Certified Reference Material (CRM: BCR-701, lake sediment) was used to test the accuracy of the procedure (Table 1). The obtained recoveries of trace metals contents of the CRM ranged for the acid soluble fraction between 89.6% and 95.6%, between 93.1% and 105% for the reducible fraction and between

Table 1

Quality control of the *aqua regia* and the BCR sequential extractions using Certified Reference Materials (Mean $\pm$ Standard deviation in mg/kg; $n=3$; R: recovery).

Metals	BCR 701 (Lake sediment)									NIM-GBW07425 (soil)		
	Acid soluble (F1)			Reducible (F2)			Oxidizable (F3)					
	Certified	Determined	R (%)	Certified	Determined	R (%)	Certified	Determined	R (%)	Certified	Determined	R (%)
Cd	7.34 ± 0.35	6.62 ± 0.42	90.2	3.77 ± 0.28	3.51 ± 0.26	93.1	0.27 ± 0.06	0.24 ± 0.09	90.4	0.13 ± 0.01	0.12 ± 0.03	92.3
Cu	49.3 ± 1.7	44.9 ± 3.1	91.1	124 ± 3	118 ± 4	95.2	55.2 ± 4.0	52.6 ± 4.8	95.3	21.4 ± 1.2	22.6 ± 3.6	105.6
Ni	15.4 ± 0.9	13.8 ± 1.2	89.6	26.6 ± 1.3	25.1 ± 2.2	94.4	15.3 ± 0.9	14.2 ± 1.4	92.8	25.4 ± 1.3	23.6 ± 3.2	92.9
Pb	3.18 ± 0.21	2.96 ± 0.32	93.1	126 ± 3	132 ± 6	104.8	9.3 ± 2.0	9.75 ± 1.34	104.8	24.7 ± 1.4	25.4 ± 3.8	102.8
Zn	205 ± 6	196 ± 9	95.6	114 ± 5	116 ± 5	101.8	45.7 ± 4.0	43.8 ± 5.5	95.8	65.0 ± 5.0	62.3 ± 7.2	95.8

90.4% and 105% for the oxidizable fraction.

Additionally, the accuracy was tested by comparing trace metals contents obtained by the sequential extraction procedure (sum of the four fractions) to that of the *aqua regia* digestion (Eq. (1)):

$$\text{Recovery}(\%) = \left(\frac{F_1 + F_2 + F_3 + F_4}{Pseudo - total} \right) \times 100 \tag{1}$$

The recoveries of the sequential extraction procedure in relation to *aqua regia* were satisfactory and ranged between 90 and 115% for Cd, 92 and 116% for Cu, 88 and 115% for Ni, 89 and 110% for Pb and 86 and 110% for Zn.

2.5. Risk assessment code

The risk assessment code (RAC) is an index, originally introduced by Perin et al. (1985), to assess the availability of metals in sediments or soils (e.g. Li et al., 2013; Sungur et al., 2014b) by applying a scale to the percentages of metals in the more labile fractions, i.e. the exchangeable and carbonate bound fractions, following the so-called Tessier's protocol, which broadly corresponds to the acid soluble fraction of the BCR procedure (Li et al., 2013; Sutherland and Tack, 2000;). According to the RAC guidelines, the soils with $<1\%$ acid soluble fraction within the total metals are considered as non-risky for the environment; 1–10% indicate low risk; 11–30% medium risk; 31–50% high risk and over 50% indicate extreme risk for environment. The RAC index was calculated as:

$$\text{RAC}(\%) = \left(\frac{F_1}{F_1 + F_2 + F_3 + F_4} \right) \times 100 \tag{2}$$

2.6. Statistical analysis

Statistical analysis was performed by the SPSS v.22 software. Paired-*t* test was used to compare the mean of the paired differences of each variable between roadside and off-road soil samples. Before running the test, data were screened for their normal distribution by the Kolmogorov-Smirnov test and the variables that departed from normality were log transformed.

3. Results and discussion

3.1. Geochemical characteristics of soils

The descriptive statistics of the physicochemical and magnetic properties, as well as the *aqua regia* extractable trace metals contents of the studied soil samples are summarized in Table 2. The soils had loam, clay loam, sandy loam, and sandy clay loam textures. Both subsets of soils had neutral to slightly alkaline pH values varying between 7.20 and 7.72, with mean values of 7.54 for

Table 2

Descriptive statistics of soil properties, magnetic measurements (magnetic susceptibility χ and percentage of frequency dependent magnetic susceptibility $\chi_{fd\%}$) and pseudototal trace metals contents in roadside and off-road soils.

	Roadside soils ($n=10$)		Off-road soils ($n=10$)	
	Range	Mean $\pm$ SD[a]	Range	Mean $\pm$ SD
Soil properties				
pH	7.20–7.72	7.54 ± 0.17	7.23–8.10	7.51 ± 0.29
EC (μS/cm)	122–264	177 ± 42.9	73.8–917	282 ± 244
SOM (%)	0.95–2.28	1.57 ± 0.42	0.64–3.09	1.85 ± 0.86
CaCO$_3$ (%)	0–39.1	20.3 ± 12.0	6.80–45.8	27.5 ± 15.1
Clay (%)	17.8–44.4	28.3 ± 9.26	15.5–38.2	23.8 ± 7.21
Silt (%)	16.5–26.8	21.2 ± 3.37	16.5–35.1	24.7 ± 6.30
Sand (%)	30.9–63.9	50.5 ± 10.2	37.1–63.9	51.5 ± 11.0
Magnetic parameters				
χ (10^{-6} m^3 kg^{-1})	0.92–5.69	1.92 ± 1.37	0.39–5.20	1.60 ± 1.35
$\chi_{fd\%}$	3.25–9.30	6.94 ± 1.98	0.16–9.50	6.12 ± 3.03
Trace metals contents (mg/kg)				
Cd	0.98–1.94	1.33 ± 0.35	0.82–1.91	1.42 ± 0.34
Cu	23.3–48.0	30.8 ± 7.47	14.5–41.3	26.8 ± 7.38
Ni	90.6–620	247 ± 169	106–656	246 ± 167
Pb	16.7–169	44.8 ± 44.5	14.1–56.5	31.1 ± 13.6
Zn	51.3–169	81.6 ± 36.3	29.2–166	71.0 ± 39.0

[a] Standard deviation.

roadside samples and 7.51 for off-road samples; such pH values are due to the presence of carbonates, averaging $20.3 \pm 12.0\%$ and $27.5 \pm 15.1\%$ in the roadside and off-road soils, respectively. The relatively high carbonates contents are related to carbonates rocks surrounding Attica's region. Mean values (± 1 standard deviation) of EC were 177 ± 43 μS/cm and 282 ± 244 μS/cm in the roadside and off-road soils, respectively, indicating a high variability in the off-road soils and the possible influence of agricultural activities. Soil organic matter (SOM) contents varied between 0.95 and 2.28% with a mean value of 1.57% in roadside samples, and between 0.64 and 3.09% with a mean value of 1.85% in off-road samples, indicating relatively low organic matter contents at both subsets.

The mean values of trace metals contents of roadside (samples A) and off-road (samples B) soils followed the same decreasing order: $\text{Ni} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$. Nickel contents always exceeded the world's average value of 29 mg/kg, (i.e. the mean value derived from recent surveys of soils throughout the world, which may serve, at least to some extent, as background values of uncontaminated soils; Kabata-Pendias, 2011). However, the levels of Ni should be ascribed to geogenic sources and not to anthropogenic contamination. Such an interpretation is in line with several previous studies reporting that the elevated Ni contents of topsoils in the Attica's region are related to the occurrence of serpentinized members of ophiolithic sequences (Argyraki and Kelepertzis, 2014; Kaitantzian et al., 2013), known to contain increased Ni amounts (Kabata-Pendias, 2011). Considering Pb, in 60%

of the roadside soils and 50% of the off-road samples the levels were above the world's average value of 27 mg/kg estimated for different soils (Kabata-Pendias, 2011), and in most cases the levels were higher than the median value reported for agricultural soils in the European continent which is 15.7 mg/kg (Reimann et al., 2013). The levels of Zn were above the world average value of 62 mg/kg (Alloway, 2013) in 50% of sample site in each subset of data.

With regard to Cu, because of the historical long-term use of this metal, direct measurements of real natural background contents are not feasible in many parts of the world. Average ambient background Cu contents of European soils away from point contamination sources vary from 11.4 mg/kg for forest soils (low anthropogenic pressure) to 15.4 and 17.0 mg/kg for agricultural and grassland soils, respectively (Oorts, 2013). With one exception in the off-road subset of samples, Cu levels were above the aforementioned background values for agricultural soils. According to the paired t-test, only Cu exhibited a statistically significant difference ($p=0.017$) between the two sub-sets, with the roadside soils being enriched compared to the off-road soils. Finally, as far as Cd is concerned, soil contents are typically found in the 0.1–1.0 mg/kg range (Smolders and Mertens, 2013). In uncontaminated soils, its contents are highly governed by soil texture and range from 0.01 to 0.3 mg/kg in sandy soils and from 0.2 to 0.8 mg/kg in loamy soils (Kabata-Pendias, 2011), because Cd shows a preference for the finer particles (Smolders and Mertens, 2013). In all of the samples examined in this study, Cd contents were equal or higher than 0.8 mg/kg, indicating anthropogenic inputs.

3.2. Mineral magnetic measurements

Magnetic susceptibility of the roadside soils ranged from 0.92 to 5.69×10^{-6} m^3 kg^{-1} and had a mean (± 1 sd) value of $1.92 \pm 1.37 \times 10^{-6}$ m^3 kg^{-1}. These values showed relatively high concentrations of ferrimagnetic minerals, i.e. magnetite and maghemite, and were within the ranges reported for highway environments (0.40–11.66×10^{-6} m^3 kg^{-1}) as reviewed by Blundell et al. (2009). However, prior to the source apportionment of the enhanced magnetic signal to automobile derived particulates, the geogenic magnetic component should be examined first. Off-road topsoils had similarly elevated χ values (range: 0.39–5.01×10^{-6} m^3 kg^{-1}; mean ± 1 sd: $1.60 \pm 1.35 \times 10^{-6}$ m^3 kg^{-1}). Vehicular derived magnetic particles are unlikely to disperse far from source (Blundell et al., 2009; Hoffmann et al., 1999), thus, traffic related sources could not solely account for the overall enhancement of χ. In both sub-sets of the soil samples, the maximum χ values were determined at station 8 (Fig. 1) and should be attributed to the local lithology, characterized by exposures of igneous ultrabasic rocks (Kelepertzis et al., 2013) which were previously found to be responsible for a significant contribution to the lithogenic magnetic minerals assemblage (Botsou et al., 2011). Since serpentinized blocks exposures are common in the Attica's region (Argyraki and Kelepertzis, 2014), it is expected that parent rocks contribute, to a certain degree, to the magnetic enhancement of the entire data set.

Furthermore, frequency dependent susceptibility ($\chi_{fd\%}$) ranged from 3.3 to 9.3% in the roadside soils, with a mean value ($\pm$ 1sd) of $6.9 \pm 2.0\%$, and from 0.2 to 9.5% (mean: $6.1 \pm 3.0\%$) in the off-road soils, indicating the presence of superparamagnetic (SP) grains at both subsets. Increased $\chi_{fd\%}$ values are often associated with natural soil forming processes (Blundell et al., 2009; Dearing et al., 1996), whereas vehicular derived particulates are coarser grained of single domain (SD) and multi-domain (MD) state (Lu et al., 2011; Yang et al., 2010). The soil samples with maximum χ had $\chi_{fd\%}$ below 4.6%, indicating the contribution of SD and MD ferrimagnetic grains.

Hoffmann et al. (1999) showed that highway dusts in Tübingen, Germany were magnetically enhanced within a distance of 2–3 m from the edge of the asphalt surface; magnetic susceptibility exhibited maxima directly on the edge of the asphalt surface, and exponentially decreased with distance until the background value was reached at distances of more than 5 m from the asphalt edge. Magnetic measurements of the present study suggest that at distances 2–10 m off the road edge, the lithogenic and pedogenic component of the magnetic assemblage is too strong and eventually is masking the pollution record. In all previous studies in which magnetic techniques had successfully detected automobile derived pollution (Beckwith et al., 1986; Hoffmann et al., 1999; Lu et al., 2011), the geogenic magnetic signal was low.

3.3. Partitioning of trace metals in the soil fractions

3.3.1. General patterns

The partitioning of trace metals in the soil fractions of the agricultural soils examined in this study are given in Table 3 and graphically illustrated in Fig. 2. In both the roadside and off-road soils, all of the studied trace metals were predominantly found in the residual fraction. This partitioning pattern suggests that a significant fraction of metals, ranging on average from 37% (Cd) to 80% (Cu), is relatively immobile under normal environmental conditions. The residual fractions of all the metals studied did not differ significantly between the roadside and off-road soils (Fig. 3), implying that this fraction is primarily of lithogenic origin. This lack of statistically significant difference between the two subsets of data, combined with the strong dependence of trace metals contents on the geological substrate, is in line with the results of magnetic measurements and explains why total metals contents failed to identify the traffic-related pollution signal in the roadside soils.

Considering the non-residual fractions, Cd and Zn were predominantly found in the acid soluble fraction (F1), averaging $28 \pm 3\%$ and $14 \pm 7\%$ of total contents, respectively, Pb was associated with the reducible fraction which comprised $24 \pm 5\%$ of total Pb, whereas Ni and Cu were associated mainly with the oxidizable fraction, accounting on average $10 \pm 5\%$ and $8 \pm 3\%$ of total contents, respectively. The potentially mobile fractions are usually composed of the initial three fractions (acid soluble+reducible+oxidizable). Thus, the potential mobility of trace metals can be expressed as the sum of the extraction yields of the first three fractions in relation to total contents. In the roadside soils the potential mobility decreased in the order: Cd (64%) > Pb (58%) > Zn (46%) > Ni (28%) > Cu (22%), whereas in the off-road soils followed the order: Cd (54%) > Pb (51%) > Zn (34%) > Cu (18%) ≈ Ni (17%). In contrast to the residual fractions of metals, the potentially mobile fractions exhibited statistically significant differences between the roadside and off-road soils, and higher contents of trace metals (except for Cd) were determined in the soils close to the road surfaces than in their off-road counterparts (Fig. 3). This finding suggests that in areas where geogenic factors contribute significantly to the total trace metals contents, sequential extraction procedures may prove beneficiary in detecting and spatially outlining pollution signals.

3.3.2. Insights in the partitioning of trace metals into non-residual fractions in roadside and off-road soils

Paired-t test was applied to compare levels of trace metals extracted in each of the non-residual fractions between the roadside and off-road soils (Fig. 3). In both sub-sets of soils, Cd contents decreased in the order: acid soluble > reducible > oxidizable fraction. Of all the metals examined in this study, Cd was the only metal for which none of the non-residual fractions differed between the roadside and off-road topsoils. Although this element is often reported to derive from vehicular emissions, such as brake linings and tyre wear (Nazzal et al., 2013; Pagotto et al., 2001; Thorpe and

Table 3
Partitioning of trace metals into soil fractions after the BCR sequential extraction procedure in the roadside (A) and off-road (B) soils (Mean ± SD[a] in mg/kg; n=10).

Element-Samples	Fractions										Sum
	Acid soluble (F1)		Reducible (F2)		Oxidizable (F3)		Residual (F4)				Σ (F1+F2+F3+F4)
	Mean ± SD	% Ratio	Mean ± SD	% Ratio	Mean ± SD	% Ratio	Mean ± SD	% Ratio			Mean ± SD
Cd-A	0.41 ± 0.12	29.1	0.35 ± 0.15	24.6	0.15 ± 0.06	10.5	0.50 ± 0.11	35.8			1.41 ± 0.33
Cd-B	0.43 ± 0.09	28.5	0.34 ± 0.09	22.7	0.17 ± 0.05	11.0	0.57 ± 0.13	37.8			1.50 ± 0.30
Cu-A	2.40 ± 0.77	7.6	1.92 ± 0.79	6.1	2.54 ± 1.66	8.1	24.6 ± 5.54	78.2			31.5 ± 7.99
Cu-B	1.52 ± 0.50	5.3	1.15 ± 0.36	4.0	2.37 ± 1.09	8.3	23.5 ± 6.35	82.3			28.6 ± 7.53
Ni-A	9.71 ± 4.54	4.0	24.9 ± 18.0	10.4	32.4 ± 29.0	13.5	173 ± 112	72.1			240 ± 159
Ni-B	6.71 ± 2.33	2.8	13.3 ± 9.78	5.5	21.2 ± 15.6	8.8	200 ± 139	82.9			241 ± 151
Pb-A	5.09 ± 3.44	11.4	11.6 ± 7.17	25.9	9.17 ± 13.66	20.5	18.9 ± 17.2	42.2			44.7 ± 40.9
Pb-B	3.30 ± 1.44	10.9	6.75 ± 2.49	22.2	5.30 ± 2.44	17.4	15.0 ± 6.11	49.5			30.4 ± 11.7
Zn-A	14.4 ± 10.3	17.6	11.2 ± 5.99	13.6	11.8 ± 9.96	14.4	44.5 ± 14.1	54.4			81.9 ± 36.3
Zn-B	8.36 ± 7.91	12.3	6.50 ± 4.31	9.6	8.18 ± 4.31	12.1	44.7 ± 17.5	66.0			67.8 ± 31.3

[a] Standard deviation.
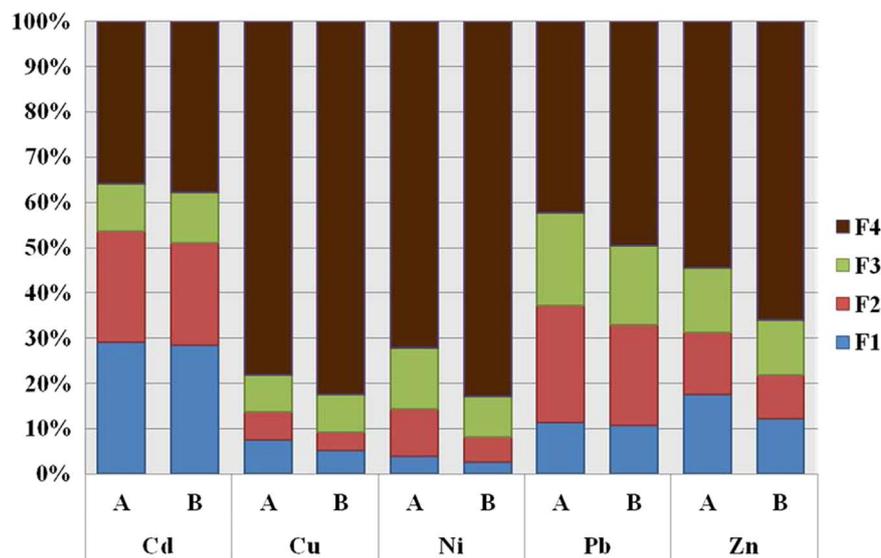
Fig. 2. Relative abundances of trace metals in the acid soluble (F1), reducible (F2), oxidizable (F3) and residual (F4) fractions following the modified BCR sequential extraction procedure of roadside (A) and off-road (B) agricultural soils.

Harisson, 2008), the lack of any significant decline of its contents with increasing distance from the road edges, even at distances of 200–400 m from the highways, indicates that in the study area Cd sources are probably related to agricultural practices. The main source of Cd in agricultural soils is the use of phosphate fertilizers, deriving from phosphate rocks, naturally enriched in Cd (Kelepertzis, 2014).

Copper in the roadside soils was equally distributed between the acid soluble and the oxidizable fraction, while in the off-road samples the oxidizable fraction clearly predominated over the acid soluble fraction (Fig. 2). The reducible fraction was of minor importance in both subsets. The acid soluble and the reducible fractions were higher in the roadside soils compared to the off-road soils (Fig. 3), whereas equal amounts of oxidizable Cu were determined in both subsets of soil samples, hence traffic related pollution appears to contribute to the acid soluble and reducible fractions. This is consistent with the findings of Hjortenkrans et al. (2008) and Bäckström et al. (2004) who reported the abundance of the acid soluble Cu in roadside soils, and Pérez et al. (2008) who showed a traffic related enrichment of soils in reducible Cu. Common sources of Cu in road surfaces include brake lining (Thorpe and Harrison, 2008), as well as corroded bodywork (Divrikli et al., 2003; Soylak et al., 2001). Sansalone and

Buchberger (1997) investigated the partitioning of metals in storm water related to highway runoff and found that Cu was predominant in the dissolved phase. Under neutral to alkaline pH values of the investigated soils, the adsorption of Cu into the solid surfaces is favorable.

Nickel is widely used in chrome plating and in highway environments derives mainly from mechanical wear and tear of bodywork and road traffic control devices (Akhter and Madany, 1993; Pérez et al., 2008; Soylak et al., 2001; Ward, 1990; Ward et al., 1977). In both subsets of soil samples the oxidizable fraction was the most abundant one, followed by the reducible and the acid soluble fractions. Significant differences between the roadside and off-road soils were observed for the acid soluble and reducible fractions of Ni, whereas, they were not detected for the oxidizable fraction (Fig. 3). Thus, it can be assumed that, as in the case of Cu, traffic pollution in the roadside soils is mainly reflected by the acid soluble and the reducible fractions.

Vehicular emissions are widely recognized as the major contributor of Pb loadings in roadside soils (Soylak et al., 2000; Turkoglu et al., 2003). After the ban on the use of Pb as a fuel additive in gasoline, the main sources of Pb in highway surfaces are brake linings (Thorpe and Harrison 2008), as well as soil erosion and transport of Pb enriched particles remaining from the leaded
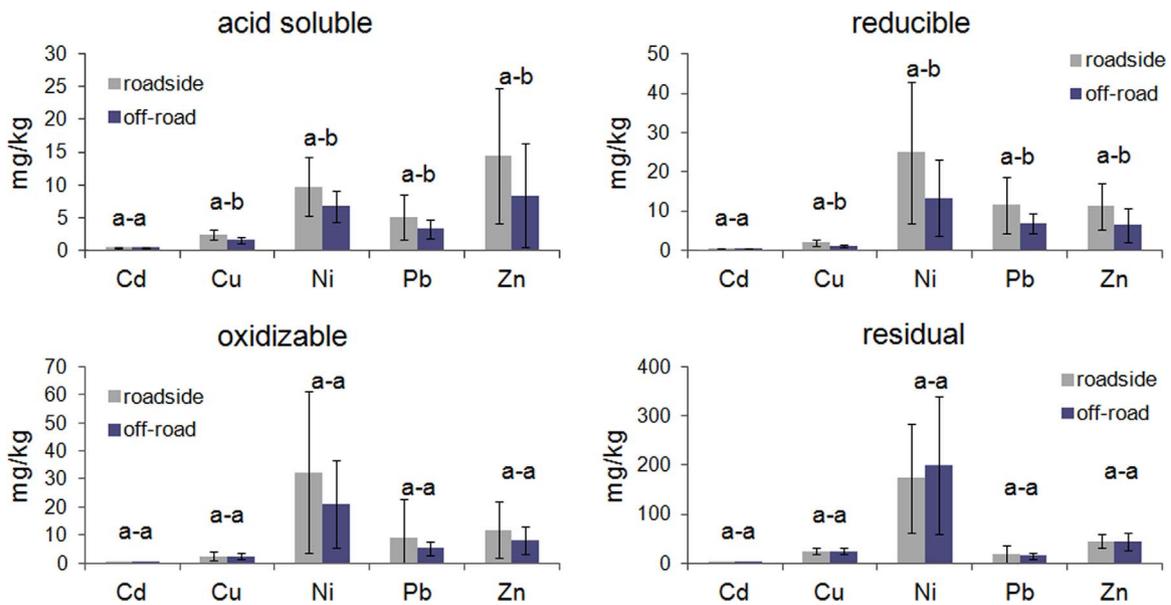
Fig. 3. Mean trace metals contents into acid soluble, reducible, oxidizable and residual soil fractions. Bars represent ± 1 standard deviation. Letters mark the statistically significant differences at the 0.05 level according to the paired *t*-test after log transformation of data.

gasoline era (Kelepertzis et al., 2016; Sutherland and Tolosa, 2000). Although Pb contents followed the phase ordering: reducible > oxidizable > acid soluble in both roadside and off-road soils, the levels of the reducible as well as the acid soluble contents were statistically significant higher in the former than in the latter (Fig. 3). A large number of previously published studies have reported the dominance of the reducible fraction, commonly associated with the Fe and Mn oxyhydroxides, in sequestering significant amounts of Pb (examples given by Hjortenkrans et al., 2008; Norrström and Jacks, 1998; Sutherland and Tolosa, 2000). In addition to the reducible fraction, the acid soluble fraction, probably corresponding to carbonates bound Pb, has been recognized as the second important phase for lead in highway environments (Harrison et al., 1981; Norrström and Jacks, 1998; Pagotto et al., 2001). The oxidizable fraction of Pb did not differ significantly between the two sub-sets, indicating that this fraction represents a stable sink for Pb.

Several sources of Zn are reported in road surfaces including tyre wear, brake linings, lubricating oil leaks, and galvanized crash barriers and road signs (Akhter and Madany, 1993; Nazzal et al., 2013; Soylak and Türkoglu, 1999; Thorpe and Harrison, 2008). The fractions ordering, in terms of Zn contents, differed between the roadside and off-road soils, and was acid soluble > reducible > oxidizable in the former, and oxidizable > acid soluble > reducible in the latter. The importance of the acid soluble fraction for Zn has been previously highlighted by Hjortenkrans et al. (2008) and Pérez et al. (2008). Similar to the other metals studied, Zn contents of the acid soluble and reducible fractions were statistically significant higher in the roadside soils compared to the off-road soils, whereas no differences were detected for the oxidizable fraction (Fig. 3). These findings indicate that traffic related pollution is primarily reflected in the more labile fractions of Zn, i.e. the acid soluble and the reducible one.

Summarizing the results presented in this section, it can be stated that the levels, as well as the differences of the partitioning schemes into the soil components effectively captured the traffic-related pollution signal in roadside soils. Of the non-residual fractions, the more mobile ones, i.e. the acid soluble and the reducible fractions, proved to be the best indicators of traffic pollution. On the contrary, similar amounts of trace metals were extracted in the oxidizable fraction of roadside and off-road soils, implying that this fraction comprised a stable sink of metals,

irrespective of their origin. Metal inputs in the soils, deriving either from anthropogenic activities or natural sources lead progressively to more stable forms of metals in the soils, and under no further metal additions, the partitioning scheme is expected to follow the order: acid soluble < reducible < oxidizable < residual (Gasparatos et al., 2015 and references therein). Thus, of the potentially mobile fractions, the oxidizable can be considered as an effective sink for trace metals. Either originally bound to organic matter or accumulated in this fraction as a result of aging effects, trace metals extracted in the oxidizable fraction are expected to be relatively stable due to the strong complexing capacity of organic matter. This is true, even in the off-road agricultural soils, where trace metals may derive from agricultural practices, or other sources. Long-term accumulation in the oxidizable fraction could thus hinder contemporaneous vehicular derived inputs of trace metals.

3.4. Risk assessment and implications on agricultural lands

Since the land adjacent to the highways is used for agriculture, the presence and potential mobility of trace metals in the soil causes environmental concerns of possible phytotoxic effects and human health risks associated with food chain contamination. The ranges of RAC values of Cd, Zn, and Pb were 24–34%, 10–23%, and 8–17%, respectively, implying that medium risks for the environment could emerge after solubilization of trace metals and subsequent plant uptake, or downward movement to groundwater (Gasparatos et al., 2015). Copper and Ni levels were below 11%, indicating low risks associated with these metals. Theoretically, the acid soluble fraction could be mobilized in response to acidification of soils, due for example to acid rain events or accidental acidic spillages (Bacon and Davidson, 2008). The actual mobility, however, will depend on soils composition and its buffer capacity to neutralize induced acidity. Under the slightly alkaline pH and the relatively high carbonates contents of the studied soils, the retention of metals in the solid surfaces is favorable, unless in the case of extreme acidification events.

The reducible fraction of metals is susceptible to mobilization if the redox potential decreases, e.g. in response to long rain periods and flooding (Hjortenkrans et al., 2008). In agricultural soils reducing conditions may be also encountered as a result of

irrigation. On the basis of the relative abundance of trace metals in this fraction, those having the highest potential to mobilization are Pb, and to a lesser extent Cd, Ni, and Zn. Finally, prolonged dry conditions combined with wind could result in the mobilization of trace metals bound to the oxidizable fraction (Hjortenkrans et al., 2008), primarily affecting Ni, Cu and to a lesser extent Pb. In agricultural soils, the oxidation of organic matter, resulting in the release of co-bounded metals, will be counterbalanced by new additions of organic matter through the application of organic fertilizers (Yang et al., 2013). Therefore, it is expected that oxidation processes will have a minimal long-term influence on the mobility of trace metals.

The data obtained in this study were compared against three sets of trace metals limits that have been established or proposed for soils for the protection of biota and human health (Table 4). The first set comprised the Ecological Soil Screening Levels (Eco-SSLs), introduced by the USEPA to provide adequate protection for ecological receptors, including plants, and to identify contaminants of potential concern that require further evaluation in a site-specific ecological risk assessment. The second set included the limits incorporated in the EU Council Directive 86/278/EEC, which concerns the protection of the environment and in particular of the soil with a pH value between 6 and 7 when sewage sludge is used in agriculture. The last set involved the Canadian quality guidelines for agricultural soils (CCME, 2007). Cadmium and Cu levels determined in this study were in most cases below the respective Eco-SSLs and the values of the EU Directive, as well as the Canadian soil quality limits indicating very low concern for the agricultural crops. Lead and Zn levels were lower than the Eco-SSLs, in the majority of samples. These metals were also lower than the upper limits of the EU's Directive and the Canadian values (except for Pb in one site). On the contrary, Ni exceeded the Eco-SSL (38 mg/kg), as well as the upper limit of EU Directive (75 mg/kg) and the recommended value of 50 mg/kg of the Canadian agricultural soil contamination guideline. Nickel exceedances were observed not only for the pseudototal contents in the soils, but for the potential mobile fractions (sum of acid soluble, reducible and oxidizable fractions) too, inferring the need for detailed, site-specific plant uptake bioassays. At this point, it should be emphasized that the application of RAC gave contradictory results in relation to the comparison of trace metal contents against quality limits for agricultural soils. In particular, Ni is not considered to trigger environmental risks according to the RAC; however, Ni levels (both pseudototal and potentially mobile) were higher than agricultural soil quality limits, indicating that considerations with regard to environmental risks arising from elevated Ni contents of agricultural soils should be based on the absolute and not the relative

Table 4
Trace metals limits (mg/kg) for agricultural soils.

	Eco-SSLs[a]	86/278/EEC[b]	CCME, 2007[c]
Cd	32[d]	1–3	1.4
Cu	70[e]	50–140	63
Ni	38[f]	30–75	50
Pb	120[g]	50–300	70
Zn	160[h]	150–300	200

[a] USEPA Ecological Soil Screening targeting the protection of plants.
[b] (EU, 1986).
[c] Canadian soil quality guidelines for the Protection of the Environment and Health.
[d] (USEPA, 2005a).
[e] (USEPA, 2006).
[f] (USEPA, 2007).
[g] (USEPA, 2005b).
[h] (USEPA, 2005c).

amounts.

Nickel uptake by plants has been found to be positively correlated with Ni concentrations in solution (Kabata-Pendias, 2011). Furthermore, the metal's origin also plays a significant role in its availability to plants. For example, it has been reported that Ni uptake by cereals is much higher when the metal has been added in the soil than from its lithogenic source (Kabata-Pendias, 2011 and references therein). Acidification of soils would decrease Ni adsorption by soil components and thus increase its plant availability. However, the mobility of Ni drastically decreases at pH values above 6.5, thus at the alkaline, calcareous soils of this study is expected to be limited. Phytotoxic concentrations range widely among plant species and generally are reported to be from 40 to 246 mg/kg (Kabata-Pendias, 2011). In this study, the most frequently encountered plantation was vineyards. Licina et al. (2010) studied the accumulation of Ni in several organs of grapevines grown on serpentinized alkaline soils. Although the authors found considerable amounts of Ni in the shoots, they did not observe toxic symptoms on the plants, nor detected significant transport from the roots to the grapes. The authors concluded on the one hand that perennial plants could be more resistant to contamination compared to annual plants; on the other hand, annual harvesting could greatly reduce human health risks arising from the consumption of grapes.

4. Conclusions

Trace metals inputs deriving from road traffic are of great environmental concern, particularly in sprawling cities, where agricultural lands extend at the margins of highways. The major findings of the present study, focusing at two major highways of the Metropolitan city of Athens, are summarized as follows:

1) Magnetic susceptibility measurements showed the abundance of ferrimagnetic minerals often encountered in highway environments. Nevertheless, equally enhanced magnetic signals in the agricultural soils at distances 200–400 m away from the road edges revealed that pedogenic and lithogenic factors were primarily responsible for the magnetic enhancement.

2) The application of sequential extraction procedure showed that all the trace metals studied (Pb, Zn, Cu, Cd and Ni) were mostly found in the residual fraction. This rather inert fraction, corresponding broadly to trace metals of geogenic origin, contributed by 37% for Cd up to 80% for Cu of the pseudototal contents. The significant contribution of lithogenic sources to the overall trace metals contents inhibited the recognition of traffic-related pollution in the roadside soils by the *aqua regia* procedure.

3) Traffic related pollution was successfully traced by trace metal partitioning into the mobile fractions. Copper and Zn exhibited significant differences between the roadside and off-road soils, both in the partitioning schemes and their contents in the mobile fractions, namely the acid soluble and the reducible fractions. Nickel and Pb followed the same distribution pattern in the two sub-sets of soils, however, the amounts extracted during the first two steps of the sequential procedure were statistically significant higher in the roadside soils compared to the off-road soils. The oxidizable fraction comprised a long-term, stable sink of metals in the off-road soils, either due to anthropogenic inputs not related to traffic pollution, or by natural aging processes.

4) The trace metals levels determined in this study were not alarming in terms of concern for the agricultural crops, except for Ni. Although Ni levels in the studied soils are considered to be controlled by lithogenic factors, vehicular emissions could also contribute to the more labile, consequentially potentiallly phytoavailable fractions. As Ni inputs to roadside soils related to

road traffic are expected to increase in response to outward expansion of Athens, future studies should be oriented towards plant uptake bioassays, including the accumulation and transport pathways from soil to the edible part of cultivated plants.

References

Abollino, O., Aceto, M., Malandrino, M., Mentasti, E., Sarzanini, C., Petrella, F., 2002. Heavy metals in agricultural soils from Piedmont, Italy. Distribution, speciation and chemometric data treatment. Chemosphere 49, 545–557.

Akhter, M.S., Madany, I.M., 1993. Heavy metals in street and house dust in Bahrain. Water Air Soil Pollut. 66, 111–119.

Alloway, B.J., 2013. Sources of heavy metals and metalloids in soils. In: Alloway, J.B. (Ed.), Heavy Metals in Soils: Trace Metals and Metalloids in Soilsind their Bioavailability. Springer, Netherlands, Dordrecht, pp. 11–50.

Argyraki, A., Kelepertzis, E., 2014. Urban soil geochemistry in Athens, Greece: the importance of local geology in controlling the distribution of potentially harmful trace elements. Sci. Total Environ. 482–483, 366–377.

Bäckström, M., Karlsson, S., Allard, B., 2004. Metal leachability and anthropogenic signal in roadside soils estimated from sequential extraction and stable lead isotopes. Environ. Monit. Assess. 90, 135–160.

Bacon, J.R., Hewitt, I.J., 2005. Heavy metals deposited from the atmosphere on upland Scottish soils: chemical and lead isotope studies of the association of metals with soil components. Geochim. Cosmochim. Acta 69, 19–33.

Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? Analyst 133 (1), 25–46.

Beckwith, P.R., Ellis, J.B., Revitt, D.M., Oldfield, F., 1986. Heavy metal and magnetic relationships for urban source sediments. Phys. Earth Planet. Inter. 42, 67–75.

Blundell, A., Hannam, J.A., Dearing, J.A., Boyle, J.F., 2009. Detecting atmospheric pollution in surface soils using magnetic measurements: a reappraisal using an England and Wales database. Environ. Pollut. 157, 2878–2890.

Botsou, F., Karageorgis, A.P., Dassenakis, E., Scoullos, M., 2011. Assessment of heavy metal contamination and mineral magnetic characterization of the Asopos River sediments (Central Greece). Mar. Pollut. Bull. 62, 547–563.

Bouyoucos, G.J., 1962. Hydrometer method improved for making particle size analyses of soils. Agron. J. 54, 464–465.

CCME, 2007. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, Canadian Council of Minister of the Environment.

Chen, H., Yuan, X., Li, T., Hu, S., Ji, J., Wang, C., 2016. Characteristics of heavy metal transfer and their influencing factors in different soil-crop systems of the industrialization region, China. Ecotoxicol. Environ. Saf. 126, 193–201.

Christoforidis, A., Stamatis, N., 2009. Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. Geoderma 151, 257–263.

Dearing, J.A., Dann, R.J.L., Hay, K., Lees, J.A., Loveland, P.J., Maher, B.A., O'Grady, K., 1996. Frequency-dependent susceptibility measurements of environmental materials. Geophys. J. Int. 124, 228–240.

Divrikli, U., Soylak, M., Elci, L., Dogan, M., 2003. The investigation of trace heavy metal concentrations in the street dust samples collected from Kayseri, Turkey. J. Trace Microprobe Tech. 21, 713–720.

EU, 1986. Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Off. J. Eur. Communities.

Gasparatos, D., Mavromati, G., Kotsovilis, P., Massas, I., 2015. Fractionation of heavy metals and evaluation of the environmental risk for the alkaline soils of the Thriassio plain: a residential, agricultural, and industrial area in Greece. Environ. Earth Sci. 74, 1099–1108.

Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. Trends Anal. Chem. 21, 2002.

Golden, N., Morrison, M., Gibson, P.J., Potito, A.P., Zhang, C., 2015. Spatial patterns of metal contamination and magnetic susceptibility of soils at an urban bonfire site. Appl. Geochem. 52, 86–98.

Harrison, R.M., Laxen, D.P.H., Wilson, S.J., 1981. Chemical associations of lead, cadmium, copper and zinc in street dusts and roadside soils. Environ. Sci. Technol. 15, 1378–1383.

Heymann, Y., Steenmans, Ch., Croissille, G., Bossard, M., 1994. Corine land cover. Technical Guide, EUR12585, Luxembourg, Office for Official Publications of the European Communities.

Hjortenkrans, D.S.T., Bergback, B.G., Haggerud, A.V., 2008. Transversal immission patterns and leachability of heavy metals in road side soils. J. Environ. Monit. 10, 739–746.

Hoffmann, V., Knab, M., Appel, E., 1999. Magnetic susceptibility mapping of roadside pollution. J. Geochem. Explor. 66, 313–326.

Huber, M., Welker, A., Helmreich, B., 2016. Critical review of heavy metal pollution of traffic area runoff: occurrence, influencing factors and partitioning. Sci. Total Environ. 541, 895–916.

Kabata-Pendias, A., 2011. Trace Elements in Soils and Plants, Fourth ed. CRC Press, Boca Raton, FL.

Kaitantzian, A., Kelepertzis, E., Kelepertsis, A., 2013. Evaluation of the sources of contamination in the suburban area of Koropi–Markopoulo, Athens, Greece. Bull. Environ. Contam. Toxicol. 91, 23–28.

Kelepertzis, E., 2014. Accumulation of heavy metals in agricultural soils of Mediterranean: insights from Argolida basin, Peloponnese, Greece. Geoderma 221–222, 82–90.

Kelepertzis, E., Galanos, E., Mitsis, I., 2013. Origin, mineral speciation and geochemical baseline mapping of Ni and Cr in agricultural topsoils of Thiva Valley (central Greece). J. Geochem. Explor. 125, 56–68.

Kelepertzis, E., Komárek, M., Argyraki, A., Šillerová, H., 2016. Metal(loid) distribution and Pb isotopic signatures in the urban environment of Athens, Greece. Environ. Pollut. 213, 420–431.

Kelepertzis, E., Paraskevopoulou, V., Argyraki, A., Fligos, G., Chalkiadaki, O., 2015. Evaluation of single extraction procedures for the assessment of heavy metal extractability in citrus agricultural soil of a typical Mediterranean environment (Argolida, Greece). J. Soils Sediments 15, 2265–2275.

Kluge, B., Wessolek, G., 2012. Heavy metal pattern and solute concentration in soils along the oldest highway of the world – the AVUS Autobahn. Environ. Monit. Assess. 184, 6469–6481.

Li, H., Qian, X., Hu, W., Wang, Y., Gao, H., 2013. Chemical speciation and human health risk of trace metals in urban street dusts from a metropolitan city, Nanjing, SE China. Sci. Total Environ. 456, 212–221.

Li, X., Thornton, I., 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. Appl. Geochem. 16, 1693–1706.

Licina, V., Antic-Mladenovic, S., Kresovic, M., Rinklebe, J., 2010. Effect of high nickel and chromium background levels in serpentine soil on their accumulation in organs of a perennial plant. Commun. Soil Sci. Plant Anal. 41, 482–496.

Lu, S.G., Wang, H.Y., Guo, J.L., 2011. Magnetic enhancement of urban roadside soils as a proxy of degree of pollution by traffic-related activities. Environ. Earth Sci. 64, 359–371.

Morse, N., Walter, M.T., Osmond, D., Hunt, W., 2016. Roadside soils show low plant available zinc and copper concentrations. Environ. Pollut. 209, 30–37.

Nazzal, Y., Rosen, M.A., Al-Rawabdeh, A.M., 2013. Assessment of metal pollution in urban road dusts from selected highways of the Greater Toronto area in Canada. Environ. Monit. Assess. 185, 1847–1858.

Nelson, D., Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter. In: Page, A.L., et al. (Eds.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, 2nd ed., ASA, SSSA, Madison, WI, pp. 539–579.

Nelson, R.E., 1982. Carbonate and gypsum. In: Page, A.L., et al. (Eds.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, 2nd ed., ASA, SSSA, Madison, WI, pp. 181–197.

Norrström, A.C., Jacks, G., 1998. Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. Sci. Total Environ. 218, 161–174.

Oorts, K., 2013. Copper. In: Alloway, J.B. (Ed.), Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability. Springer, Netherlands, Dordrecht, pp. 367–394.

Pérez, G., López-Mesas, M., Valiente, M., 2008. Assessment of heavy metals remobilization by fractionation: comparison of leaching tests applied to roadside sediments. Environ. Sci. Technol. 42, 2309–2315.

Pagotto, C., Rémy, N., Legret, M., Le Cloiec, P., 2001. Heavy metal pollution of road dust and roadside soil near a major rural highway. Environ. Technol. 22, 307–319.

Peijnenburg, W.J.G.M., Zablotskaja, M., Vijver, M.G., 2007. Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. Ecotoxicol. Environ. Saf. 67, 163–179.

Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanette, M.L., Orio, A.A., 1985. Heavy metal speciation in the sediments of northern adriatic sea. A new approach for environmental toxicity determination. Heavy Met. Environ. 2, 454–456.

Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J. Environ. Monit. 1, 57–61.

Reimann, C., Flem, B., Fabian, K., Birke, M., Ladenberger, A., Négrel, P., Demetriades, A., Hoogewerff, J., The GEMAS Project Team), 2013. Lead and lead isotopes in agricultural soils of Europe – the continental perspective. Appl. Geochem. 27, 532–542.

Sansalone, J.J., Buchberger, G.S., 1997. Partitioning and first flush of metals in urban roadway storm water. J. Environ. Eng. 123, 134–143.

Saracoglu, S., Soylak, M., Eli, L., 2009. Extractable trace metals content of dust from vehicle air filters as determined by sequential extraction and flame atomic absorption spectrometry. J. AOAC Int. 92, 1196–1202.

Scoullos, M., Botsou, F., Zeri, C., 2014. Linking environmental magnetism to geochemical studies and management of trace metals. Examples from fluvial, estuarine and marine systems. Minerals 4, 716–745.

Smolders, E., Mertens, J., 2013. Cadmium. In: Alloway, J.B. (Ed.), Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability. Springer, Netherlands, Dordrecht, pp. 283–311.

Soylak, M., Türkoglu, O., 1999. Trace metal accumulation caused by traffic in an agricultural soil near a motorway in Kayseri, Turkey. J. Trace Microprobe Tech. 17, 209–217.

Soylak, M., Elci, L., Dogan, M., 2000. Lead concentrations of dust samples from Nigde City-Turkey. Fresenius Environ. Bull. 9, 036–039.

Soylak, M., Akkaya, Y., Elci, L., 2001. Monitoring trace metal levels in Yozgat-Turkey: determinations of some metal ions in roadside soils. Trace Elem. Electrolytes 18, 176–180.

Sungur, A., Soylak, M., Ozcan, H., 2014b. Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability. Chem. Speciat. Bioavailab. 26,

219–230.

Sungur, A., Soylak, M., Yilmaz, S., Özcan, H., 2014a. Determination of heavy metals in sediments of the Ergene River by BCR sequential extraction method. Environ. Earth Sci. 72, 3293–3305.

Sungur, A., Soylak, M., Yilmaz, E., Yilmaz, S., Ozcan, H., 2015. Characterization of heavy metal fractions in agricultural soils by sequential extraction procedure: the relationship between soil properties and heavy metal fractions. Soil Sediment Contam.: Int. J. 24, 1–15.

Sutherland, R.A., Tolosa, C.A., 2000. Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii. Environ. Pollut. 110, 483–495.

Tack, F.M.G., Verloo, M.G., 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. Int. J. Environ. Anal. Chem. 59, 225–238.

Thompson, R., Oldfield, F., 1986. Environmental Magnetism. Allen And Unwin, London.

Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: a review. Sci. Total Environ. 400, 270–282.

Turkoglu, O., Saracoglu, S., Soylak, M., 2003. Trace metal levels in soil samples from crossroads in Kayseri-Ankara motorway. Trace Elem. Electrolytes 20, 225–229.

USEPA, 2005a. Ecological Soil Screening Levels for Cadmium Interim Final, OSWER Directive 9285.7-65. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

USEPA, 2005b. Ecological Soil Screening Levels for Lead Interim Final, OSWER Directive 9285.7-70. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

USEPA, 2005c. Ecological Soil Screening Levels for Zinc Interim Final, OSWER Directive 9285.7-73. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

USEPA, 2006. Ecological Soil Screening Levels for Copper Interim Final, OSWER Directive 9285.7-68. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

USEPA, 2007. Ecological Soil Screening Levels for Nickel Interim Final, OSWER Directive 9285.7-76. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

Ward, N.I., 1990. Multielement contamination of British motorway environments. Sci. Total Environ. 93, 393–401.

Ward, N.I., Brooks, R.R., Roberts, E., Boswell, C.R., 1977. Heavy-metal pollution from automotive emissions and its effect on roadside soils and pasture species in New Zealand. Environ. Sci. Technol. 11, 917–920.

Werkenthin, M., Kluge, B., Wessolek, G., 2014. Metals in European roadside soils and soil solution – a review. Environ. Pollut. 189, 98–110.

Yang, S., Zhou, D., Yu, H., Wei, R., Pan, B., 2013. Distribution and speciation of metals (Cu, Zn, Cd and Pb) in agricultural and non-agricultural soils near a stream upriver from the Pearl River, China. Environ. Pollut. 177, 64–70.

Yang, T., Liu, Q., Li, H., Zeng, Q., Chan, L., 2010. Anthropogenic magnetic particles and heavy metals in the road dust: magnetic identification and its implications. Atmos. Environ. 44, 1175–1185.

Yildirim, G., Tokalioğlu, S., 2016. Heavy metal speciation in various grain sizes of industrially contaminated street dust using multivariate statistical analysis. Ecotoxicol. Environ. Saf. 124, 369–376.