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Soil *versus* plant as indicators of agroecosystem pollution by potentially toxic elements

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Abstract

The major route of potentially toxic elements (PTEs) to humans is the intake through food. They enter the food chain principally by plants uptake from the soil and, to a less extent, through foliar deposition. The soil-to-plant transfer as part of the biogeochemical cycle of these elements is a complex and hardly predictable process. In this study, we investigated the capability of soils and plants to indicate PTEs inputs in an intermingled urban-rural landscape of south Italy affected by legal and illegal waste disposal and dumping. For this aim, 172 agricultural soil and plant (edible part) samples were collected in pairs from 47 municipalities and analyzed for 12 PTEs (As, Be, Cd, Co, Cu, Cr, Ni, Pb, Se, Tl, V, Zn). Soil extractions with 1 M NH_4NO_3 and 0.05 M EDTA pH 7 were applied to assess PTEs bioavailability. Results were examined according to plant species and main soil chemical properties. For Pb and Cd, the soil-to-plant transfer factors (TF) and the corresponding soil benchmark concentrations were also investigated. Zinc, Cu, Cd, and Pb were the only PTEs of anthropic origin severely polluting from 10 to 16% of the soils, but only in a very few cases exceeded physiological or EU legal critical values in the edible part of the plants. An evaluation of human risk due to the ingestion of these elements was tried; no risk for consumers for Zn, Cu, and Pb, while for Cd three values slightly exceeded the tolerable daily intake. Therefore, we conclude that crops cultivated in the studied area could represent only a moderate risk for human health. No correlation was found between soil and plant data, which likely highlights different pollution inputs. A large variability characterized the Pb and Cd TF, making it difficult to establish a unique benchmark concentration for the studied agricultural soils.

Key words: agricultural soils / health risk / soil benchmark concentration / transfer factors / vegetables

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1 Introduction

In the Campania Region (south Italy), a large plain area in the provinces of Naples and Caserta, known as Campania Plain and corresponding to the National Interest Priority Site (NIPS) "Litorale Domizio-Agro Aversano", has recently been subjected to a mass media campaign provoked by illegal dumping of wastes and their burning. *Anonymous* (2014) correlated this phenomenon to injuries to the health of the population living in the area. Several studies have investigated the type and concentration of potentially toxic elements spread in Campania Plain soils, as well as their origin (geogenic or anthropic), highlighting the absence of a diffuse soil pollution (*Capra* et al., 2014, and literature cited in it). Nevertheless, despite the absence of data certifying the contamination of the food chain, the agriculture-based economy of the area has been suffering from public perception that its products might be contaminated. As consequence, under the pressure of public opinion, national and regional agricultural and environmental authorities promoted investigations aimed to evaluate the contamination of agricultural soils and foodstuffs produced in the area.

Considering that plant roots take up water and soluble ions, it is unlikely that foodstuffs contain organic pollutants whose bioavailability is usually reduced in soils by adsorption or complexation (*Wu* and *Zhu*, 2016). So, the highest concern was about contamination by potentially toxic elements (PTEs; *Kabata-Pendias*, 2010), some of which are essential for microorganisms, plants, and animals (including humans) at low concentrations (*Nagajyoti* et al., 2010). The first challenge was how to define an agricultural soil as actually polluted. In Europe (*Carlon*, 2007), differentiating site-specific land uses such as residential or industrial, there are different screening values for several PTEs, above which a soil can be defined as potentially contaminated. Screening values are predominantly based on total or 'pseudototal' contents of PTEs in soil with no clear trend in regard to screening values for potentially unacceptable risk for metals and metalloids related to countries. Italian screening values are the lowest ones for most metals and metalloids. Only few countries (*i.e.*, Germany and Austria) have specific screening values for agricultural soils considering mobility and bioavailability of the pollutants.

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For assessing pollution of agricultural soils it is crucial to assess the risk of root uptake of PTEs and their accumulation in edible plant parts. Therefore, the risk of contamination of the food chain should be related to the bioavailable fraction rather than to the total content of PTEs in cropland soils (*Adamo* et al., 2014). The bioavailable fraction is that part of the PTEs total content that is or can be made available for absorption by living organisms (*Adamo* et al., 2017). For vegetables, the PTEs bioavailability depends on the chemical forms in which they occur in soil and on the nature of their binding to the different soil geochemical fractions (*Adamo* et al., 2017). The plant availability of the PTEs basically depends on the equilibrium conditions between the soil solid constituents and the soil solution. The PTEs occurring as simple or complex ions in the soil solution are readily bioavailable, whereas the PTEs which are prone to be mobilizable from the mineral and organic solid constituents to the soil solution are potentially bioavailable. The potential bioavailability is a site-dependent property being a function of soil type and properties such as pH, redox potential, temperature, organic matter, and clay content (*Adamo* et al., 2017).

Furthermore, to determine a soil contamination the site-specific background values should be taken into account, with the aim to discern a high content of PTEs due to geogenic origin from the anthropic contamination. Several surveys report that the soils of our study area (Fig. 1), originating from volcanic materials mixed with alluvial ones, have high content of several mineral elements with values sometimes higher than the legal screening values (*Cicchella* et al., 2005; *Albanese* et al., 2007; *Lima* et al., 2012). For this reason, for the study area the baseline values for Be, Tl, and V were set at 6.3, 2.7 and 150 mg kg^{-1}, respectively (*ARPAC-ISPRA*, 2010).

Considering that the European legislation has established maximum levels of lead (Pb) and cadmium (Cd) in various subgroups of vegetables (*EC*, 2006), with the aim to minimize dietary exposure and safeguard public health, these two contaminants have been considered with priority. Their effects on human health are well known: Cd can damage the kidneys and is carcinogenic to humans (*Järup* et al., 1998; *IARC*, 2006; *Järup* and *Akesson*, 2009). Lead affects the central nervous system, the male fertility (*Giaccio* et al., 2012) and increases the risk of cancer (*IARC*, 2006). According to the European Food Safety Authority, vegetables are the main food categories contributing to EU population Pb and Cd exposure (*EFSA*, 2012a; 2012b). *Esposito* et al. (2015) have recently analyzed Pb and Cd concentrations in fruits and vegetables produced in the Campania Region excluding any risk for human health deriving from foodstuff consumption. Only 3 among 750 analyzed samples (0.4%) were found to exceed the European thresholds, thus, denying any negative effect of environmental factors, such as geological origin of soils or pollution from the illegal disposal of wastes, on food safety.

In this paper, through a paired soil and plant sampling design, we investigated the capability of soils and plants to highlight PTEs inputs in a fragmented urban-rural landscape of south Italy affected by illegal waste disposal and dumping. With the aim to have a more complete picture of the environmental quality of the study area, with particular reference to the spread of contaminants into the soils and from there into the

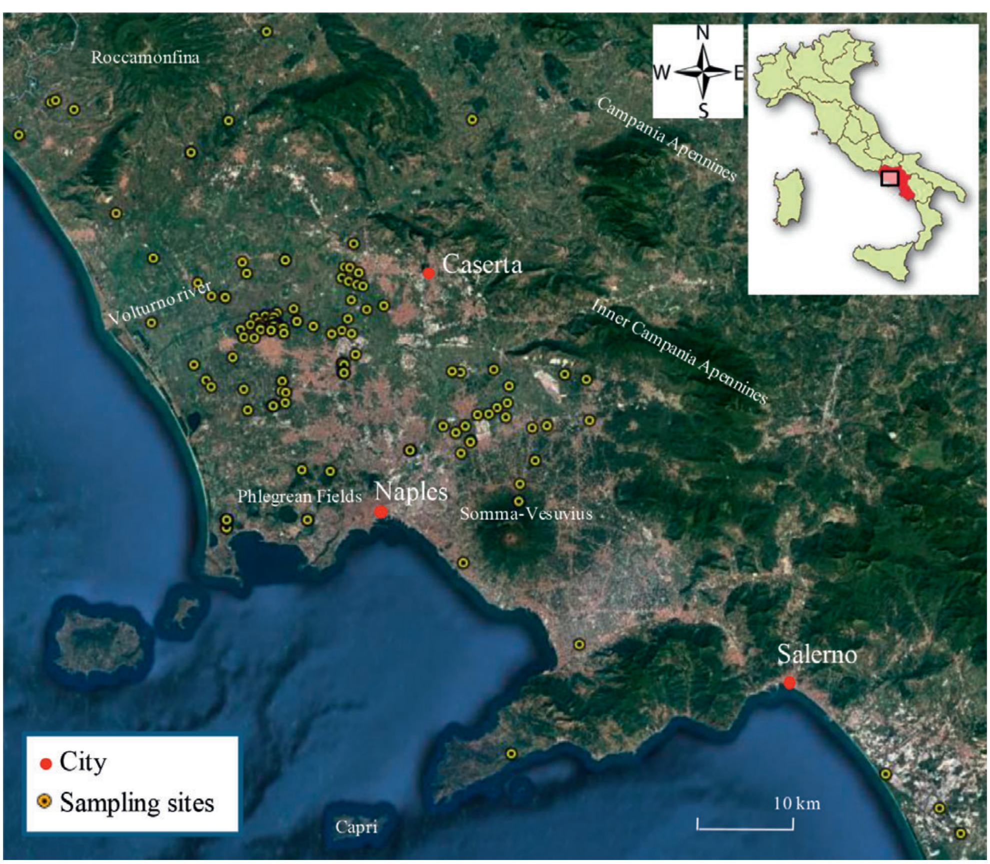

Figure 1: Location of soil and plant sampling sites.

food chain, an ample set of metals and metalloids (As, Be, Cd, Co, Cu, Cr, Ni, Pb, Se, Tl, V, and Zn) was analyzed in soils and food plants. The influence of soil properties and plant species on the bioavailability and uptake of PTEs from potentially polluted agricultural sites was analyzed. With regard to Pb and Cd, the potential human health risk *via* consumption of vegetables and the relative limits in agricultural soils were evaluated.

2 Material and methods

2.1 Study area

Soil and plant sampling was mostly carried out in the Campania Plain, from the territory of 45 municipalities in the provinces of Naples and Caserta, and only limitedly (2 municipalities) in the province of Salerno (Fig. 1). The plain, which covers an area of approximately 140,000 ha, constitutes the largest plain of the Campania Region (south Italy). From a geological viewpoint, the plain is a large graben formed during the Tertiary Period and filled with Holocene alluvial sediments partially overlying pyroclastic materials in addition to Plio-Pleistocene lacustrine, palustrine, and marine sediments (*Capra* et al., 2014). The mineralogical composition of stratified geo-lithological substrates mainly consists of primary and secondary carbonates and volcanic materials. Soil formation in the plain is influenced by alluvial and colluvial processes with presence of both detrital–alluvial sediments from Volturno river and the fall of pyroclastic materials from the volcanic complexes of Roccamonfina on the north and Phlegrean Fields and Somma–Vesuvius on the south. According to the Naples Province soil map provided by *Di Gennaro* and *Terribile* (1999) and to the Agro Aversano and Carinolese soil maps provided by the *Campania Region* (pers. comm.) and according to the WRB system of soil classification, the majority of the studied soil samples belong to Chernic Vitric Andosols, Hypereutric Vitric Andosols, Hypereutric Cambisols, Haplic Phaeozems, Vitric Andosols, and Molli-Vitric Andosols. The formers are typically found in the Phlegrean Pediment Plain, where soils are very thick, well drained and at times characterized by the presence of a cemented ash horizon made by the Vesuvian *Avellino Pumice surge* deposits within the first 1 m depth (*Di Gennaro* and *Terribile*, 1999). Besides, Vitric Andosols and Molli-Vitric Andosols are typically found in the Somma–Vesuvius Pediment Plain as well as in the pediment plains of carbonate mountains of inner Campania Apennines (*Campania Region*, pers. comm.). Instead, the soil samples collected in the eastern part of the Volturno River alluvial plain, bordered by the Roccamonfina volcano and the Massico Mountain in the north, mostly belong to Calcaric Cambisols, Molli-Gleyic Cambisols, and Fluvic Cambisols (*Campania Region*, pers. comm.). According to the soil regions study of Italy (*Costantini* et al., 2004), the area has a humid climate, second mesothermic, with a slight water deficit in the summer. From 1985 to 2005, average annual air temperature and mean annual precipitation were 18.7°C and 818 mm, respectively (*Capra* et al., 2014).

The territory has recently been under the attention of media because of the extensive legal and illegal use of soils to dispose and dump potentially toxic wastes and for the numerous illegal waste burnings. Public opinion claims that this situation is the cause of increase of cancers and shorter lifespan of people living in the area. Authoritative researchers have recently suggested that Campania Region could be a perfect field study for a monitoring research program, as their poisoned fields could serve as a giant experiment in the new science of 'exposomics' (*Anonymous*, 2014). However, despite the perception encouraged by the media, the area, characterized by a still prevailing agricultural vocation, accommodates about 38,000 farms producing 40% of the entire agricultural output of Campania (*Di Gennaro*, 2014). Agriculture is very intensive, mainly consisting of irrigated lands used for horticulture, fruit trees, vineyards, and forage crops.

2.2 Soil and plant sampling

172 agricultural soil and plant samples were collected in pairs in the period December 2013–September 2015. The soil in contact with the plant roots to a depth of 20 cm (A_p horizons) was collected. 42 different plant species including vegetables, fruits and grass were collected (Tab. 1). Soil and plant samples (about 500 g each) were placed in labeled plastic and paper bags, respectively, and rapidly transported to the laboratory.

2.3 Soil and plant analysis

The main soil physical and chemical properties were determined on air-dried, 2 mm sieved soil, according to the Italian official methods of soil analysis (*MiPAF*, 2000). Soil pH was determined potentiometrically by applying a 1.0 : 2.5 soil : water ratio, organic carbon according to the Walkley and Black method, cation exchange capacity (CEC) in $BaCl_2$ + TEA solution at pH 8.1, and carbonates by pressure Dietrich–Fruehling calcimeter. Particle size analysis (Andreasen's pipette method) was carried out after wet sieving by sedimentation in aqueous medium.

The pseudototal contents of As, Be, Cd, Co, Cr, Ni, Pb, Cu, Se, Tl, V, and Zn, defined as PTEs by *Alloway* (1995) and normated by Italian legislation (D.Lgs 152/06), were measured in pulverized soil sub-samples using microwave-assisted acid digestion in acqua regia *EPA* 3051A/2007. Concentrations of metals in the digestion solutions were determined in accordance with *EPA* 6010C/2007 using inductively coupled plasma-mass spectrometry (ICP-MS; Agilent 7700 series, Agilent Technologies). Procedural blanks were usually below quantification limits, and reference standard materials were used to check accuracy and precision of digestion and ICP analysis procedures. The accuracy for most elements was within ± 15%. The variability between analytical replicates was lower than 15%. On about half of the soil samples, selected on the basis of the total PTE content in soil or in the coupled plant sample, the readily and potentially bioavailable amounts of several PTEs were extracted from the 2 mm sieved soil with 1 M NH_4NO_3 (*DIN 19730*, 2008) and 0.05 M EDTA pH 7 (*EUR 19774 EN*/2001; *Rauret* et al., 2001), respectively. Concentrations of elements in the extraction solutions were determined using inductively coupled plasma-

Table 1: List of plant species sampled in pair with soil from the territory of 45 municipalities of Campania (south Italy).

Botanical family	Common name	Scientific name
Brassica leaf vegetables ($n = 43$)	Rocket, Cabbage, Broccoli, Kohlrabi, Turnip greens, Friarielli, Savoy cabbage	*Eruca sativa, Brassica oleracea, B. oleracea, Brassica rapa sylvestris, B. ruvo*
Non-*Brassica* leaf vegetables ($n = 9$)	Chicory, Endive, Lettuce	*Cichorium intybus, C. endivia, Lactuca sativa*
Cereals ($n = 13$)	Wheat, Corn	*Triticum durum, Zea mays*
Fruits ($n = 44$)	Apple, Medlar, Strawberry, Peach, Black cherry, Cherry, Plum, Apricot, Lemon, Orange, Grapes, Kiwi, Nut, Melon	*Malus domestica, Eriobotrya japonica, Fragaria vesca, Prunus persica, P. cerasus, P. avium, P. domestica, P. armeniaca, Citrus sinensis, Vitis vinifera, Actinidia chinensis, Juglans regia, Cucumis melo*
Legumes ($n = 8$)	Bean, Green bean, Lupin bean, Pea	*Phaseolus vulgaris, Vicia faba, Lupinus albus, Pisum sativum*
Root vegetables ($n = 6$)	Parsley, Fennel, Onion, Garlic	*Petroselinum crispum, Foeniculum vulgare, Allium cepa, A. sativum*
Vegetables ($n = 33$)	Pepper, Tomato, Chili pepper, Eggplant, Potato, Pumpkin, Courgette	*Capsicum annuum, Capsicum, Solanum lycopersicum, S. melongena, S. tuberosum, Cucurbita maxima, C. pepo*
Grass ($n = 16$)	Grass	*Festuca spp, Lolium spp.*

atomic emission spectroscopy (ICP-OES) (Optima 7300DV, Perkin Elmer).

Determination of total PTEs concentrations in plant samples was carried out after acid digestion (6 mL of HNO_3 at 65%, 2 mL of H_2O_2 at 30%) in a microwave oven with temperature and pressure control. The digestion solutions were analyzed using ICP-MS (Agilent 7700 series, Agilent Technologies). The recovery rate of PTEs content varied between 71 and 92%, with a limit of detection (LOD) of 0.3 μg kg^{-1} and a limit of quantification (LOQ) of 1.0 μg kg^{-1} for all analyzed elements.

2.4 Data analysis

In order to elaborate the data, all values below the LOQ were set at half of the LOQ (*Glass* and *Gray*, 2001; *ISS*, 2004). Univariate statistical analysis was perfomed on all the plant and soil data, and for the purpose of data presentation, tables with minimum, maximum, median, and MAD (median absolute deviation) values or box plots were used. The median and MAD values are the best indicator of central tendency and data spread in the case of asymmetrical and non-normal distribution of the data (*Reimann* and *Filzmoser*, 2000), as in the case of this study (symmetry and normality of the distribution were checked with Skewness and Kurtosis coefficient and with Shapiro–Wilk test, results of the test not shown). The box plot are widely used in geochemical studies for data representation; they give overall information about the univariate data distribution (*Daszykowski* et al., 2007; *De Vivo* et al., 2016). Principal component analysis (PCA) was performed with the purpose to obtain a general overview of correlations existing between the amounts of elements extraxted by ammonium nitrate or EDTA and soil properties. The PCA analysis is one of the multivariate statistical analyses used by many authors in order to facilitate the visualization of meaningful correlations (*Guillén* et al., 2012). The PCA based on the correlation matrix (Pearson) was performed using XLstat software (2009 version), Varimax with Kaiser Normalization was used as the rotation method in the analysis in order to maximize factor variance. The transfer factor (TF) from soil to plant was calculated as the ratio of element concentration in plant (data on dried basis) by its total concentration in soil.

3 Results and Discussion

3.1 Contents of PTEs in soils

The collected soil samples, mostly coming from the Campania Plain territory, cover a large range of physical and chemical properties (Fig. 2). This is generally common in alluvial plains. In the Campania Plain, where the pedogenic material is mostly of alluvial origin, the variability derives from the contribution, variable in terms of quantity and nature, of pyroclastic materials to soil formation and from the addition of exogenous earth materials to soils during past reclamation actions. The soil pH ranges from 4.7 to 8.6 (with a median of 7.4). These values are in agreement with the content of carbonates of the soils which are absent in acidic soils or reach a maximum value of 489 g kg^{-1} in alkaline soils, with a median value of 9.6 g kg^{-1}. The organic carbon content of the soils, ranging from poor (4.0 g kg^{-1}) to very rich (36.5 g kg^{-1}), with a median value of 13.0 g kg^{-1}, likely reflects differences in field management. Cation exchange capacity, ranging from 5.3 to 40.6 cmol kg^{-1} (median of 19.5 cmol kg^{-1}), resembles the generally sandy to loamy texture of the soils. The considerable variability in soil texture and related chemical properties

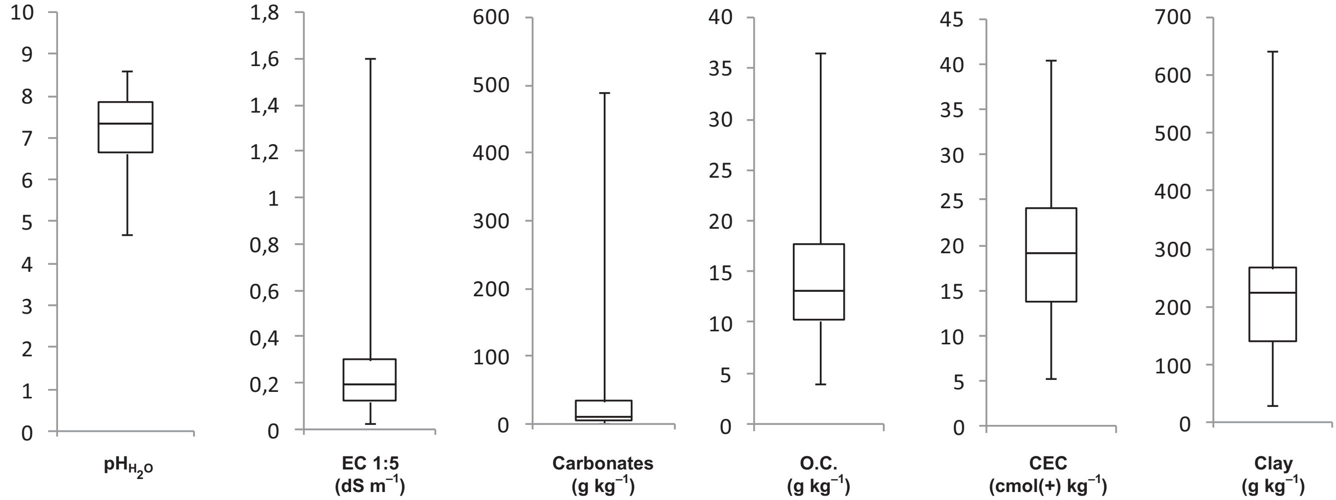

Figure 2: Main soil properties. Each plot represents minimum and maximum (whiskers) and median (bar) values measured in 172 samples. The box ranges from 25 to 75th percentile. For acronyms see main text.

is consistent with the findings by *Capra* et al. (2014) and *De Vivo* et al. (2016), suggesting a different mineralogical paragenesis of the geo-lithological substrates for the agricultural soils of Volturno River's lower basin.

The pseudototal contents of PTEs in the soils are given in Fig. 3. In Italy, in absence of specific screening values (SV) for agricultural use, values for potentially unacceptable risk for residential soil use are applied (D.Lgs 152/06 column A). In this study, only for the soils collected in the territory of the Campania Plain, the total content of PTEs in soil can also be compared to the soil background reference values defined by *ISPRA* (Institute for Protection and Environmental Research) in collaboration with *ARPAC* (Campania Region Environmental Protection Agency) (*ARPAC-ISPRA*, 2010) and to the natural background values measured by *Lima* et al. (2012). On the basis of these SV, about half of the analyzed soil samples were not potentially polluted for any of the normed PTEs. Among the polluted samples (at least by one metal), about 10% exceeded the SV for Be, Tl, or V, but the excess for most cases was very close to the background levels, indicating a geogenic rather than an anthropic contamination. In no case a contamination was found by Ni, and in very few cases Cd, Cr, and Co exceeded the SV. The most common contaminations regarded the elements Se, Zn, Pb, As, and Cu, reaching maximum concentrations of 8.7, 1134, 230, 43.3, and 570 mg kg^{-1}, respectively. These maximum values were always below the SV for soil destined to industrial use as defined by D.Lgs 152/06 column B (Se: 15; Zn: 1500; Pb: 1000; As: 50; Cu: 600 mg kg^{-1}), and the percentage of soil samples characterized by PTEs levels above SV for residential soil use were low, with the exception of Se (Fig. 3).

The most severe contamination was found for Zn and Cu whose toxicity threshold is very low as compared to the other elements (*ATSDR*, 2015). They are micronutrients for plants and animals, even if this latter aspect could be disadvantageous because it allows an easier entrance in the food chain. Also Se at low doses is an essential oligo-element for humans and a beneficial element for plants; generally, the background values of Se in soil from the Campania Plain did not exceed 1 mg kg^{-1} (*Lima* et al., 2012), therefore, the higher values detected in the studied soils likely come from anthropic sources. For many of the PTEs, the highest values in soils were found in the municipalities of Nolan area and in some municipalities of Naples and Caserta. Chromium had its maximum in the municipalities of the Salerno area well known as one of the main Italian tanning district (*Albanese* et al., 2013).

It has been reported that in urban and peri-urban agricultural sites, as the studied sites, soil contamination by Pb occurs near roadsides, often associated with Zn and Cd (*Garcia* and *Millan*, 1998), whereas the highest values of Cu may be attributed to the use of Cu-based pesticides in agriculture (*Lima* et al., 2012). Also Se is added in many agricultural products (insecticides, fertilizers, and foliar sprays) and probably these are the main sources of Se contamination in the studied soils (*Kabata-Pendias*, 2010).

In agricultural soils, the mobility and bioavailability of PTEs should be considered, rather than their total content, in order to assess the potential transferability of elements to the plants and ultimately to animals and humans through the food chain. Extraction of soil with 1 M NH_4NO_3 solution is used to determine readily soluble element contents, this soil extraction method should help to improve risk assessment of soil contamination (*Adamo* et al., 2017) and some European countries (Germany and Slovakia) also fixed limit values of extractable elements with this method (*Carlon*, 2007). According to 1 M NH_4NO_3 extraction, Cu and Zn were the most readily soluble and plant available elements in the studied soils (Tab. 2). In about 20% of the analyzed soil samples, Cu and Zn amounts extracted by NH_4NO_3 exceeded the threshold values (1 and 2 mg kg^{-1}, respectively) defined in the German Federal Soil Protection and Contaminated Sites Ordinance (*BBodSchV*, 1999) and in the Slovakia Soil Protection Law (*ASP*, 2004) to prevent the transfer of metals from soils to plants. For all the other analyzed elements, the amounts extracted with NH_4NO_3 were always below the limits of quantification of the method, indicating their negligible mobility and

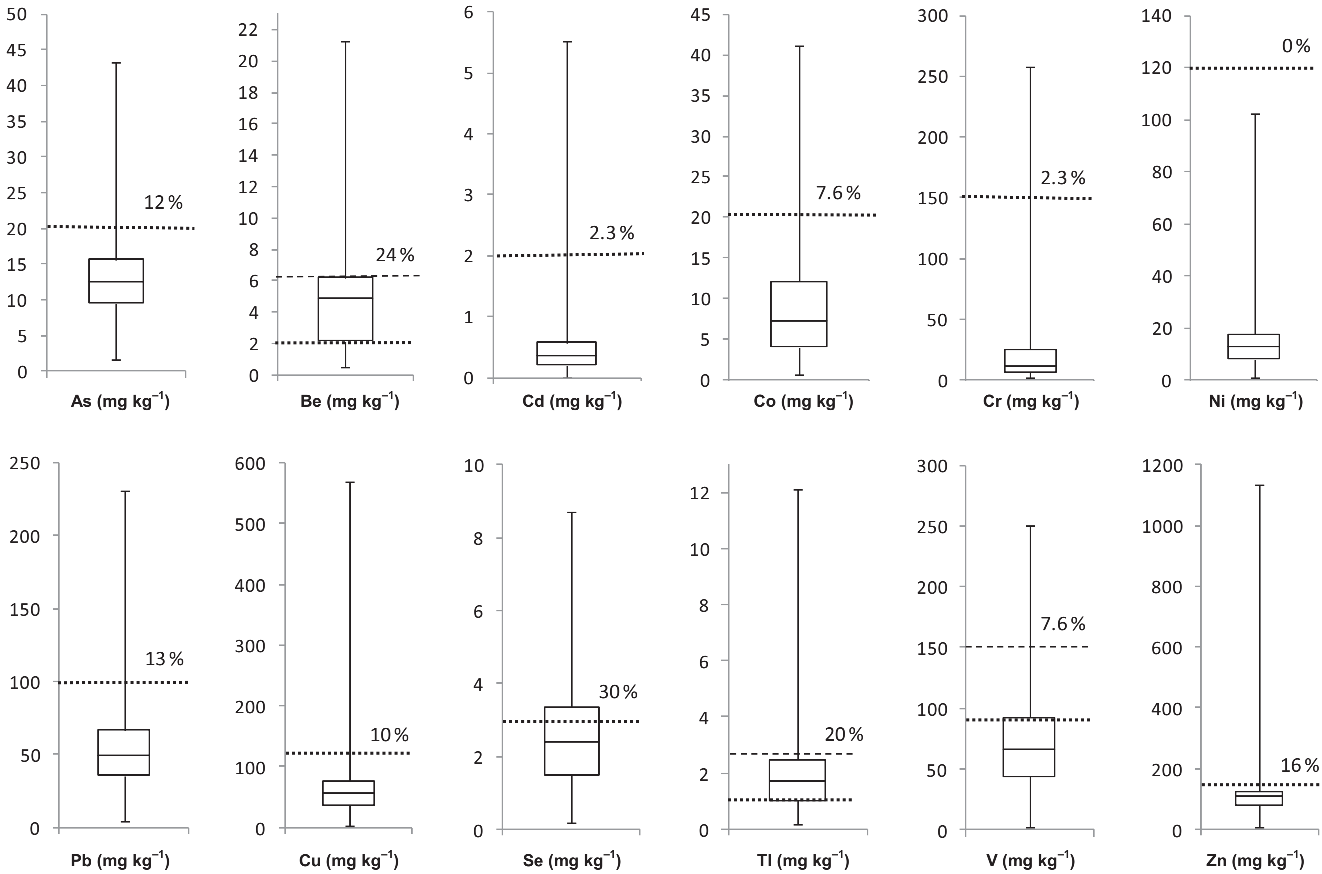

Figure 3: Pseudototal contents of PTEs in soils. Each plot represents minimum and maximum (whiskers) and median (bar) values measured in 172 samples. The box ranges from 25 to 75th percentile. Dot line indicates the Italian legal screening value for residential soil use (D.Lgs. 152/06); Dashed line indicates the background value of the studied area (*Lima* et al., 2012). The numbers on the lines indicate the percentage of the samples exceeding the screening value or background value.

Table 2: Amount (mg kg^{-1}) of PTEs extracted with 1 M NH_4NO_3 from 85 soil samples.

	As	Be	Cd	Co	Cr	Ni	Pb	Cu	Se	Tl	V	Zn
Samples > LOQ[a] (%)	4	1	0	1	0	4	0	78	0	0	0	85
Min	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.25	0.25	0.05	0.05
Max	0.32	0.12	0.05	0.22	0.05	0.17	0.05	13.8	0.25	0.25	0.05	9.46
Median	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.19	0.25	0.25	0.05	0.40
MAD[b]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.29
TV[c]	0.4		0.1			1.5	0.1	1		0.1		2
% of soils that exceed TV[c]	0		0			0	0	20		NA[d]		18

[a]LOQ: limit of quantification;
[b]MAD: median absolute deviation;
[c]TV: Germany and Slovakia threshold value;
[d]NA: not applicable.

plant availability. As a complementary way to measure the mobility and bioavailability of PTEs in polluted soil samples, the 0.05 M EDTA extraction proposed by the European Community (*EUR 19774 EN*/2001) was applied. With the exception of Se and Tl (always below the limits of quantification of the method), the amounts of PTEs extracted from the studied soils with 0.05 M EDTA were several times higher than those extracted with 1 M NH_4NO_3 (Tab. 3), indicating a substantial pool of potentially bioavailable PTEs in soils. However, in analogy with the NH_4NO_3 results, this pool was remarkable only for the main soil pollutants Cu and Zn, and, only for

Table 3: Amount (mg kg–[–1]) of PTEs extracted with 0.05 M EDTA pH 7 from 85 soil samples.

	As	Be	Cd	Co	Cr	Ni	Pb	Cu	Se	Tl	V	Zn
Samples > LOQ[a] (%)	88	21	56	91	79	79	100	100	0	0	100	100
Min	0.05	0.05	0.05	0.02	0.05	0.05	1.88	1.80	0.25	0.25	0.30	1.48
Max	2.78	2.36	1.52	2.87	8.86	3.19	159	379	0.25	0.25	8.12	567
Median	1.15	0.05	0.11	0.31	0.19	0.27	8.90	35.8	0.25	0.25	1.40	8.97
MAD[b]	0.37	0.00	0.06	0.19	0.08	0.16	4.01	24.8	0.00	0.00	0.72	4.75

[a]LOQ: limit of quantification;
[b]MAD: median absolute deviation.

EDTA, for Pb with maximum values of 379, 567, and 159 mg kg^{-1}, respectively.

In soil, the relationship between total, readily, and potentially available pools of PTEs is site-specific mainly depending on properties, such as pH, CEC, organic matter, and clay content, governing the elements solubility, adsorption, precipitation (*Puschenreiter* and *Horak*, 2000; *Pinto* et al., 2015). In the studied soils, the PTEs NH_4NO_3-extractable pool appeared negatively correlated with the soil pH, CEC, and clay content (Fig. 4a). This is not surprising because, as expected, metal solubility decreases as pH increases and high values of clay and CEC indicate a high potential of soils to retain PTEs (*Orhue* and *Uzu*, 2011). Carbonate content seemed not to be correlated with the PTEs amounts extracted by NH_4NO_3, except for Zn (negative correlation), whereas organic carbon content seemed loosely positively correlated, again with the exception of Zn (no correlation). The EDTA extractable pool appeared mainly governed by organic carbon, carbonate, and clay content rather than pH (Fig. 4b). The EDTA-extractable elements can be grouped in two pools: Zn, Cd, Pb, Cr, and Cu, which were closely positively correlated with organic carbon and carbonate content; As, Co, V, and Be, that were closely positively correlated with clay content. This is in accordance with the importance of these soil properties for respectively cationic and anionic elements retention (*Rieuwerts* et al., 1998; *Zeng* et al., 2011), and with the physical and chemical properties of the soils in the studied area having organic carbon and clay content varying more than pH. *Capra* et al. (2014) also found that in the agricultural soils of the Volturno River's lower basin soil organic matter is an important sink for both geogenic and anthropogenic PTEs, suggesting secondary accumulation processes probably favored by the formation of organo-metal complexes.

3.2 Contents of PTEs in edible parts of plants

Collected plant samples (*n* = 172; see Tab. 1) were divided into eight main foodstock categories ("Cereals", "Non-*Brassica* leaf vegetables", "Legumes", "Grass", "Vegetables", "Fruits", "*Brassica* leaf vegetables", "Root vegetables"), as suggested by 420/2011 *EU* regulation. The "Grass" category (*Festuca* spp. + *Lolium* spp.) will be discussed separately from the others because the concentrations are referred to standard 14% forage moisture levels, and so these values are not comparable to those of other categories for which PTE levels are referred to fresh weight (FW).

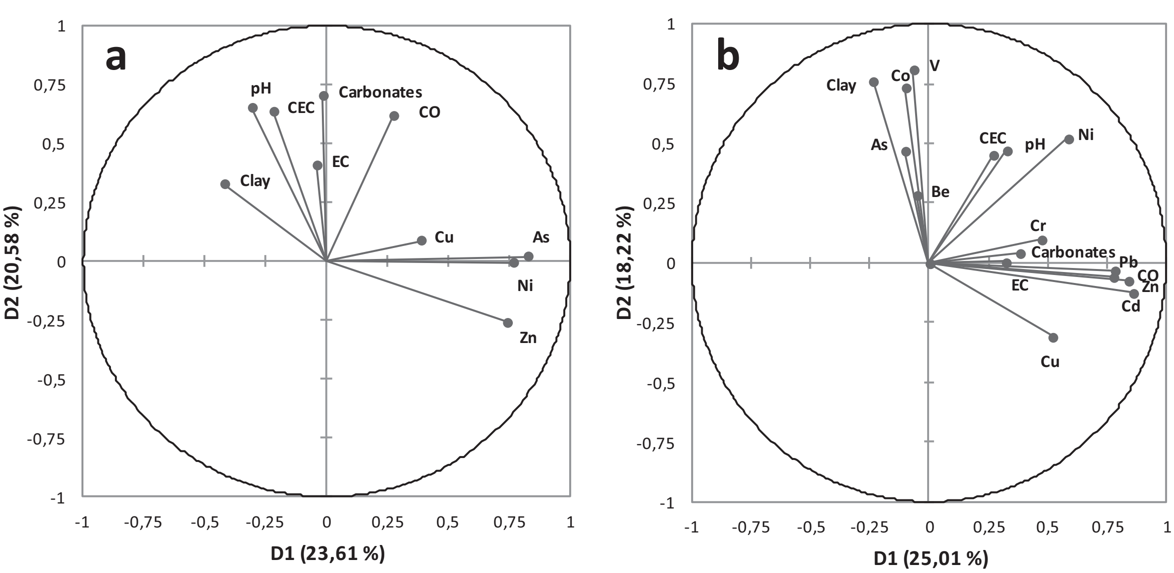

Figure 4: Principal component analysis for the NH_4NO_3 (a) and EDTA (b) extractable PTEs amounts based on the soil properties (analysis performed with exclusion of the elements always below the LOQ).

Among the analyzed PTEs, a special attention was given to Zn, Cu, Pb, and Cd because they were most widespread in the area (Zn and Cu; see Fig. 3), and the only ones regulated by EU (Pb and Cd, 420/2011 *EU* regulation).

Concerning Zn (Fig. 5), in "Cereals" 38% of the samples exceeded the LOQ with a maximum value of 2.1 mg kg^{-1} FW, ten times lower than values measured by *Onianwa* et al. (2001) in Nigerian food, in which the mean concentration of Zn was 25–36 mg kg^{-1} in sweet corn and 27–37 mg kg^{-1} in wheat grains. In "Non-*Brassica* leaf vegetables" 67% of the samples had detectable Zn levels with a maximum of 52 mg kg^{-1} (in one lettuce sample). This value is in agreement with amounts reported by *Kabata-Pendias* (2010) for lettuce (range 44–73 mg kg^{-1}). In "Legumes", "*Brassica* leaf vegetables" and "Root vegetables", 50, 54 and 71% of the samples exceeded LOQ. The maximum values were 14 mg kg^{-1} FW (in one peas sample), 11.5 mg kg^{-1} (in one turnip greens sample), and 5.7 mg kg^{-1} FW (in one onion sample). These values were lower than mean levels found in other studies from different countries (29 mg kg^{-1} for legumes, 24–31 mg kg^{-1} for cabbage, 6–18 mg kg^{-1} for tubers; *Onianwa* et al., 2001; *Radwan* and *Salama*, 2006; *Kabata-Pendias*, 2010). In "Vegetables", 42% of the samples had values higher than LOQ, with a maximum of 46 mg kg^{-1} FW (in one tomato sample) higher than values obtained in an Egyptian market-basket survey carried out by *Radwan* and *Salama* (2006) for tomatoes (6.17–9.81 mg kg^{-1}). In "Fruits", 60% of the samples exceeded the LOQ, with a maximum of 41 mg kg^{-1} FW (in one peach sample) higher than the range (1–2 mg kg^{-1}) found by *Peganova* and *Edler* (2004) for the fruit category.

Copper concentration exceeded the LOQ in most of the analyzed samples (Fig. 5), with percentages of 100% for "Root vegetables" and "Legumes", 84% for "*Brassica* leaf vegetables", 78% for "Non-*Brassica* leaf vegetables", 74% for "Fruit", 64% for "Vegetables", and 38% for "Cereals". The category with the highest maximum value was "Non-*Brassica* leaf vegetables" (9.5 mg kg^{-1} FW), slightly higher than values reported for lettuce (range 6–8 mg kg^{-1}) by *Kabata-Pendias* (2010). For "Cereals" the maximum value was 3.2 mg kg^{-1} FW, lower than levels found by *Škrbić* and *Onjia* (2007) in a Serbian survey of microelements in wheat grain (range 3.6–7.7 mg kg^{-1}). Similarly, "Root vegetables" and "Fruits" had maximum values of 1.1 mg kg^{-1} and 2.2 mg kg^{-1}, respectively, lower than levels reported by *Hu* et al. (2013) and *Oteef* et al. (2015) for these categories (3–5 mg kg^{-1} and 2.7–6.4 mg kg^{-1}). For "Vegetables" (8.7 mg kg^{-1}) and "*Brassica* leaf vegetables" (4.5 mg kg^{-1}), the highest Cu values were similar to those reported elsewhere (6–9 mg kg^{-1} and 6.2 mg kg^{-1}, respectively) (*Hu* et al., 2013).

Cadmium concentration exceeded the LOQ in 85% of "Cereals", 89% of "Non-*Brassica* leaf vegetables", 50% of "*Brassica* leaf vegetables", and 57% of "Root vegetables" samples (Fig. 5). "Legumes" never showed Cd presence. In "Fruits" the mean of 0.012 mg kg^{-1} was lower than 0.041 mg kg^{-1} detected by *Esposito* et al. (2015) in a study carried out in the Campania Region. The maximum values were always lower than the EU limits of 0.2 mg kg^{-1} for "Cereals", "Non-*Brassica* leaf vegetables", "Legumes", "*Brassica* leaf vegetables", and of 0.1 mg kg^{-1} for "Root vegetables". On the contrary, for "Vegetables" and "Fruits" the percentage of samples that exceeded Cd LOQ was 20% and 40%, respectively, with val-

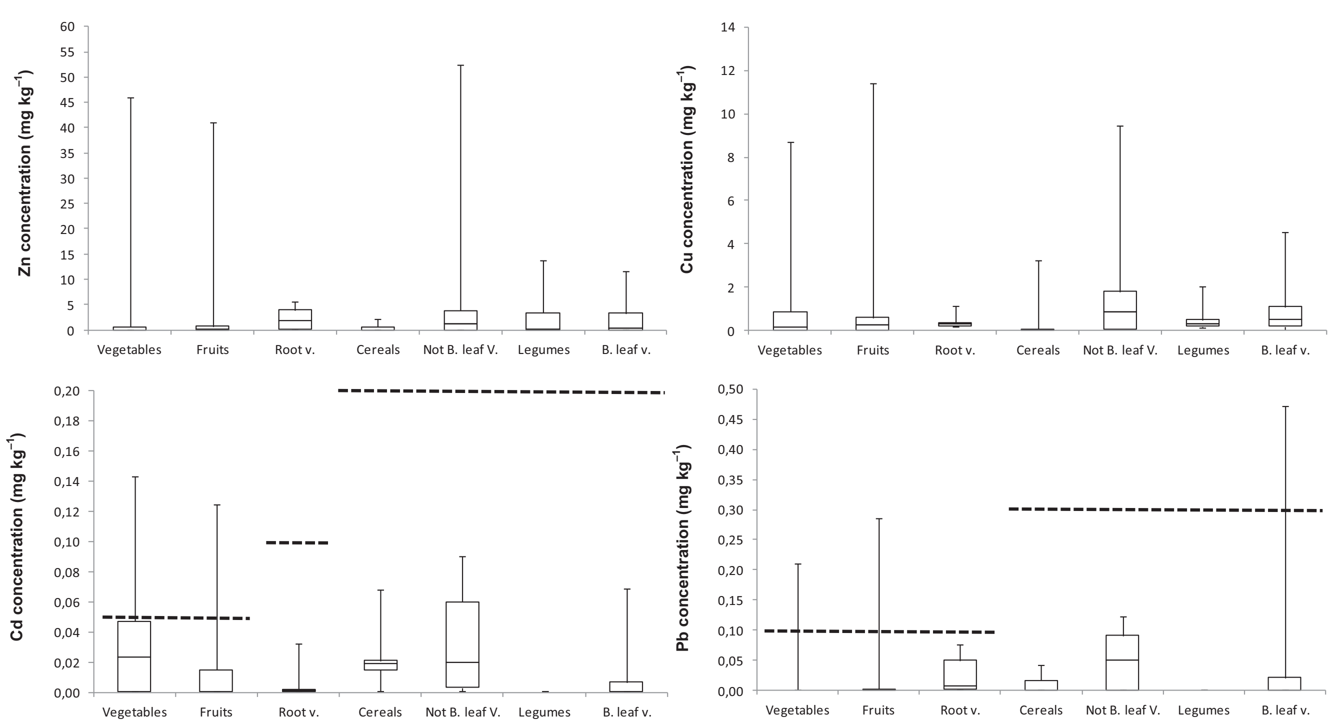

Figure 5: Concentrations of Zn, Cu, Cd, and Pb in plants (mg kg^{-1} FW). Dashed line indicates the EU limits (*EU*, 2011). Each plot represents minimum and maximum (whiskers) and median (bar) values measured in 172 samples. The box ranges from 25 to 75th percentile.

ues exceeding the EU limit of 0.05 mg kg^{-1} in seven samples of vegetables and three of fruits.

The Pb concentration in "Cereals", "Non-*Brassica* leaf vegetables", and "Root vegetables" exceeded Pb LOQ in 38%, 67%, and 71% samples, respectively (Fig. 5). The maximum values were 0.04 mg kg^{-1} FW ("Cereal"), 0.10 mg kg^{-1} FW ("Non-*Brassica* leaf"), 0.07 mg kg^{-1} ("Root vegetables"). The "Legumes" category never showed the presence of Pb. "Vegetables", "Fruits", and "*Brassica* leaf vegetables" samples containing Pb at quantifiable levels were 9%, 26%, and 28%, respectively. The maximum values were 0.2 mg kg^{-1} FW ("Vegetables"), 0.3 mg kg^{-1} FW ("Fruits"), 0.5 mg kg^{-1} FW ("*Brassica* leaf vegetables"). The EU legal limits are 0.3 mg kg^{-1} ("Cereals", "*Non-Brassica* leaf vegetables", "Legumes"), and 0.1 mg kg^{-1} ("Root vegetables"). Only one sample of turnip greens (0.47 mg kg^{-1} FW), one sample of tomato (0.21 mg kg^{-1} FW), and two samples of fruit exceeded the EU limits (*EU*, 2011).

In "Grasses" Zn was detectable in 44% of the analyzed samples with a maximum of 36 mg kg^{-1} (Fig. 6). This value was similar to values found in other studies (28–47 mg kg^{-1}; *Bergmann*, 1975; *Metson* et al., 1979). The 69% of the samples contained Cu at detectable level with a maximum of 1.3 mg kg^{-1}, much lower than values found by *Davis* et al. (1974) and by *Metson* et al. (1979; 9.6–10.5 mg kg^{-1}). Cadmium and Pb were detectable only in 50% and 38% of the analyzed grass samples with maximum values of 0.07 and 0.3 mg kg^{-1} never exceeding the EU limits of 1 and 30 mg kg^{-1} respectively (*EU*, 2013).

The concentrations of all the other PTEs were very low (Tab. 4). Usually, for each category, < 50% of the samples showed element levels higher than LOQ and so medians in different plant categories were equal to LOQ. "Cereals" were not contaminated by Be, Co, and Tl; instead, "Legumes" by Tl. Only in few cases medians higher than LOQ were found. This was true, in particular, in "Root vegetables" for Be and Cr (median 0.013 and 0.024 mg kg^{-1}FW, respectively), in "Non-*Brassica* leaf vegetables" for Ni (median 0.007 mg kg^{-1} FW), in "Legumes" and "Grass" for Se (medians 0.010 mg kg^{-1} FW and 0.032 mg kg^{-1} FW, respectively). Vanadium was the element showing the highest median values (0.49 mg kg^{-1} FW in "Cereals", 0.026 mg kg^{-1} FW in "Grass", 0.001 mg kg^{-1} FW in "Root vegetables", 0.002 mg kg^{-1} FW in "Vegetables"). The diffuse presence of V is probably related to its natural abundance in the earth crust (mean concentration 136 mg kg^{-1}) (*ATSDR*, 2015) and in the studied soils (see Fig. 3).

Considering the range of values among different plant categories, "*Brassica* leaf vegetables" showed maximum values for Tl (1.32 mg kg^{-1} FW), Be (1.23 mg kg^{-1} FW), and As (0.46 mg kg^{-1} FW). "Grass" showed maximum levels of Se (4.16 mg kg^{-1} FW) and V (1.38 mg kg^{-1} FW); instead, in "Fruits" category the highest values were found for Ni (2.84 mg kg^{-1} FW) and Co (0.49 mg kg^{-1} FW). "Vegetable" showed only a maximum level for Cr (4.33 mg kg^{-1} FW). Comparing our results with literature data, it was found that Be was always lower than in other studies, in particular for bean (below LOQ) and peas (0.014 mg kg^{-1} FW). In an Egyptian study it showed levels of 2.2 µg kg^{-1} FW and 109 µg kg^{-1} FW, respectively (*Awadallah* et al., 1986). We never detected Co in "Cereals", whereas in the USA *Barceloux* and *Barceloux*, (1999) found values ranging from 0.2 to 0.6 mg kg^{-1}. Nickel values were always lower than those given by the *Expert Group on Vitamins and Minerals* (*EVM*, 2002) in particular for green vegetables (0.088 mg kg^{-1} FW) and fresh fruits (0.038 kg^{-1} FW). Se values for "Cereals" (0.033 mg kg^{-1}) were higher than those (0.02 mg kg^{-1}) reported by *EFSA* (2009a). However, as reported by *WHO* (2011), food with high protein concentration as cereals usually show high Se levels (0.1–10 mg kg^{-1}).

3.3 Comparison between concentrations of PTEs in soils and food plants and health risk assessment

The concentrations of Zn, Cu, Pb, and Cd in the edible parts of plants did not show any direct correlation with the total concentrations of the elements in the relative soil (correlation coefficient between –0.115 and 0.030), even considering the different plant categories separately (data not shown).

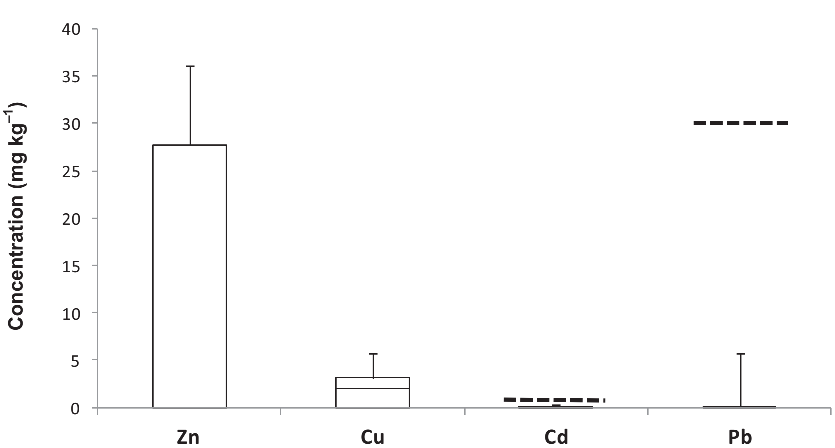

Figure 6: Concentrations of Zn, Cu, Cd, and Pb in the "Grass" category. Dashed line indicates the EU limits (*EU*, 2013). Each plot represents minimum and maximum (whiskers) and median (bars) values measured in 172 samples. The box ranges from 25 to 75th percentile.

Zinc levels in plants were in the range 0.005–12.6 mg kg^{-1}, except for five outlayers: a lettuce (52.5 mg kg^{-1}; soil concentration 1.32 mg kg^{-1}), a tomato (45.9 mg kg^{-1}; soil concentration 73.6 mg kg^{-1}), a peach (41.0 mg kg^{-1}; soil concentration 12.4 mg kg^{-1}), a pepper (17.2 mg kg^{-1}; soil concentration 631 mg kg^{-1}), and a pea sample (13.7 mg kg^{-1}; soil concentration 91.9 mg kg^{-1}). With the exception of pepper, these highest Zn levels in plants were not associated with correspondingly high levels of Zn in soil. In turn, high Zn levels in soil did not produce any high Zn value in the related plants. Zinc is a

Table 4: Concentrations (mg kg^{-1} FW) of As, Be, Co, Cr, Ni, Se, Tl, and V in plants.

		As	Be	Co	Cr	Ni	Se	Tl	V
Brassica leaf vegetables	Samples > LOQ[a] (%)	33	33	40	16	60	37	21	23
	Median	0.0005	0.0005	0.0005	0.0005	0.0210	0.0005	0.0005	0.0005
	MAD[b]	0.0000	0.0000	0.0000	0.0000	0.0205	0.0000	0.0000	0.0000
	Max	0.4590	1.2300	0.1250	1.9300	0.6540	0.3630	1.3230	0.0870
Non-*Brassica* leaf vegetables	Samples > LOQ[a] (%)	44	22	67	22	55	33	22	44
	Median	0.0005	0.0005	0.0010	0.0005	0.0070	0.0005	0.0005	0.0005
	MAD[b]	0.0000	0.0000	0.0005	0.0000	0.0065	0.0000	0.0000	0.0000
	Max	0.0800	0.0300	0,1600	0.1710	0.1560	0.1630	0.6200	0.7170
Cereals	Samples > LOQ[a] (%)	7	0	0	7	15	7	0	70
	Median	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.4880
	MAD[b]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.4880
	Max	0.0760	0.0005	0.0005	0.3110	0.7010	0.4170	0.0005	1.0880
Fruits	Samples > LOQ[a] (%)	25	27	22	43	57	25	22	45
	Median	0.0005	0.0005	0.0005	0.0005	0.0090	0.0005	0.0005	0.0005
	MAD[b]	0.0000	0.0000	0.0000	0.0000	0.0095	0.0000	0.0000	0.0000
	Max	0.0410	0.2410	0.4910	0.7850	2.8360	0.0980	0.0500	0.4340
Legumes	Samples > LOQ[a] (%)	25	38	25	25	12	63	0	25
	Median	0.0005	0.0005	0.0005	0.0005	0.0005	0.0100	0.0005	0.0005
	MAD[b]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0095	0.0000	0.0000
	Max	0.2140	0.1470	0.0390	0.3150	0.6240	0.0500	0.0005	0.5240
Root vegetables	Samples > LOQ[a] (%)	33	67	67	83	67	33	50	67
	Median	0.0005	0.0068	0.0010	0.0140	0.0038	0.0005	0.0005	0.0073
	MAD[b]	0.0000	0.0063	0.0003	0.0135	0.0033	0.0000	0.0000	0.0068
	Max	0.0100	0.1140	0.0380	0.3210	0.2580	0.0310	0.0300	0.0420
Vegetables	Samples > LOQ[a] (%)	24	6	12	24	18	9	21	48
	Median	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
	MAD[b]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	Max	0.1950	0.3090	0.4110	4.3290	0.8390	1.2460	0.1240	0.9270
Grass	Samples > LOQ[a] (%)	31	31	56	6	44	62	25	62
	Median	0.0005	0.0005	0.0140	0.0005	0.0005	0.0315	0.0005	0.0260
	MAD[b]	0.0000	0.0000	0.0135	0.0000	0.0000	0.0310	0.0000	0.0255
	Max	0.0410	0.0310	0.0660	0,1220	2.3060	4.1600	0.0380	1.3790

[a]LOQ: limit of quantification;
[b]MAD: median absolute deviation; The minimum values are 0.0005 for all elements in all plant categories.

metal normally present in the environment and at trace concentration is a micronutrient for plants (*Oteef* et al., 2015). For many crop plants as lettuce, tomato, pepper, peach, and peas, the Zn natural concentrations are defined (*BDA*, 2015). In our study, even when Zn levels in soils were above legal screening values or natural background, Zn levels in plants were mostly around their natural values, indicating no transfer of contamination from soil to plant, with consequent absence of health risk arising from food consumption. This applies also if we assume the ingestion of the most contaminated samples. On the basis of the portions recommended by the Italian Society of Human Nutrition (200 g of tomato and pepper; 150 g of peas and fruit and 80 g of lettuce; *LARN*, 2012), Zn human intake would be: 4.20 mg per portion of lettuce, 9.18 mg per portion of tomato, 6.15 mg per portion of peach, 3.43 mg per portion of pepper, 2 mg per portion of peas. These values are in all cases lower than the level of 25 mg d^{-1} in adults recommended by *LARN* (2014).

The range of Cu concentrations in all analyzed plants was 0.005–6.18 mg kg^{-1} with three samples showing outlayer levels: a grape (11.4 mg kg^{-1}; soil concentration 20.5 mg kg^{-1}), a lettuce (9.47 mg kg^{-1}; soil concentration 77.2 mg kg^{-1}), and a pepper (8.71 mg kg^{-1}; soil concentration 60.7 mg kg^{-1}). As for Zn, the highest Cu levels in plant were not associated with high soil values, as well as the highest Cu concentrations found in soil did not cause any Cu accumulation in the related plants. However, it must be considered that Cu is a micronutrient (*Oteef* et al., 2015), and its natural content in grapes, for instance, is 0.06 mg 100 g^{-1} of product (*BDA*, 2015). According to the recommended Cu assumption for adults of 0.7 mg d^{-1} and the maximum tolerable level of assumption of 5 mg d^{-1} (*LARN*, 2012), there is no health risk deriving from consumption of our food plants, even in the case of 'outlayers' consumption. On the basis of the portions recommended by the Italian Society of Human Nutrition (150 g of grape, 80 g of lettuce, 200 g of pepper; *LARN*, 2012) Cu assumptions would be 1.71 mg per portion of grape, 0.76 mg per portion of lettuce, 1.74 mg per portion of pepper.

Lead and Cd are 2^{nd} and 7^{th} in the top 20 priority list of hazardous substances (*Rehman* et al., 2017). In our study, Cd levels in plants ranged between 0.001 and 0.076 mg kg^{-1}, with six outlayers: two tomato samples (0.143 and 0.125 mg kg^{-1}), one peach (0.125 mg kg^{-1}), one pepper (0.117 mg kg^{-1}), one lettuce, and one eggplant all with a value of 0.090 mg kg^{-1}. With the exception of lettuce, all these concentrations exceeded the current EU limits (*EU*, 2011), but again, the total content of Cd in soil was not correlated with the Cd concentration in the edible parts of analyzed plants. Nevertheless, we must consider that human Cd uptake *via* food is affected by the presence of Zn, Fe, and Ca competing with Cd for absorption (*EFSA*, 2009b). *EFSA* (2009b) established a tolerable weekly intake of Cd (TWI) of 2.5 μg kg^{-1} body weight (bw), so dividing this value by 7 d, the corresponding tolerable daily intake would be 0.36 μg kg^{-1} bw. Comparing the Cd intakes resulting from the six outlayers it appears that three of these (two tomatoes, 0.48 μg kg^{-1} bw and 0.42 μg kg^{-1} bw, and one sample of pepper, 0.39 μg kg^{-1} bw) slightly exceed this value, even considering the ingestion of one of them per day. It is crucial to underline that this scenario regards only the particular condition in which an adult eats the most contaminated food plants.

The concentration of Pb in the analyzed plants was in the range 0.005–0.472 mg kg^{-1} (turnip greens) irrespective of the soil content, with only one sample of wild plant as outlayer (1.32 mg kg^{-1}). Also for Pb, *EFSA* (2010) established a Provisional Tolerable Weekly Intake (PTWI) of 25 μg kg^{-1} bw. A comparison between this PTWI with the outlayer was not carried out, because the sample is a forage. As observed for the other elements, the highest Pb levels in plants were not associated with correspondingly high values in soil. Taking into account that food plants contribute for 16% to the Pb human exposure (*EFSA*, 2010), our Pb results can be considered positive. The scenario found for Cd and Pb, even if few samples exceeded the EU limits, is in line with another study carried out by *Esposito* et al. (2015) investigating the same elements in vegetables and fruits grown in the Campania Region of Italy.

As for total content, also the bioavailable amounts of PTEs extracted from soil by ammonium nitrate and EDTA were not correlated with levels in plants (correlation coefficients between –0.098 and 0.120), even considering the different categories of plants separately (data not shown). For example, the above-mentioned peach sample, outlayer for the Zn concentration (41 mg kg^{-1}), corresponds to a soil with amounts of bioavailable Zn (0.25 mg kg^{-1} in ammonium nitrate and 3.20 mg kg^{-1} in EDTA) even lower than those found in soils hosting plants with normal Zn content; similarly, the tomato outlayer for the Zn content (45.9 mg kg^{-1}), corresponds to a soil with amounts of Zn extracted in ammonium nitrate and EDTA of 0.36 and 18.3 mg kg^{-1}, while other two tomato samples with Zn concentrations of 0.14 mg kg^{-1} and $<$ LOQ, respectively, were associated with soils with ammonium nitrate and EDTA-extractable amounts of Zn of 2.76 and 6.44 (the first) and 0.11 and 44.8 mg kg^{-1} (the second). The lettuce outlayer for the Cu concentration (9.47 mg kg^{-1}) corresponded to a soil with amounts of Cu extracted in ammonium nitrate and EDTA of 0.18 and 38.6 mg kg^{-1}, while another lettuce sample containing only 1.79 mg kg^{-1} of Cu corresponded to a soil with bioavailable amounts of Cu of 7.76 (ammonium nitrate) and 149 (EDTA) mg kg^{-1}; one of the tomato outlayers for Cd content (0.143 mg kg^{-1}) was associated with a soil with bioavailable amounts of Cd $<$ LOQ in ammonium nitrate and of 0.13 mg kg^{-1} in EDTA, very similar to bioavailable amounts found in soils hosting tomato plants with much lower Cd concentrations (0.054 mg kg^{-1}). Similar contrasting examples were found for Pb; an apricot sample with a Pb concentration of 0.29 mg kg^{-1} was associated with a soil with amounts of Pb extracted in EDTA of 4.84 mg kg^{-1}, while another apricot sample with a Pb content $<$ LOQ was associated with a soil with much higher amounts of Pb extracted in EDTA (22.9 mg kg^{-1}). In both cases, soils had amounts of Pb extractable by ammonium nitrate $<$ LOQ.

The discrepancy between the soil and plant data observed in this work might be related to differences between the two systems in terms of concentrations and origin of PTEs they can host. Zinc and Cu are metals normally occurring in soil and in trace concentration are micronutrients for plants (*Kabata-Pendias*, 2010). Their occurrence in the soil–plant system can also be anthropogenic when released into the environment by humans. Differently, Cd and Pb are usually soil exogenous contaminants and no micronutrients. Their occurrence in plants can be related predominantly to anthropogenic activities (*Oteef* et al., 2015). Therefore, the total content of all these elements in soil can indicate natural or anthropogenic pollution when values are higher than 'normal' (local background or legal limits), regardless of the element concentration in plant showing any deviation from 'normality'. On the other hand, when the level of these elements in plants are well above the 'normal' concentrations in absence of a likewise increased soil total or bioavailable level, most likely this contamination can be related to air-borne deposition (*Pandey* et al., 2009; *Gebrekidan* et al., 2013).

Under most conditions, a PTE present in a vegetable/fruit must have existed in the rooting zone of the plant, at least in a slightly soluble form. The ammonium nitrate and EDTA extractions used in this study are considered indicative of the readily and potentially plant-absorbable amounts of PTEs in soil. Nevertheless, in this study no correlation was found among the concentrations of Zn, Cu, Cd, and Pb found in plants and their bioavailable content in soil as assessed by these extractions. This result reinforces the consideration that the mineral element composition of fruits and vegetables is a distorted reflection of the mineral composition of the soil in which the plants grow and that the soil–plant system is highly specific for different elements, plant species, and environmental conditions (*Adamo* et al., 2017). The assumption that a high total and bioavailable PTE content in soil is associated with an enhanced plant uptake and therefore to a higher-than-'normal' PTE concentration in the plant tissues cannot be applicable to all circumstances. Moreover, the elements may accumulate in an organ other than the one considered and the plants, unless they are hyperaccumulators, do not absorb indiscriminately elements from soil, but maintain a nutrient homeostasis (*Clemens*, 2001). Therefore, extreme caution must be applied when results of soil chemical extractions (mostly devised for nutritional purposes and validated in specific soil–plant–climate contexts) are interpreted in terms of pollutant phytoavailability.

3.4 Deriving Pb and Cd limits for agricultural soils from plant uptake: Preliminary results

In Europe only few countries adopt screening values specific for agricultural soils (*Carlon*, 2007). The agricultural use of soil is often addressed by legislations deriving screening values on the basis of assumptions and modeling which differ from those applied to industrial and residential contaminated sites. In Italy, the Environmental Health Risk Assessment model (EHRA), based on a probabilistic estimation of exposure, was provided by the Italian Human Health Department (*ISS*, 2012) to support decisions relating to the management of agricultural contaminated sites. In deriving soil screening values (below which there is not apparent risk to human receptors) EHRA considers, above all, the risk associated to the ingestion of food-plants produced within the contaminated area. In this context, it is crucial to take into account the potential transfer of contaminants from soil to plant and to identify contaminant concentration values in plants (Cveg) for the protection of human health. The transfer of contaminants from soil to plant is associated with the bioavailability of the contaminants in soil which in turn depends on the characteristics of the soil as well as of the contaminants. In EHRA, transfer factors (TF) from soil to vegetables are defined as:

$$TF = Cveg/Csoil, \tag{1}$$

where C*veg* is the human health-risk based concentration of the contaminant in vegetables; C*soil* is the benchmark concentration of the contaminant in soil to be estimated expressed in mg kg^{-1} dry weight.

Applying this equation we estimated the benchmark concentrations of Pb and Cd in the studied soils below which no apparent risk to human health should arise from food-plants production. Firstly, with the paired total contents of Pb and Cd in soil (C*soil*, see Fig. 3) and vegetables (C*veg*, see Fig. 5) measured in our study area, the experimental TF values were calculated. Then, the benchmark C*soil* was derived as:

$$Csoil = Cveg/TF. \tag{2}$$

The TF values for Pb and Cd were calculated for each plant category and the values at 20^{th}, 50^{th}, and 90^{th} percentile are reported in Tab. 5. The TF values appear highly variable for most of the plant categories, but this is not surprising because the TF values are soil and plant-specific (*Smolders*, 2001; *Mirecki* et al., 2015). Furthermore, the TF values are not constant for any concentration of element in soil, but, as already reported in literature (*Adamo* et al., 2014; *Mirecki* et al., 2015), decrease as the element concentration in soil increases (data not shown). In our study there is no clear trend of TF values for the plant categories. At the 90^{th} percentile, "Root vegetables" and "Cereals" show the highest and lowest Cd TF values, respectively, while "Non-*Brassica* leaf vegetables" and "Cereals" show the highest and the lowest Pb TF values, but these trends are not the same at 20^{th} and 50^{th} percentile. In any case, the Pb TF values are always lower than Cd TF values for each plant category, indicating a higher plant absorbability of Cd with respect to Pb because of the higher mobility of Cd in soil and in accordance with other studies reported in literature (*Jolly* et al., 2013; *Mirecki* et al., 2015).

Considering the TF values at 20^{th}, 50^{th}, and 90^{th} percentile and as the C*veg* limit values defined for various fruits and vegetables by EC Reg. 1881/2006, the soil benchmark values for Pb and Cd (C*soil* = C*veg*/TF) were calculated (Tab. 5). Median Pb benchmark values for the studied soils ranged from a minimum of 59 mg kg^{-1} (for "Vegetables") to a maximum of 425 mg kg^{-1} (for "*Brassica* leaf vegetables"). For Cd this median range was from 0.2 (for "Root Vegetables") to 22 mg kg^{-1} (for "Non-*Brassica* leaf vegetables"). When the more precautionary TF values at 90^{th} percentile are considered, Pb and Cd benchmark values (mg kg^{-1}) ranged between 20 ("Fruits") and 96 ("Non-*Brassica* leaf vegetables"), and 0.01 ("Fruits" and "Root vegetables") and 3 ("not *Brassica* leaf vegetables"), respectively. Some of these benchmark values are unlikely low and in some cases lower than the background values of some areas of Campania Region (*Lima* et al., 2012), presumably highlighting difficulties and inadequacy of the EHRA model to face the problem of agricultural soil benchmark values definition.

4 Conclusions

Accumulation of potentially toxic elements in food plants resulting from cropping on contaminated agricultural soils is of major concern due to the potential human-health risk involved. The results of this investigation carried out in a National Interest Priority Site (NIPS) of Italy, where illegal waste dumping and burning were related to injuries to population health, show that the only PTEs occurring in 10–16% of analyzed soils in amounts above legal limits or natural background are Cu, Zn, Pb, and Cd. The low toxicity and the phys-

Table 5: Transfer factors (TF) and estimated benchmark concentrations of Pb and Cd in the studied soils (C*soil* in mg kg^{-1}). Only paired soil and vegetable samples with metal concentration > LOQ were considered; the "Legumes" category did not satisfy this condition for all samples.

Plant categories	Percentile	TF Pb	TF Cd	C*soil* Pb	C*soil* Cd
Brassica leaf vegetables	90th	3.9×10^{-2}	7.3×10^{-1}	50	0.9
	50th	1.7×10^{-2}	1.1×10^{-1}	425	8
	20th	5.7×10^{-3}	7.0×10^{-2}	540	35
Non-*Brassica* leaf vegetables	90th	1.2×10^{-1}	4.4	96	3
	50th	1.4×10^{-2}	4.9×10^{-1}	223	22
	20th	1.1×10^{-2}	1.1×10^{-1}	662	36
Cereals	90th	4.4×10^{-3}	6.3×10^{-1}	51	0.2
	50th	1.6×10^{-3}	3.2×10^{-1}	139	0.4
	20th	3.3×10^{-4}	1.8×10^{-1}	692	0.6
Fruits	90th	3.6×10^{-2}	31	20	0.01
	50th	5.0×10^{-3}	1.2	144	0.3
	20th	9.3×10^{-4}	5.2×10^{-2}	766	7
Root vegetables	90th	2.0×10^{-2}	67	26	0.01
	50th	2.4×10^{-3}	2.5	209	0.2
	20th	7.6×10^{-4}	1.2×10^{-2}	660	42
Vegetables	90th	4.7×10^{-2}	7.7	35	0.11
	50th	2.8×10^{-2}	2.3	59	0.4
	20th	2.1×10^{-2}	4.6×10^{-1}	80	1.8

iological concentrations of Cu and Zn in the edible organs of crops grown in the area would exclude any risk for human health due to the presence of these metals in crops. Based on consumption and concentration of Cd in the few most contaminated food plants, daily Cd intake values represent only a moderate risk for human health.

The results of this investigation unveil that the concentrations of PTEs in food plants are not related to changes in the total and bioavailable content of PTEs in soil following natural or anthropic pollution processes. However, our data suggest that both soils and plants (edible parts) can be considered reliable indicators of longstanding (mainly soil) and recent (mainly plants) pollution events.

Preliminary results defining agricultural soil benchmark values on the basis of the paired soil and plant data show large variability of transfer factors among and within plant categories. This means that the Environmental Health Risk Assessment model (EHRA), proposed by the Italian Human Health Department, needs further development and consideration. The general theoretical intuition behind EHRA approach may still be valid, but its empirical application to our data produces unlikely low values so that the majority of the studied soils would be unsuitable to be used for food-plants production. In the investigated area (Campania Plain) soil formation and properties are strongly affected by co-existence of volcanic and sedimentary materials, thereby influencing soil classification. This pedological peculiarity has a great influence on PTEs total contents and behavior in the soil environment and must be taken into consideration when Reference Values and Action Levels for Agricultural land use have to be established at a regional or sub-regional level.

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