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Potentially toxic elements in soils of Campania region (Southern Italy): Combining raw and compositional data

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ABSTRACT

Concern about health effect of Potentially Toxic Elements (PTEs) has led to an increasing global attention about their concentration levels in the environment. Soil geochemistry has been widely used as a tool for environment monitoring. This study investigates topsoil geochemistry of Campania region (Southern Italy) and (i) allows a reliable overview of the PTEs (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn) concentration in soils, (ii) enable the investigation of the main factors governing PTEs geochemical variation on a regional scale. Over 7300 topsoil samples were collected from the survey area, which occupies an area of about 13.600 km^2. Samples were analyzed for pseudo-total content of 53 elements (major and trace elements) by ICP-MS after aqua regia digestion. Data analysis was performed taking into account both raw data and their compositional nature as a tool for the PTEs environmental evaluation and origin investigation.

As, Be, Cu, Pb, Sn, Tl, V and Zn in soils of Campania region show higher median concentration levels than Italian and European ones. In addition, all PTEs exceed the residential/ recreational intervention limit (CSC^A) set by Italian legislation. The variation structure of compositional data had been visualized using compositional (clr) biplots and displaying the individual sample observations according to their parent rock. Clr-biplot analysis allowed us to recognize geochemical processes controlling most of soil chemical signatures. Multivariate analysis has been performed and three principal components were determined. PC1 is controlled by enrichment of elements deriving from dominant parent rocks of the area (siliciclastics and volcanoclastics). On the other hand, PC1 reveals the presence of an elemental association dominated by Na, K, U, Th, Zr, Ti, Tl and Be (clr variables), which are pathfinder element of soils developed from volcanic parent material. The second (PC2) component well discriminates the geochemical mobility of the elements in soils. The third (PC3) component reveal the presence of an anthropogenic association (Hg, Sb, Pb, Sn, Au, Ag) which depict a marginal contribution in soil geochemistry of the study area. The generation of clr-biplot helped us in a deeper interpretation of single element spatial distribution patterns. As, Be, Sn, Tl and V spatial distribution shows dominance in soil developed from volcanic products of the main volcanic complexes. Our study showed that element such as Be, Sn and Tl naturally exceed the contamination thresholds in almost the entire territory, due to a quite elevated background concentration values. Hence, Campania region con not be considered entirely contaminated (at this scale) by such elements. Co, Cd, Cr and Ni are more abundant where siliciclastic parent rocks occur.

1. Introduction

Potentially toxic elements are naturally occurring, ubiquitous chemicals in the soil environment which essentially originate from the weathering of parent materials and pedogenetic processes (Tazikeh et al., 2018) giving rise to spatial variability of their concentration levels. Nevertheless, population growth, rapid urbanization, exponential consumption of resources (land, food, water, air, fossil fuels and

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minerals), industrial activities and waste products have been leading in the last decades to PTEs remobilization, input and accumulation in soils. PTEs pollution has spread broadly over the globe, perturbing the environment and posing serious hazards to food safety worldwide and human health (Tóth et al., 2016; Atamaleki et al., 2019). About 2.8 million sites in Europe produce potentially polluting activities and the number of polluted sites is expected to increase worldwide (Payá Pérez and Rodríguez, 2018). Hence, PTEs occurrence in soil is one of the main concerns in the scientific and policy debate about geochemical data demand and health risk assessments. Geochemical mapping, performed at different sample densities and map scales, is considered to be the best available tool to report spatial variation of chemical elements concentrations. However, regarding Europe, there is no agency that is responsible for mapping at the global or even the continental scale. Hence, several soil survey and related researches on a global/continental (Salminen et al., 2005; Xie et al., 2012; Smith et al., 2014; Reimann et al., 2014), and national, regional and local scale (Cicchella et al., 2014, 2015, 2018; De Vivo et al., 2009, 2016; Ohta et al., 2015; Thiombane et al., 2018; Zuo et al., 2016; Zuzolo et al., 2018a) have been conducted by applied geochemist all over the world for different purposes, i.e., mineral exploration, assessment of soil quality providing broad and relevant knowledge about the geographical distribution of the elements. In recent years, this rising attention about environmental contamination has sometimes generated alarmism and strong public claim of soil remediation plans. Public awareness about environmental and health issues, pushed the political attention led the Regional Government of the Campania Region (Southern Italy) to implement a project named “Campania Trasparente”, funding the Istituto Zooprofilattico del Mezzogiorno (IZSM) aimed at the production of an integrated monitoring plan, for a better territory knowledge at regional scale. This in order to make clarity, separating often unjustified emotions from scientific evidence. This study is part of it and focused on topsoil geochemistry characterization.

Geochemical data are usually reported as concentrations in units of mg/kg or weight percent (wt%) and discussed as single variable (Cicchella et al., 2008a; Cicchella et al., 2015; Cheng et al., 2014; Gosar et al., 2016; Reimann et al., 2014) for documenting contamination (natural, anthropogenic or mixed) and predicting the spatial distribution (concentration) of a chemical element. However, from the statistical point of view, geochemical data are compositional and belong to closed system as each element is a part of a whole (Aitchison, 1986; Pawlowsky-Glahn and Buccianti, 2011; Buccianti et al., 2015). Several researches (Reimann et al., 2012; Buccianti et al., 2015) demonstrated that the interpretation of geochemical processes may be not fully captured taking only the absolute values or the logarithm of concentrations. The Compositional Data Analysis (CoDA) (Pawlowsky-Glahn and Buccianti, 2011) is an approach more appropriate to elaborate and interpret geochemical processes.

This study aimed to (i) enable a reliable overview of the concentration of PTEs (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn) in soils of entire Campania regional territory, (ii) better understand the compositional behavior in relation to parent rock material and human impact, (iii) identify areas with PTEs hazardous concentration levels.

2. Materials and methods

2.1. Background information of the survey area

The Campania Region is located in southwestern Italy and occupies an area of about 13.600 km^2 (Fig. 1). Sedimentary (limestones, dolostones, siliceous schists and terrigenous sediments)and volcanic rocks, spanning from the Triassic to recent age (Fig. 1), mainly represent the lithological outcrops in the study area. Several basins (Campanian Plain, Sele River Plain) mainly characterized by lacustrine - marine deposits, often alternating and covered by volcanics occur (Vitale and Ciarcia, 2013). Volcanic rocks consist of potassic and ultrapotassic lavas and pyroclastic deposits (De Vivo et al., 2010). In the last fifty years the landscape of the Campania Region (Southern Italy) has been strongly transformed by urban sprawl (which increased fivefold) and intensification of agriculture in the coastal plains and hills. Contemporary mountain areas and in the inland hills had been abandoned (Di Gennaro and Innamorato, 2005; Migliozzi et al., 2010). The main urban centers of the coastal strip has welded together in a metropolitan continuum which occupies approximately 15% of the region, from Caserta (North) to Sele Plain (South). This urban strip hosts about 72% of the population of the Campania Region, resulting in high anthropic impact and soil degradation (Migliozzi et al., 2010). Agricultural production represents one of the main economic activities of the Campania Region, as it is strongly positively influenced by the widespread presence of pyroclastic deposits. Despite the natural fertility of the soil, Campania is the foremost consumer of fertilizers in Southern Italy and nitrogen fertilizers represent 50% of the regional consumption per year (Albanese et al., 2007; ISTAT, 2013). More detailed description of geological and land use features of Campania region has been clearly emphasized by several authors (Lima et al., 2003; Thiombane et al., 2019; Zuzolo et al., 2018a).

2.2. Sampling and analytical procedures

“Campania Trasparente” project database on soils consist of 7300 surface soil samples (topsoil) and about 1500 bottom soils, collected from the Campania Region (almost 13,600 km^2). In this paper we only discuss data on top soils.Sampling density guarantee the representativeness of the entire regional territory. The sampling procedure and samples preparation followed the international guidelines established by GEMAS sampling protocol (Reimann et al., 2014). At each sampling site, 1.5 kg of soil was collected from a depth between 0 and 20 cm below the ground surface after removal of the vegetation cover. Each sample represents a composite material taken from each vertex of a 1 m square and its central point to provide a representative sample of the area, in accordance with internationally adopted method described in detail by Salminen et al. (1998). Field observations such as coordinates, topography, local geology, land use, and any additional detail related to anthropic activities in the surroundings were recorded on a field observations sheet at each sampling site. After being dried with infra-red lamps at a temperature below 35 °C (to avoid mercury volatilization), the 7300 samples were sieved to retain the 2 mm fraction (which correspond to the fraction where the vast majority of the reactive surfaces in soil are found) excluding any gravel or larger detritus (≥2 mm, wherein elements may be physically protected). The sieved samples were analyzed after the aqua regia digestion (Bureau Veritas Minerals, 2017), using a combination of inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) analyses to determine the “pseudototal” concentration of 53 (major and trace) elements. The pseudo-total term is used due to incomplete dissolution of the soil mineral matrix using an aqua regia digestion and is useful to evaluate the potential risk (Gupta et al., 1996).

2.3. Data analysis and map production

Statistical data analysis was carried out using R which is a free software environment for statistical computing and graphics. Values below the detection limit were replaced by half of the detection (Birke et al., 2017). Descriptive statistic was summarized and it included minimum, maximum, mean, median, percentiles, standard deviation, median absolute deviation, robust coefficient of variation (Table 1). The last two parameters represent robust measure of spread (Reimann et al., 2008). Classical statistical and spatial data analysis of raw data were performed. However, geochemical data are compositional and this aspect should be considered to reduce the influence of data closure in

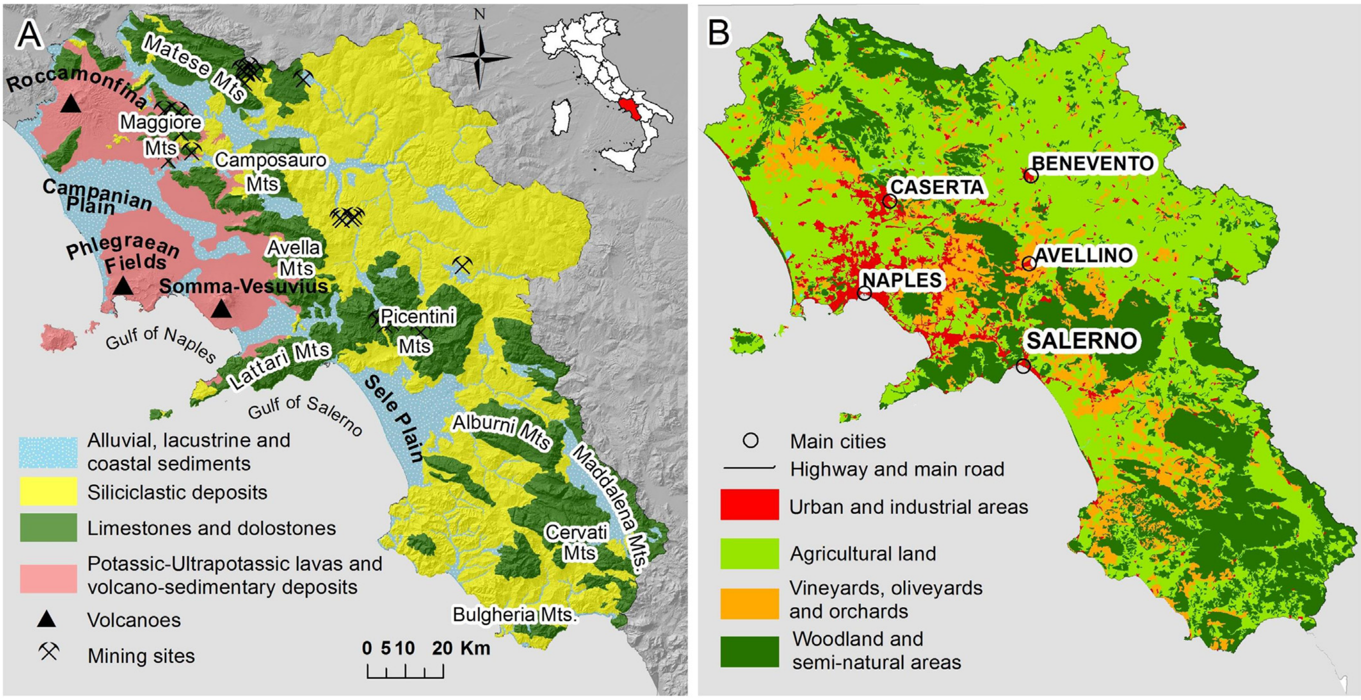

Fig. 1. Simplified geological map (A) and land use (B) of the Campania region (southern of Italy).

the identification of geochemical processes (Liu et al., 2016). In geochemistry, compositional data are obtained transforming the original raw data (i.e. mg/kg or % of an element in a sample) into new variables which describe quantitatively relative contributions to a whole (Aitchison, 1986; Pawlowsky-Glahn and Buccianti, 2011; Buccianti et al., 2015). The centered log-ratio (clr) transformation (introduced by Aitchison, 1986) is one of the prevailing function adopted in geochemical studies (Boente et al., 2018) to account for compositional nature of geochemical data and remove closure effect. It uses the geometric mean to normalize the composition. Hence we considered this type of log-ratio transformation to open our data and better visualize their multivariate structure, constructing the compositional (clr) biplot (Aitchison and Greenacre, 2002; Filzmoser and Hron, 2011).

2.4. Compositional (clr) biplot

The biplot is a widely and powerful 2D graphical representation used with multivariate data sets to describe and display the relationships between observations and variables which are expressed as dots and rays, respectively (Kempton, 1984). The singular value decomposition and its interpretation as a linear biplot has proved to be a powerful tool for analyzing many forms of multivariate data. Here we applied the clr-biplot methodology, which adapt to the case of compositional data. Aitchison and Greenacre (2002) and Otero et al. (2005) stated that the clr-biplot facilitates the analysis of all geochemical variables. In the clr-biplot, rays and links provide information on the variability of a logratio in a compositional data set. Rays represent the log-ratio and the lengths of the rays are directly proportional to the clr-variance of the corresponding chemical element included in the two components displayed. The length of the ray cannot be interpreted as a single original part but as a representation of its dominance to an "average part" in the composition (Filzmoser et al., 2012) The distance between two log-ratio can be indicated by the link (vector connecting the endpoints) between the two rays vertices. Hence, the closer the vertices are, the more proportional the concentrations of the chemical elements are (Aitchison and Greenacre, 2002). The angle between any two rays provide information about the correlation between the log-ratios. Consequently, the orthogonality of the links suggests that uncorrelation of the log-ratios can be expected (Thiombane et al., 2018). The clr-biplot was achieved using CoDaPack software (Comas-Cufí and Thió-Henestrosa, 2011), which returned, as a numerical result, the Principal Components and the cumulative proportion explained with each component.

3. Results and discussion

3.1. Geochemical pattern identification

The generation of clr biplot (Fig. 2) allows us a better interpretation of single element distribution and spatial patterns. It explains almost all Euclidean variability (~70%) based on 31 elements. Of the 53 elements analyzed, we focused on the complete cases (5533 samples) of the 30 elements to better understand and reveal the relative multivariate compositional structure. The first three Principal Components (PC1, PC2, and PC3, accounting for 39%, 20%, and 9%, respectively as shown in Table 3).

The fingerprint of the parental material is well recognizable even if complex processes related to the soil formation have generated wide overlaps in soil chemistry (as also stated in Buccianti et al., 2015). High scores on the first principal component (Fig. 2A and B) refer to clay-dominant soils developed from siliciclastic deposits, which are characterized by a dominance of Fe, Mn, Ni, Co, Cr, (clr variables) for instance, where a dominant role is played by the presence of Mn and Fe hydroxides, which determine the co-precipitation of other elements, such as Ni, Co, Cr (Quantina et al., 2002). Such elemental suite is characterized by relative immobility, compared to other more mobile elements. On the other hand, the compositional biplot better distinguish samples from different parent rock material (Fig. 2B), along the first principal component. PC1 depicts the presence of two cluster of elements (clr variance) both reflecting the potassic and ultrapotassic rocks formations (Peccerillo, 2019 and ref. therein) from which soils developed: U, Th, Zr, Ti, Tl and Be on one side and Na,K on the other. These two different group characterizing samples with volcanic parent material well reflect the age of volcanic products, which span from 0.6 Ma up to our recent time: the relative enrichment of Na and K is a pathfinder of younger volcanic lithologies, strongly pronounced in soils

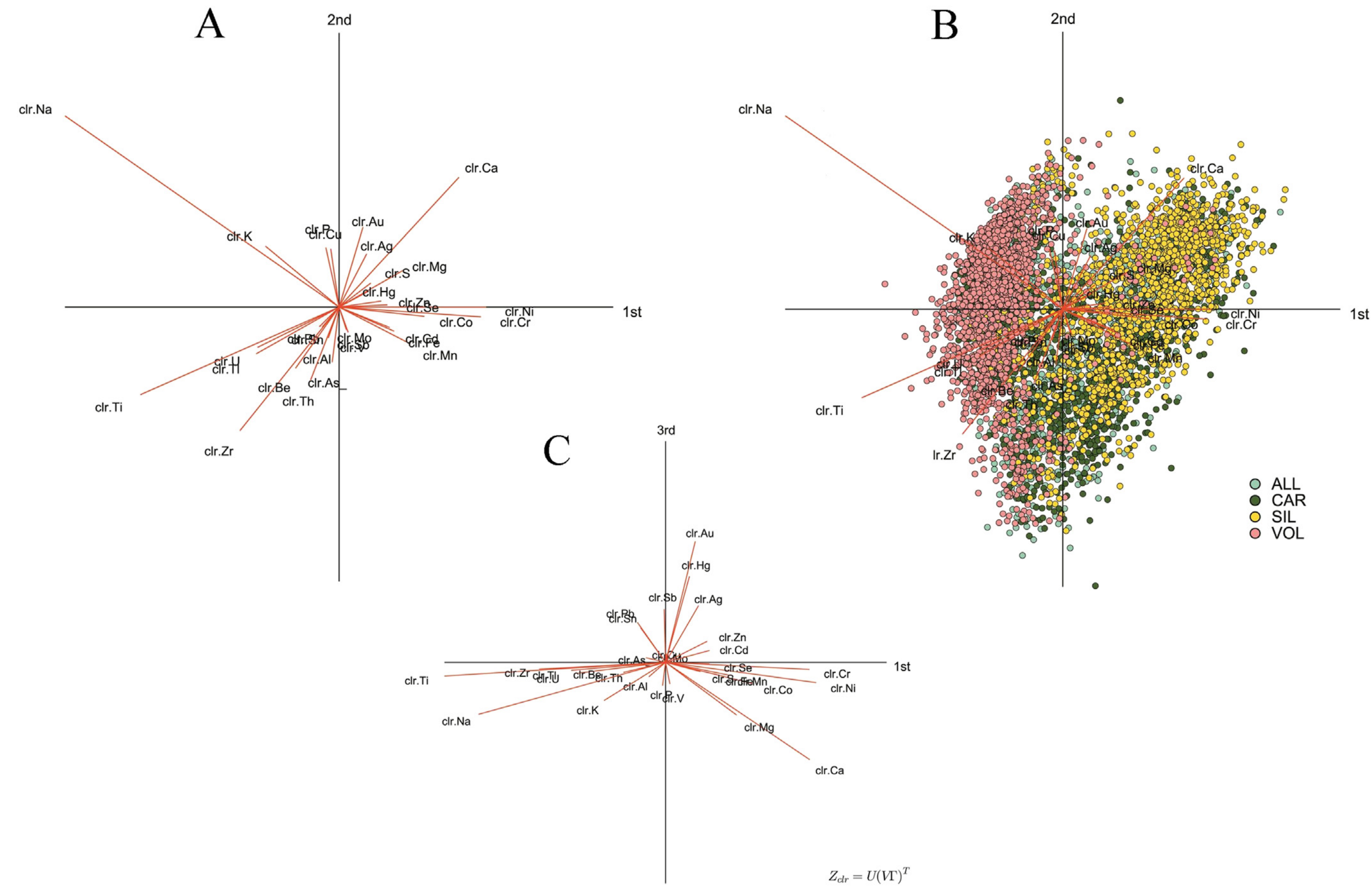

Fig. 2. Clr-biplot of the full composition of Campania topsoil dataset (n = 5533). The left plot (A) displays the 1st and 2nd component without the individual sample observations; the right plot (B) shows association between variables and the observations distributed according to their parent rock: ALL = alluvial, lacustrine and coastal sediments, SIL = siliciclastic deposits, CAR = carbonate rocks, VOL = volcanoclastic deposits. (C) displays the 1st and 3rd principal components.

of the Vesuvian area (as shown in Thiombane et al., 2019). The clr-variance of Pb and Sn logratios in the first two components is negligible (indicating no dominance of such elements on the whole) even if the angle suggest a good correlation with this group. The volcanic cluster (a1, see Table 3) stands in opposition to Ca along the first principal component, which is interpreted as the relative enrichment effect of Ca input in soils in correspondence of siliciclastic-carbonate deposits.

PC2 approximates elemental geochemical mobility in soil: losses by surface runoff and leaching of mobile element such as Ca, K, Na and P (depletion) leading with time to a passive enrichment of Th, Ti and Zr (a4 group, see Table 3), which are considered to be immobile elements (Stiles et al., 2003). Mobile elements derive mainly from leachable minerals such as apatites, feldspars and micas, whereas immobile elements are either concentrated in residual phases or strongly adsorbed by secondary minerals (Middelburg and van der Weijden, 1988). Very shorts ray in Fig. 2A represent elements such as Hg, Sb, Pb, Sn indicating that the first two components not fully capture their behavior. In fact, these elements present a high length of communality contributing to the (a5) group (Hg,Sb,Pb,Sn,Au,Ag, see Table 3) and may suggest the effect of an anthropogenic enrichment, since they have no relationship with pathfinder logratios of volcanic soils (e.g., Th,Be,-Ti,Tl,U,Na,K) as displayed in Fig. 2C. Clear enhancement in Au and Ag have been recognized in correspondence to the main urban areas of Campania region (Zuzolo et al., 2018a). Nevertheless, the aforementioned anthropogenic association (a5) reveal an overall marginal contribution in soil geochemistry of the study area. Hence, the majority of soil chemical features are controlled by parent rock material and weathering (geochemical and pedochemical) processes, which normally have a large influence on the nature of the resulting soil.

3.2. *Potentially toxic elements concentrations in topsoil of Campania region (Southern Italy)*

Summaries of elemental concentrations are fundamental starting

Table 3
Explanation of the first three Principal Components (PCs) extracted from the clr-transformed data of the Campania (Southern Italy) topsoil database. Cumulative proportion explained with each component is showed.

Component	% of variance explained	Association	Interpretation
PC1	39	(a1)Ca,Ni,Cr,Co,Mg,Mn,Fe,Cd,Zn	(a1) Reflects siliciclastic deposits underlying the study area
		(a2)Th,Be,K,U,Tl,Zr,Na,Ti,As	(a2) Reflects volcanic parent rock material underlying the study area
PC2	20	(a3)Na,Ca,K,P	(a3) Indicate parts that are mobile during weathering
		(a4)Ti,Th,Zr	(a4) Indicate enrichment of such parts in intensely weathered soils.
PC3	9	(a5)Hg,Sb,Pb,Sn,Au,Ag	(a5) suggest the effects of elemental anthropogenic enrichment
		(a6)K,Na,Mg,Ca	(a6) Reflects enrichment of alkali metals in soils which are commonly involved in plant nutrition

Table 1
Statistics of PTEs from multi-element database (n = 7300) of Campania region (Southern Italy).

Element	MIN	P5	MEDIAN	MEDIAN Italian soils[a]	MEDIAN European soils[b]	MEAN-log	MEAN	P75	P95	MAX	SD	MAD	CVR %
As	0.6	3.5	11.7	7.6	5.5	10.5	12.3	15.1	21.6	930.3	14.3	5.5	46.9
Be	0.1	1	4.7	0.8	0.5	3.8	4.6	6.3	8.5	17.9	2.4	2.8	59.9
Cd	0	0.1	0.3	0.3	0.2	0.3	0.4	0.5	1.3	11.1	0.5	0.2	62.2
Co	0.8	5.1	12.1	11.7	7.5	11.4	12.5	14.8	21.1	88	5.3	4.2	34.3
Cr	0.8	6.4	19.3	33.6	20	19	24	30.9	51.2	808.4	24.6	12.6	65.3
Cu	2.5	19.2	50.4	32	15	59.4	86	106.8	249.5	2394	97.2	35.2	69.9
Hg	0.003	0.016	0.041	0.033	0.03	0.046	0.07	0.1	0.2	6.8	0.1	0	61.5
Ni	0.4	5.4	17.1	31.5	15	18.2	22	28.9	47.4	155.6	14	9.2	53.8
Pb	3.1	13.9	47.1	22.0	16.0	45.3	59.9	66.6	139.6	2052.2	70.8	27.2	57.7
Sb	0.01	0.17	0.52	0.30	0.20	0.54	0.79	0.79	2.07	42.80	1.42	0.30	57.02
Se	0.1	0.1	0.4	0.4	0.4	0.3	0.4	0.5	0.8	2.4	0.3	0.3	74.1
Sn	0.2	0.9	2.9	1.0	0.7	2.7	3.5	4.1	7.9	125.6	4.5	1.8	61.3
Tl	0.1	0.2	1.4	0.2	0.1	1.1	1.4	2.0	2.6	69.0	1.1	0.9	67.6
V	4	26	65	34	25	61.2	67.7	89	115	234	28.5	32.6	50.2
Zn	3.9	45.9	85.9	62.0	45.0	89.7	103.6	110.8	210.4	3210.6	91.1	30.2	35.2

[a] = agricultural soil (Ap) samples of Italy (Cicchella et al., 2018); [b] = agricultural soil (Ap) samples of Europe (Reimann et al., 2014); Min = minimum value; P = percentile, P5 = 5th percentile, P75 = 75th percentile, P95 = 95th percentile; MEAN-log = the geometric mean (equal to the mean of the log transformed data-back transformed); MAX = maximum value reported; SD = standard deviation; MAD = median absolute deviation standardised to conform with the normal distribution; CVR: robust coefficient of variation. (per cent). n = 7300, all values in mg/kg.

point of any geochemical study. The main statistical parameters for 15 PTEs in topsoil of Campania region (Southern Italy) are presented in Table1. Data were also compared to the contamination thresholds (CSC) established by Italian legislation for soils (Legislative Decree 152/2006, 2006), in order to discuss our results. The Italian legislation set two different contamination thresholds: CSC^A corresponding to the concentration limit for residential/ recreational use of soil and CSC^B as concentration limit for commercial/ industrial use of soil. These values are shown in Table 2, with the corresponding percentage of sample exceeding them. Our data showed that As, Be, Cu, Pb, Sn, Tl, V and Zn in soils of Campania region have a median concentration level higher (almost double) than Italian and European ones, suggesting a regional geochemical enrichment of such elements. In the majority of cases MEDIAN and MEAN-log are comparable, while they are considerably lower than the MEAN, indicating a right-skewed distributions for all elements. Accordingly to MAD and CVR% values in Table 1, the homogeneity/stability of PTEs in the survey area is considerably lower suggesting that these elements occurrence may be part of different processes. In particular, CVR% (which is independent of the magnitude of the data and thus of the data measurement units) may give a first idea of the high elemental spatial variability in our study area.

Elements such as Sn, Be, Tl, V, Cu, Zn and Pb are also characterized by the highest percentage of samples above the CSC^A. The Sn, Be and Tl percentages shown in Table 2 seem impressive since more than half of the samples would seem "contaminated" compared to the Italian legislation. Nevertheless, exceeding of CSC^B can be considered negligible for all elements, with the exception of Be characterized by 84 (about 1.15% of total sampling point) "contaminated" samples. However, previous studies at national scale (Cicchella et al., 2015) determined that these elements naturally exceed Italian statutory limit for soil due to their geogenic source (Peccerillo, 2019, and ref. therein), with consequent high background concentrations (e.g., Be and Sn exceed the limit for residential/recreational use of soil on the whole territory of southern and central Italy).

3.3. *Potentially toxic elements spatial patterns in topsoil of Campania region (Southern Italy)*

Spatial patterns of element variation in soil were constructed according to MIDW interpolation and classified into nine classes by Concentration Area (C-A) plot in order to better interpret their occurrence, geochemical abundance and spatial variability. The C-A plot is useful to consider the spatial scale of the distribution of the data in selecting thresholds of the distribution function, by looking at the fractal structure of the data (Cheng et al., 1994; Cheng and Agterberg, 1995; Reimann et al., 2008; Zuo and Wang, 2016). Moreover the elemental spatial distribution of sampled points exceeding the contamination threshold (CSC^A and CSC^B) set by Italian legislation (Legislative Decree 152/2006, 2006) is presented as dot map.

Table 2
Percentage of PTEs in topsoil samples from Campania region (Southern Italy) exceeding [(A)] the Italian statutory limit for residential use of soil (Legislative Decree 152/06, 2006).

Element	CSC^A	CSC^B	% of samples above CSC^A	% of samples above CSC^B
As	20	50	7.45	0.42
Be	2	10	63.77	1.15
Cd	2	15	1.82	0
Co	20	250	5.33	0
Cr	150	800	0.30	0.01
Cu	120	600	22.42	1.01
Hg	1	5	0.32	0.01
Ni	120	500	0.01	0
Pb	100	1000	10.35	0.10
Sb	10	30	0.25	0.04
Se	3	15	0	0
Sn	1	350	73.20	0
Tl	1	10	61.69	0.05
V	90	250	23.80	0.00
Zn	150	1500	11.00	0.05

CSC^A is the contamination thresholds for residential use of soils established by Italian legislation for soils (Legislative Decree 152/2006, 2006); CSC^B is the contamination thresholds for industrial/commercial use of soils established by Italian legislation (Legislative Decree 152/2006, 2006). All concentrations are in mg/kg.

3.3.1. *Be, Tl, Sn*

The previously presented summaries of elemental concentrations showed that Be, Tl and Sn data are have peculiar characteristics given that they are abundantly present in all the analyzed samples. Looking at their spatial distribution (Fig. 3) it is evident that Be distribution is defined by two distinct populations of data: the first one with Be concentration values lower than 4.1 mg/kg and the second one with Be data above that concentration. The latter defines a large Be enrichment, mainly concentrated in topsoils developed directly over pyroclastic deposits and over carbonate massifs characterized by the presence of

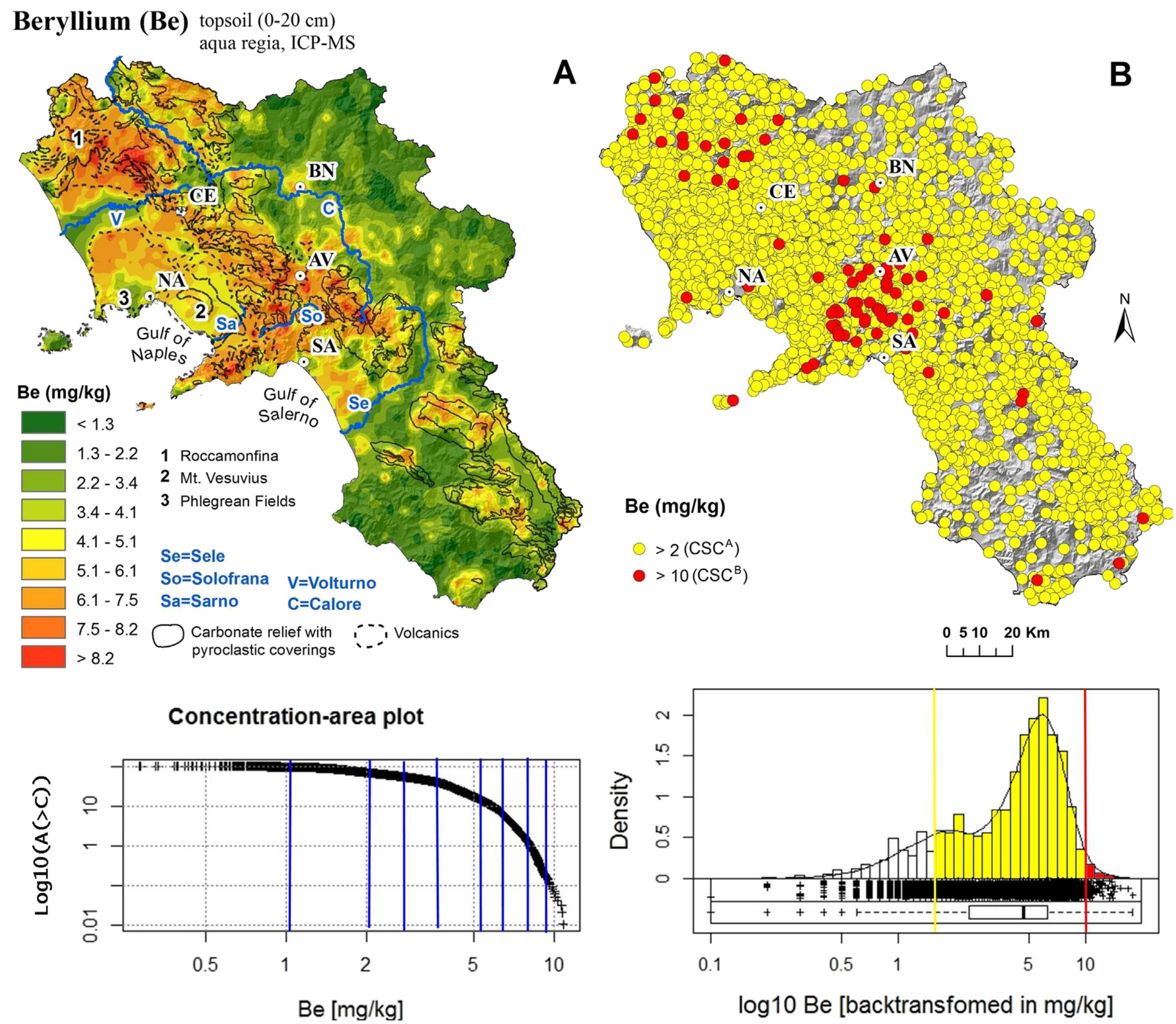

Fig. 3. Spatial distribution of Be in topsoil of Campania region (southern Italy). A) interpolated map classified according to Concentration-Area (CA) plot (lower left). B) Dot map illustrating the Be data exceeding the CSC[A] (contamination thresholds for industrial/commercial use of soils) and CSC[B] (contamination thresholds established by for residential use of soils) set by Italian legislation (Legislative Decree 152/2006, 2006); these data are also displayed in edaplot (bottom right).

widespread pyroclastic coverings. Berillyum concentrations close to the average (4.1–6.1 mg/kg) are found all around the Mt. Somma-Vesuvius. Conversely, the highest Be concentration (> 8.2 mg/kg) is found around the Roccamonfina volcanic complex and in the southeastern part of the Mt. Vesuvius (from the Sorrento Peninsula to Avellino). In these areas many samples exceed the intervention limit for commercial/industrial use of soil (CSC[B]), which are visible as two separate cluster (Fig. 3B). The Be enrichment in soils of these areas can be explained by different processes, both natural. In the eastern part of the Mt. Somma-Vesuvius volcanic products of the Ottaviano (~8000 BCE) and Avellino (~3800 BCE) eruptions are present (Di Crescenzo et al., 2007). These volcanic products are particularly enriched in incompatible elements, such as B, Be and Li (Paone, 2008; Peccerillo, 2019). In particular, Be concentration in Ottaviano and Avellino volcanic product (26–30 and 14–31 mg/kg, respectively) is double compared to the those of other Plinian eruptions (Paone, 2008), due to the longer period of magma differentiation and the magma deriving from mantle wedge significantly enriched in Pb, B and Be-containing sediments (Paone, 2008). The source of Be enrichment in soils all around Roccamonfina may be the same of that found on the carbonate massifs, where are present as well covers of pyroclastics from different Ignimbrites events (De Vivo et al., 2001; Rolandi et al., 2003; Rolandi et al., 2019). Petrik et al. (2018a) suggested that Be anomaly in topsoils developed over the oldest pyroclastic deposits in Roccamonfina and over carbonatic massifs is mainly due to advanced pedogenesis processes, which led to the development of strongly altered Eutrisilic Andosoils and 'terra rossa' soils. Terra rossa is the chemical weathering product of limestone (with karstic nature) under oxidizing conditions excelled by climate conditions, especially in the Mediterranean regions. The spatial patterns of Be in topsoils of Campania region may support the hypothesis of other authors (Liu et al., 2013; Muhs and Budahn, 2009; Yaalon, 1997; Sandler et al., 2015; Vingiani et al., 2018) that terra rossa cannot have been formed exclusively from authoctonous source (e.g., the insoluble residue of chemical weathering of carbonate rocks), but they might have received external materials, such as volcanic ash, alluvial mud or eolian dust, during pedogenesis. Exceeding of contamination threshold is well spatially distributed on the whole territory, due to the natural high concentration of Be in soils of Campania region and, more extensively, of the whole territory of southern and central Italy, covered by layers of pyroclastics from the different explosive eruptions occurring in the Campania region (De Vivo et al., 2010; De Vivo et al., 2019).

The same feature is highlighted by Tl and Sn point distribution (Figs. S1 and S2 in Supplementary material), characterized by samples above the CSC^{A} covering more 50% of whole territory. The spatial distribution pattern of Tl is very comparable with that of Be, suggesting a common origin. Tha C-A classified map of Tl (Fig. S2) depict two distinct data populations: the first under and the second over the concentration of 1.2 mg/kg. Thallium abundance and distribution is related to topsoils developed over alkali pyroclastic rocks, since k-alkaline rocks are particular enriched in Tl (Calderoni et al., 1983). Moreover, Calderoni et al. (1985) found that at Roccamonfina Fe and Mn enriched sediments are powerful Tl sink. Iron is also one of the major clay's chemical elements of the "Terra rossa", probably deriving from dissolved eolian dust (Merino and Banerjee, 2008). The C-A classified map of Sn (Fig. S2 A and S2B) reveals the presence of different patterns of geogenic and anthropogenic origin. Areas covered by Sn concentration lower than 3.1 mg/kg are found where siliciclastic formation occurs, characterized by lower Sn natural background values. (De Vivo et al., 2016; Cicchella et al., 2018). Conversely, Sn topsoil content ranging from 3.1 and 11 mg/kg essentially derive from geolithological control, due to the development of soils on volcanic rocks (as it is for Be and Tl). However, the C-A classification allows to discriminate local hotspots (with the highest Sn values > 19 mg/kg) for which the anthropic source contribute cannot be excluded.

3.3.2. As, Se, V

The C-A map showing As spatial distribution (Fig. 4) highlight the presence of As enrichment related to volcanic rocks and pyroclastic ashfall sediments around large volcanic edifices. However one of the most noticeable high As area (> 21 mg/kg) with several samples exceeding the intervention limit for residential use of soil (CSC^{A}) can be followed in a NW–SE direction (as also previously found by Petrik et al., 2018b) which coincides with the presence of the carbonate massifs characterized by the presence of pyroclastic ashfall sediments. The elevated abundance of As, in these zones could be explained by a double sources (allochtonous and authoctonous, respectively), as also found for Be. The presence of a pyroclastic covering could be the primary "allochtonous" source of high As concentration in this areas. In addition, the development of "terra rossa" soils led to As enrichment (as well as for other element), since it tends to adsorb to clay minerals, secondary Fe-, Al-oxy-hydroxides and organic matter (Reimann et al., 2009). Anomalous As distribution pattern (above 50 mg/kg, which also correspond to CSC^{B}) are visible all around Bagnoli brownfield site. This metal(loid) enrichment is due to springs and spas active in volcanic geothermal systems (Albanese et al., 2010; Minolfi et al., 2018a). This is also confirmed in the waters of spas of the volcanic area of Ischia island (e.g. As average of 155 μg/l, with values up to 1500 μg/l, Lima et al., 2003).

Regarding Se distribution, C-A map (Fig. S3 in Supplementary material) shows that soil of inlands are impoverished, with values < 0.175 mg/kg, which correspond to the reference threshold value for the risk assessment of soil potentially Se deficient (Tan et al., 2002). Reimann et al. (2014) set that large parts of Europe's agricultural soil is deficient in this element, while excessive concentrations (> 0.881 mg/kg) can be reached along coastal areas due to the steady input via marine aerosols in combination with a strong affinity to bind to organic matter in soil. Our high density Campania soil data don't highlight a strong coastal effect. An enrichment is found in alluvial plains (Sele, Volturno, Solofrana and Sarno) and where "Terra rossa" soil occurs. As a matter of fact, the behaviour of Se in highly calcareous soil is of special concern, because Se becomes easily water soluble when soil is low in sesquioxides (Kabata-Pendias, 2010). Thus, since Terra rossa is characterized by accumulation of hydrate iron sesquioxides, Se enrichment is explained. It is notable that no sampled soils exceed Se intervention limits (both CSC^{A} and CSC^{B}), whereas a large part of these soils are Se deficient.

Spatial distribution patterns of V (Fig. S4 in Supplementary Material) follow quite well those of elements such as Be and As, suggesting a common double source, which is both geogenic and pedogenetic (as widely discussed for these elements). Generally, V naturally present in soil has a low mobility and tends to sorb to Fe and Mn-hydroxides, clay and organic matter. It's remarkable that the V concentration in volcanic rocks from the Phlegraean Fields (40–55 mg/kg) is a half or even one-third lower than those found around Roccamonfina and Mt. Somma-Vesuvius volcanic complexes. This difference could be probably related to the different eruptive age of the mentioned volcanic complexes (Campi Flegrei, overall, younger than Mt. Somma-Vesuvius and Roccamonfina), therefore reflecting different stages in pedogenetic processes (Zuzolo et al., 2018b).

3.3.3. Co, Cd, Cr, Ni

The CA-classified Ni concentration map (Fig. S5 in Supplementary material) reveals two distinct populations of Ni values (one less and one above 22 mg/kg). The first one, indicating low content Ni areas, falling in correspondence of soils developed over volcanics. An increase in Ni content is found toward silico-iclastic rocks. The threshold limit for Ni (120 mg/kg) for residential areas set by the Italian legislation (D Lgs. 152/2006, 2006) is exceeded by only one sample, which falls within a high content Ni area, in the northern part of Benevento province, which is characterized by outcropping of siliciclastic sediments (clays, marls, sandstones, conglomerates) and flysch units. In the same quite elevated concentrations of Mn (up to 5599 mg/kg) are present (Zuzolo et al., 2017). The presence of Mn oxides and their high sorption capacity determines co-precipitation and consequent enrichment of trace elements such as Co, Cr and Ni (Quantina et al., 2002). This is confirmed by the strong association (also revealed by the clr-biplot) between Ni, Cr and Co. Other high values (> 55 mg/kg) can be found in soils developed on sedimentary and calcareous units, such as the Vallo di Diano, Alburni Mountains, up to the southern coastal areas. Here Ni tends to accumulate in alkaline soil, due to its tendency to be absorbed by clay minerals and Fe—Mn hydroxides. In these areas the higher content of Cr (> 40 mg/kg) was also found (Fig. S6 in Supplementary material). Chromium anthropic contamination in the Solofra basin is likely related to the tannery district, which is potentially the principal source of this element (Albanese et al., 2013).

The C-A classified map of Co (Fig. S7 in Supplementary material) underlines high Co levels in the southern sector and the eastern area related to reduction of its mobility due to the adsorption and co-precipitation effects operated by Fe and Mn oxides and hydroxides occurring mostly in the sedimentary deposits such as marl-sandstone, conglomerate and siliciclastic flysch deposits. The soils developed from these type of rocks are characterized by high Co natural levels. Regarding to The spatial distribution of Cd shows remarkably high values (> 3.8 mg/kg) where Terra rossa soils occur (Fig. S8 in Supplementary material), in correspondence of carbonate massifs (Matese, Alburni and Cervati Mts). Cadmium has been proved to be remarkably high in this type of soils also in other Italian regions (e.g., Sicily), due to its strong affinity for Mn oxides in soils (Bellanca et al., 1996). The association of Cd with Mn-oxides is of considerable importance in environmental assessment because its mobility and consequently the bioavailability may be significantly increased in moderate reducing conditions (Bellanca et al., 1996).

3.3.4. Hg, Pb, Sb, Zn

The spatial distribution of Hg abundance is associated with the most urbanized areas of the region (Fig. S9 in Supplementary material). The C-A interpolated map (Fig.S9 A) shows concentration > 0.35 mg/kg in correspondence of Naples and Caserta, where intensive vehicle traffic

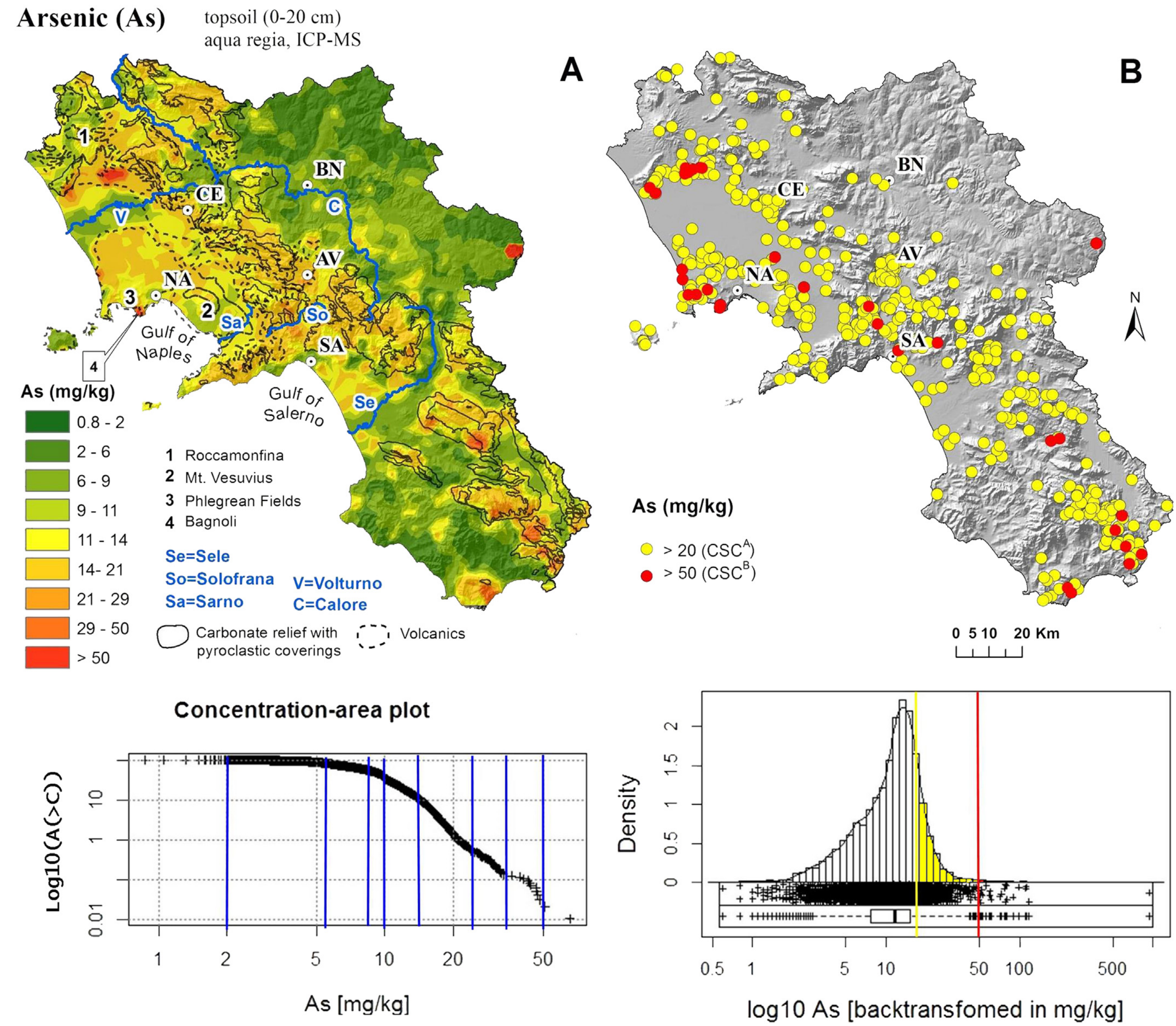

Fig. 4. Spatial distribution of As in topsoil of Campania region (southern Italy). A) interpolated map classified according to Concentration-Area (CA) plot (lower left). B) Dot map illustrating the As data exceeding the CSC^A (contamination thresholds for industrial/commercial use of soils) and CSC^B (contamination thresholds established by for residential use of soils) set by Italian legislation (Legislative Decree 152/2006, 2006); these data are also displayed in edaplot (bottom right).

occurs. Anomalous Hg content has been found also in correspondence of the Phlegraean Fields, corresponding to the upper limit of baseline values (Cicchella et al., 2005) and sourced from hydrothermal activity of volcanic centers (Tarzia et al., 2002; Lima et al., 2003; De Vivo et al., 2016). In this area Bagnoli brownfield site falls, and different authors (Tarzia et al., 2002; De Vivo and Lima, 2018; Albanese et al., 2010) stated the existence of a local overlap of PTEs contamination from geogenic (mainly hydrothermal) and anthropogenic (industrial) sources. Scattered Hg spot contaminations exceeding Italian legislation thresholds, can be found between Naples and Caserta provincial territories. Among these, the Hg soil anomaly around Acerra is remarkable (> 5 mg/kg) and is potentially related to the presence of a waste incinerator plant. Petrik et al. (2018c) also hypothised that some high abundances of Hg in soils of Campania region might be related to dense fault networks and precipitation rates (the latter promoting organic-rich topsoils accumulating Hg).

As regards Pb, its spatial distribution (Fig. 5) is controlled by different processes both geogenic and anthropogenic ones. The C-A plot highlights that the concentration of 50 mg/kg correspond to the enrichment threshold. Value lower than this threshold can be found in the eastern part of the Apennine chain, to the south of Matese Mts, where various silico-clastic rocks are the main parent material from which soils developed. A NW-SE trending moderate concentration zone (35–50 mg/kg) almost coincides with the carbonate massifs of the Apennine chain characterized by widespread pyroclastic coverings (Minolfi et al., 2018b). This NW-SE trend approximately separates the low Pb value area (in the east) with the high Pb concentration zone (in the west), as also displayed for other element distribution such as As, Be, Tl and Sn. The higher Pb content in the western area is related to the overlapping of soil volcanic source and the presence of the highest urbanized areas of the region. In the latter areas the concentration of 65 mg/kg has been assumed as the lower limit of natural background value (De Vivo et al., 2016). Hence, values above it can be considered anomalous and pollution related. As matter of fact, the Pb contaminated areas are certainly influenced by vehicular traffic and roads network. Other previous studies confirm the mixing between geogenic

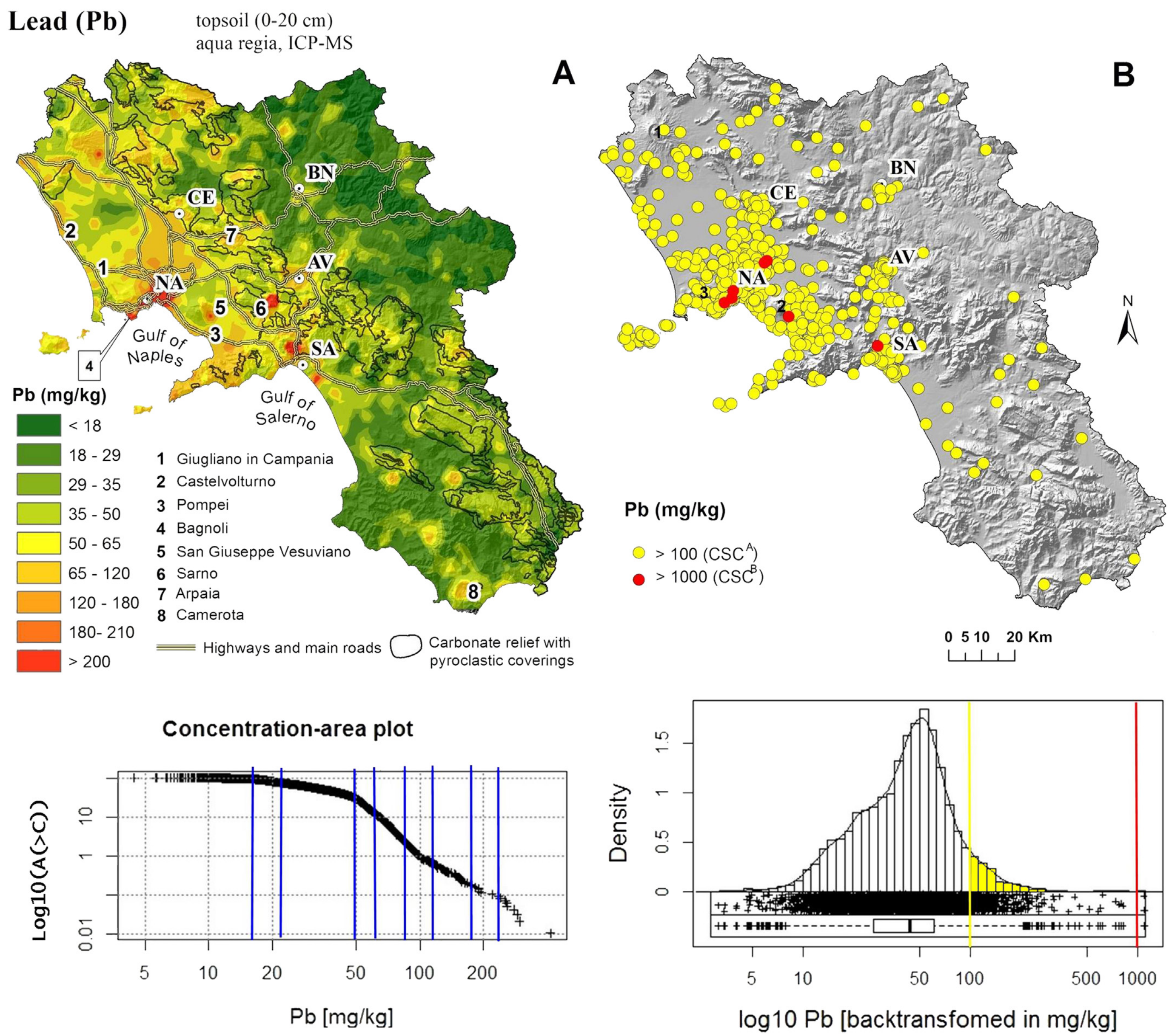

Fig. 5. Spatial distribution of Pb in topsoil of Campania region (southern Italy). A) interpolated map classified according to Concentration-Area (CA) plot (lower left). B) Dot map illustrating the Pb data exceeding the CSC[A] (contamination thresholds for industrial/commercial use of soils) and CSC[B] (contamination thresholds established by for residential use of soils) set by Italian legislation (Legislative Decree 152/2006, 2006); these data are also displayed in edaplot (bottom right).

and anthropogenic sources based on Pb isotope data (Cicchella et al., 2008b; Rezza et al., 2018).

Similar pattern distribution occurs for Sb and Zn (Fig. S10 and Fig. S11 in Supplementary material, respectively). Cicchella et al. (2005) established that areas characterized by intermediate values (between 1 and 3 mg/kg) might reflect both geogenic and anthropogenic contribution. Hence, areas with Sb content > 3 mg/kg may be considered polluted. The high Sb zones correspond to the urban area of Napoli, which have clearly an anthropogenic origin due to motor vehicle traffic as also showed for Pb. Overall, most of the regional territory shows low content of Sb in soils, except for high densely populated areas where few samples exceed the contamination thresholds. The distribution of Zn concentration data (Fig. S11 in Supplementary material) reveals high spatial continuity of elevated concentration levels (> 55 mg/kg) following the metropolitan continuum which occupies approximately 15% of the region, from Caserta (North) to Sele Plain (South). It is interesting to note the high Zn contents in soils sampled on the carbonate relief, where weathering led to formation of terra rossa soil. Vingiani et al. (2018) found that element such as Cr, Cu, Zn, Ni, As and Pb are highly concentrated in terra rossa soils and their content is higher than that of European soils in general. In addition, Bellanca et al. (1996) found that Zn (and also Cr) is mainly present in the 'residual' fraction, where well crystalline Fe oxides probably remain along with silicate phases. Hence, in these areas its bioavailability should be negligible.

3.3.5. Cu

The Cu map (Fig. S 12 in Supplementary material) shows the highest concentration values in the vesuvian area (> 350 mg/kg), controlled by the volcanic origin of soils and by the secondary volcanic activity. Neverthless, here these high concentrations are most probably related as well to the agricultural activities (mostly vineyards) taking place on the slopes of the volcano, indicating an overlap of different sources (one geogenic and the other anthropogenic). Other anomalous Cu content in soils (> 78 mg/kg) are evident in correspondence of most "wine regions". In fact Cu is plenty used as a fungicide in vineyards and in 2016 > 3 thousand tons of fungicides (including Cu-based inorganics) were used in Campania region. (CREA, 2018). Other research (Micó et al., 2006; Adrees et al., 2015; Albanese et al., 2015), notice that agricultural soils have higher Cu concentrations compared to other land uses, indicating a link between Cu accumulation in topsoil and agricultural practices.

4. Conclusions

This study is part of a wider project named "Campania Trasparente" and managed by Istituto Zooprofilattico del Mezzogiorno (IZSM) aimed at an integrated monitoring plan on the regional territory. In this study we focused on topsoil geochemistry characterization. Compositional biplot analysis allowed us to recognize geochemical processes controlling most of soil chemical signatures. Soil chemistry is mainly controlled by enrichment of elements deriving from dominant parent rocks of the area (silico-clastics and volcanoclastics). PTEs are related to high geogenic contribution and, marginally, to anthropogenic pollution.

The Campania region (Southern Italy) is characterized by several PTEs exceeding the contamination thresholds (CSC) established by Italian legislation for soils (Legislative Decree 152/2006, 2006). However, the occurrence in soil of elements such as As, Be, Sn and Tl is mainly controlled by geological features and pedogenetic processes, and hence, such soils, are not pollution controlled.

Highly urbanized (Naples and Salerno), highly industrialized (Solofra) and intensely cultivated areas (Sarno River Basin), are characterized by the high dominance of the anthropogenic elements association (Pb, Sb and Zn). These elements spatial patterns well trace the metropolitan continuum which occupies approximately 15% of the region, from Caserta (North) to Sele Plain (South). Additional important information about geochemical processes, determining the distribution of PTEs in the Campania soil environment, were gained following the CoDA approach through the production of a clr-biplot. It helped us to verify the elemental behaviour and relationships, allowing a better and deeper interpretation. Chemical weathering plays an important role in PTEs abundance and re-distribution processes especially in soils over the carbonate massifs. Here, advanced pedogenetic processes and the co-presence of allochtonous sources (e.g., pyroclastic coverings) determined high content of element such as As, Be, Cd, Ni, Se, Tl and V. It is notable that soil of inlands are depleted in Se (an essential nutrient for many plants and animals content). This should be noticed since values < 0.175 mg/kg correspond potential Se deficiency which might have vital consequence to agricultural productivity and, consequently, to human health. This study demonstrated that soil chemical composition of Campania region is expression of geological features, pedogenetic processes and anthropic sources, which depict a high spatial geochemical heterogeneity and data population overlaps on the investigated scale. This study described origin and environmental evaluation of PTEs in the surface living environment, which may affect agriculture production and human and ecosystem health.

A future goal is to better assess the risk presented by metals in the environment to human and ecological receptors, improving knowledge (i) of the influence of environmental characteristics on metal speciation and (ii) metal speciation within an organism, through a cross-disciplinary approach essential to address environmental health threats.

CRediT authorship contribution statement

Daniela Zuzolo: Conceptualization, Methodology, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Domenico Cicchella:** Visualization, Supervision. **Annamaria Lima:** Supervision. **Ilaria Guagliardi:** Validation. **Pellegrino Cerino:** Resources. **Antonio Pizzolante:** Resources. **Matar Thiombane:** Validation. **Benedetto De Vivo:** Conceptualization, Supervision. **Stefano Albanese:** Data curation, Visualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2020.106524.

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