



Environmental screening for the assessment of potentially toxic elements content in PGI soils from the Mediterranean region (Italy and Turkey)

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Abstract

To provide a contribution to the Thematic Strategy for Soil Protection, here we present the results of a study focused on the potentially toxic elements (PTE) content in agricultural soils' representative for the Mediterranean region. To reach this aim, samples of 22 Italian (NE Peloritani Mountains, Sicily) and 18 Turkish (Amik Plain, Hatay) soils were collected and analyzed to evaluate their PTE content. The Italian and Turkish sites have been selected because they represent very important cultivation zones. In Amik Plain (Turkey), the dominant crops consist of cotton, wheat, corn and olives, whereas in NE Peloritani Mountains, Sicily (Italy), an appreciate citrus variety, known as the "Interdonato lemon", guaranteed by Protected Geographical Indication label, is produced. The collected results include: (1) the assessment of PTE levels in soils; (2) the identification of the PTE sources; (3) the relationships between PTE contents and soil properties (pH, electrical conductivity, organic matter, CaCO₃, and clay). Several multivariate statistical methods such as correlation matrix, cluster analysis and main component analysis were applied to individuate the anthropogenic vs natural origin of the PTE sources. The detected PTE levels are in decreasing order Mn > Zn > V > Cr > Cu > Ni > As > Pb > Co > Sb > Se > Cd for the Italian soils, and Mn > Ni > V > Zn > Cr > Cu > Pb > Co > As > Se > Sb > Cd for the Turkish soils. The overall obtained results allowed to define: (a) a main lithogenic source for PTE detected in the Italian soils, except for Zn which origin is also associated to anthropogenic input; (b) a lithogenic origin for all of the PTE detected for the Turkish soils, with an associate anthropogenic contribution for Cr, Ni, V, Cu and V. The results obtained in this work enhance the knowledge in the individuation of PTE pollution sources in agricultural soils of the European Mediterranean region.

Keywords PCA · CDA · PGI · Potentially toxic elements · Soil quality · Soil parameters

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Introduction

Overview

Nowadays, the changes of land use pattern are a consequence of urban-industrial expansion due to an excessive infrastructure development. The increasing of these activities causes a sensible reduction of soil qualities and then, pollution becomes an important environmental issue, especially, in the developed countries. In this regard, the contaminants can be very dangerous, according to their persistence and toxicity and, among them, the potentially toxic elements (PTE) can be extremely hazardous for the living beings (e.g., Biasioli et al. 2006; Ullah et al. 2017; Wuana and Okieimen 2011).

The PTE distribution in soils is controlled by parent-rock geochemistry, climatic and geomorphologic conditions, time of weathering exposition, soils texture, living organisms (bacteria, fungi, vegetation and animals) and several anthropogenic inputs (Pinto et al. 2017). In general, sources of PTE are considered to be of anthropogenic origin and the degree and extent of pollution have been among the main topics of the environmental sciences (e.g., Pinto et al. 2014, 2015, 2017; Almeida-Silva et al. 2013; Andrejkovičová et al. 2016).

A distinction is often made between soil contamination originating from clearly confined sources (local or point source contamination) and soil contamination caused by diffuse sources (Qu et al. 2020; Xu et al. 2020).

Pollution by PTE in agricultural soils is a particularly pressing concern since it affects food safety and security. In particular, the accumulation of PTE elements in soils above certain levels entails multiple negative consequences for all the ecosystems and other natural resources (Doran and Zeiss 2000; Brussaard et al. 2007; Kibblewhite et al. 2008; Wellnitz and Poff 2001; Setälä et al. 2005). Moreover, contamination of soils with PTEs is of worldwide concern due to their ability to be transferred into the human food chain via many pathways (Lim et al. 2008; Ji et al. 2008; Varrica et al. 2014 Rinklebe and Shaheen 2017; Rinklebe et al. 2019; Antoniadis et al. 2017a, b, 2018; Edelstein and Ben-Hur 2018).

The PTE pollution in agricultural fields mainly refers to the Northern, Central European countries (e.g. Lado et al. 2008; Tavazzi et al. 2012; Smolders 2013; Six and Smolders 2014; Weissengruber et al. 2018), whereas a few studies were developed about this issue in the southern Europe, particularly in the Mediterranean region (e.g., Kelepertzis 2014; Odabasi et al. 2010; Yuce et al. 2005; Abollino et al. 2002; Acosta et al. 2014).

In this framework this paper addresses the attention to soils used to produce a prestigious variety of citrus known

as “Interdonato lemon”, labeled with the Protected Geographical Indication (PGI) and original of the NE Peloritani Mountains (Italy) (Disciplinare di produzione della indicazione geografica protetta “Limone Interdonato Messina”, 2013) and cotton, corn and olive growing soils (Turkey). Due to the importance of those areas as production zones, for the European commercial market, it would be necessary to evaluate the PTEs content of these cultivation soils.

The environmental screening of PTE is very important, especially to evaluate the soil healthiness in agricultural fields. Some inorganic elements are, in fact, strictly related to anthropogenic input, which could be more mobile to the respect of the lithogenic ones (Micò et al. 2008). This condition could represent a threat for the human health, because the consumption of agri-food products could facilitate the bioaccumulation of dangerous inorganic elements in the human body. To reach the goal it is important to verify the presence of some elements in vegetable crops, especially in soils characterized by high PTE concentrations.

This paper accounts for the experimental environmental screening of selected Turkish and Italian soils coherently with the EC rules “towards a thematic strategy for soil protection” (EC 2006) and aims to propose a reference for maintaining or improving the soil quality.

We collected and analyzed soil samples from the Messina province (NE Peloritani Mountains Italy) and the Amik Plain (Turkey), and determined both the content and the source of the PTEs. Moreover, some agricultural properties considered as necessary to develop a comprehensive environmental screening (e.g., organic matter content, texture and mineral composition), have been also determined. Finally, using multivariate statistical methods we obtained information about the possible sources of pollution (e.g., Dragovic et al. 2008; Blaha et al. 2008; Franco-Uría et al. 2009; Shan et al. 2013).

Studies areas

The Messina province (Sicily, Italy) is located in Sicily (Italy) over the NE Peloritani Mountains. The area is characterized by a warm and temperate climate with a mean rainfall value equal to 726 mm/year and an annual average temperature of 18.2 °C. The studied soils fall in the geographic domains of the Peloritani Mountains (NE Sicily, Italy), which are characterized by high relief traversed by short, seasonal rivers and torrents, geologically form the Peloritani Chain.

The Peloritani chain is the southernmost portion of the Calabrian-Peloritani arc, an arc-like structure connecting the NW–SE-trending Italian Apennines with the Sicilian (East–West) and North African Maghrebis. The Peloritani Chain consists of a stack of continental crust units

involving Pan-African and Variscan crystalline basements and remnants of original Meso-Cenozoic sedimentary cover rocks, locally affected by an Alpine overprint (e.g., Bonardi et al. 2008; Cosenza et al. 2015). The structural setting of the Peloritani Chain involves nine Alpine tectonic units, which from top to bottom are: Aspromonte, Mela, Piraino, Mandanici, Alì, Fondachelli, San Marco d'Alunzio, Longi-Taormina and Capo Sant'Andrea units (Carbone et al. 2008, 2011).

The investigated soils lie on rocks belonging to the Mandanici unit, which include phyllites and metarenites, actinolitic amphibolite schists, quartzites and marbles, and are covered by clastic-terrigeneous sedimentary rocks dating back to the Pleistocene. Several polymetallic mineralized occurrences are located essentially within the Mandanici unit, in lithologic packages characterized by marble layers and graphitic schists, often associated with fluorite, barite, galena and pyrite (Cosenza et al. 2015).

The investigated agricultural soils are imposed on terraced grayish floods, formed by sandy-silty gravels with clasts deriving, in turn, from dismantling and erosion of the underlying metamorphic rocks of the Mandanici Unit.

The Amik plain, Hatay Province (Turkey), exhibits a typical Mediterranean climate with 1124 mm annual precipitation and 18 °C average annual temperature (Gün and Erdem 2003; Kiliç 2011).

The study region, one of the most important agricultural areas of southeastern Turkey, has a border with Syria and, surrounded by Reyhanlı, Kırıkhan, and Antakya city and Serinyol town. Overall, about 85% of the Turkish territory

is located at an average altitude of 450 meters, with intermediate national values of around 1128 m b.s.l. The study area is one of the most rapidly industrializing regions of Turkey.

The southeastern Anatolia is characterized by a complex and articulated geological framework, which includes a number of tectono-magmatic/stratigraphic units, such as the metamorphic massifs, the ophiolites, the volcanic arc units and the granitoid rocks (Karaoglan et al. 2013).

The ophiolites of southeastern Turkey occur in two belts, namely the Peri-Arabic belt ophiolites and the Southeast Anatolian ophiolites (Fig. 1a). The ophiolites, the arc-related units and granitoids in the southeast Turkey are important tectono-magmatic units for the late Cretaceous tectonic evolution of the southern Neotethyan ocean (e.g., Sengör and Yilmaz 1981; Mackintosh and Robertson 2012; Yuce 2018; Karaoglan et al. 2013).

In the study area, the base stratigraphic units outcrop as shallow marine character of Upper Triassic–Cretaceous carbonate and ophiolites, which are emplaced in the area during Upper Cretaceous.

The Southeast Anatolian ophiolites typically display the complete ophiolite stratigraphy, including mantle tectonites, ultramafic to mafic cumulates, gabbros, isolated diabase dykes, sheeted dyke complex, plagiogranite and volcanic products (e.g., Parlak et al. 2004, 2009; Karaoglan et al. 2013).

The youngest units of study area are represented by Quaternary succession of Alluvium (Özer et al. 2004). The base of the studied area is dominated by typical

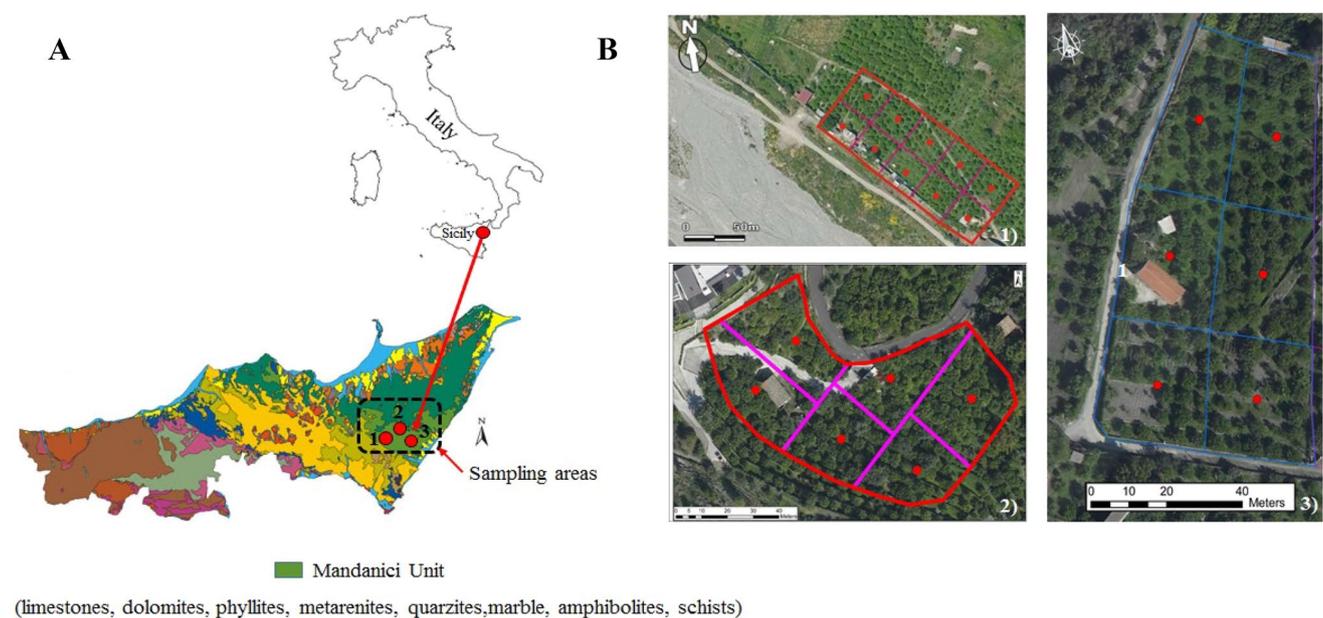


Fig. 1 Geological sketch map of Eastern Sicily (a) (Bonardi et al. 1976) with, in particular, the Mandanici Unit falling into the sampling areas (1, 2, 3). Map of PGI soils sampling (b)

environments of shallow sea (lower Paleozoic), and by Mesozoic carbonates and ophiolitic rock.

The sedimentary deposits which are placed at the head of the stratigraphic column and which are more recent than the Quaternary ones are typically alluvial (gravel, sand, clay) and are found above a thickness of alkaline basalts of the transitional series with sodium affinity (e.g., Özer et al. 2004; Italiano et al. 2017).

The Amik Basin is a graben basin covered by alluviums and lacustrine sediments. At past, Amik Lake was located in the middle of the basin, however it was drained and dried up. In the basin, the major soil orders include Entisol, Inceptisol, Vertisol, Alfisol, and Mollisol (Kılıç 2011).

Materials and methods

Soil sampling and chemical analyses

Forty representative soil samples, 22 from Italy (see Fig. 1a, b) and 18 from Turkey (Fig. 2a, b), were collected over the selected areas. The sampling sites were recorded and georeferenced by a DGPS (differential global position system).

1 kg of topsoil sample was collected from the surface horizon (30–45 cm) of all the investigated soils, and each sample analyzed in triplicate.

In the laboratory, the soil samples were air-dried at room temperature, sieved and analyzed for PTEs (Cd, Co, Cr, Cu, Pb, Zn, Mn, Fe, Ni, V, As, Sb and Se). Total PTEs were extracted by acid digestion and analyzed with an inductively coupled plasma mass-spectrometer (ICP-MS).

The instrumental equipment is made of a ICP-MS Agilent 7500cx (Agilent Technologies), with a quadrupole powered by a 27.12 MHz radiofrequency solid state generator, and an ASX-520 autosampler (Cetac Technologies Inc., Omaha, NE, USA).

The equipment was tuned before any analytical session and the adopted method was optimized to reduce the spectral (polyatomic and isobaric) and non-spectral interferences that could significantly affect the multi-analyze determinations.

To check any loss or cross contamination, all replicates (along with blanks), were analyzed three times. Finally, to obtain the quantitative determinations, the external calibration procedure with the multi-elemental standard solutions was performed.

Calibration standards were prepared at concentration ranges suitable for the investigated elements: from 0.020 to 2 mg/kg for As, Co, Cd, Cr, Sb, Pb and Se; from 0.020 to 5 mg/kg for Cu and Ni; from 0.5 to 50 mg/kg for Mn, V and Zn elements.

Each solution was digested by microwave and, then, analyzed by ICP-MS with the same experimental conditions used for soil samples.

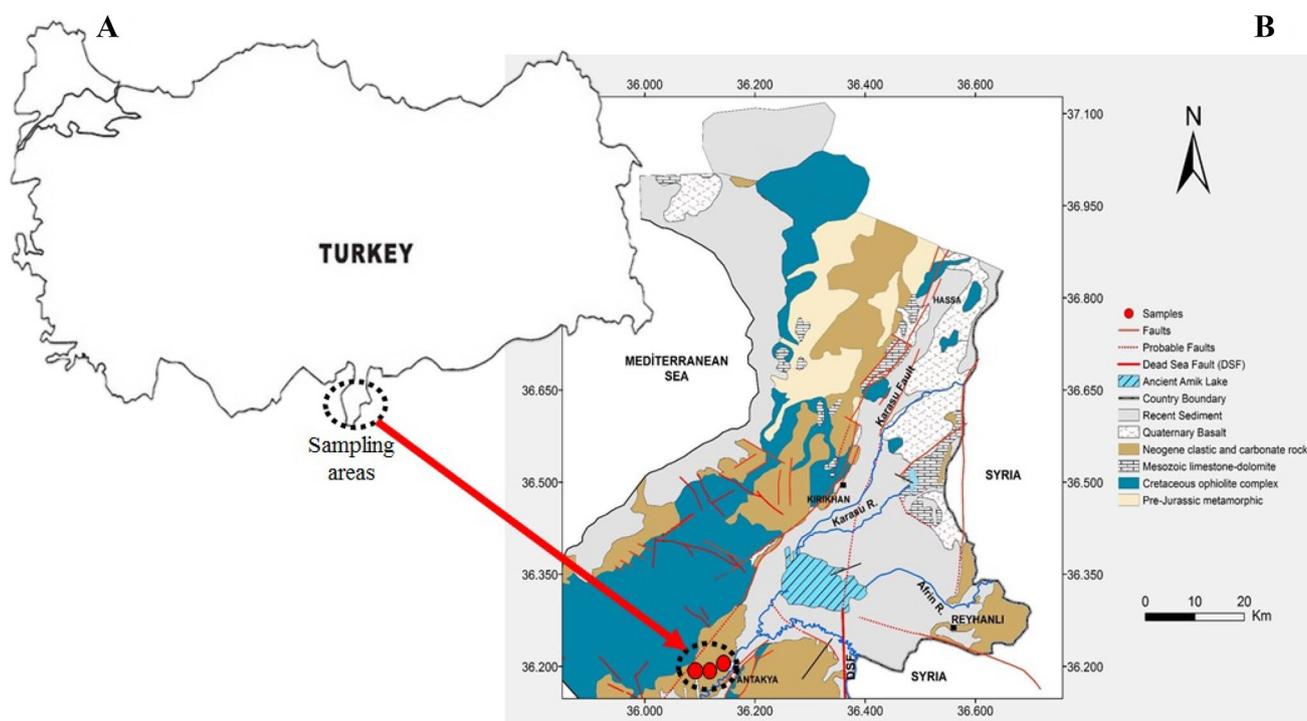


Fig. 2 Soils sampling areas of cultivation sites (Guzelburc, Turkey) (a). Geological setting of Hatay province (Turkey) (b) (Yuce et al. 2014)

The calibration curves were realized using six different concentrations per analyze and, in detail, each point was obtained by six replicates. Blanks were also run along with multi-elemental standard solutions ($n = 6$ at each level). The accuracy of method was checked by analyses of the certified reference materials (CRMs), IAEA/SOIL-7 (International Atomic Energy Agency) and NBS 2711 (Montana Soil).

Sample preparation

Soil samples were air-dried for several days, sieved to 2 mm, finely ground in an agate mortar, and then, stored in a closed bottle. Sample digestion was carried out in a closed vessel: (a) 0.5 g of sample was transferred into a Milestone digestion vessel; (b) 1 mL of H_2O_2 , 5 mL of HNO_3 and 3 mL of HF were added; (c) the PTFE vessels were sealed and tightened using a torque wrench prior to digestion.

The mineralization procedure was carried out by microwave digestion system (Ethos 1 Milestone, Bergamo, Italy), setting the following temperature program: 0 °C to 200 °C in 10 min (step 1) and 200 °C held for 10 min (step 2), with a constant microwave power of 1000 W. After cooling down to room temperature, the digested samples were diluted with ultrapure water and, then, stored at 4 °C.

Analytical blanks were also prepared with the same procedure. Heavy metal concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). All measurements were performed in triplicate. According to D.M. 13/9/1999 (Metodi ufficiali di analisi chimica del suolo) soil properties have been determined as following: (a) the pH was determined in water suspension (in proportion 1:2.5); (b) the electrical conductivity was measured using the saturation paste extract (ECe); (c) the organic matter levels was calculated by Walkley–Black method; (d) the carbonates content (%) was determined using the Bernard calcimeter; (e) the particle-size distribution was defined through sieving of dry soils.

Statistical analyses

The statistical analyses were performed using a dedicated software named “Statistica 13.0”. Descriptive statistical analysis (range, mean, standard deviation, coefficient of variation, skewness and Kolgomorov-Smirnov test) was conducted as a first step towards an exploratory analysis of heavy metal data. Moreover, with the correlation analysis was assessed the possible relationship among the PTE and pH.

The Principal Component Analyses (PCA) results were mapped in a 3D graphical interface with the aim to make an easier interpretation of results.

Pearson and Correlation matrixes were respectively employed to identify the relationships between heavy metal

contents and soil properties, whereas the evaluation of “Spearman coefficient” was used to improve the robustness of statistical treatments and to determine the dataset distributions (-normal or not normal-).

Cluster Analysis (CA) was also performed to increase the chemometric goodness and to individuate the geochemical differences among samples on dendrogram. Before proceeding with the PCA elaboration, the data matrix was subjected to preliminary statistical treatments. In detail, the Kaiser–Meyer–Olkin (KMO) test was run to measure the sampling adequacy, for each considered variable; instead, the Bartlett test was used to assess the equality of variance in different samples.

Results and discussion

Descriptive statistics

Descriptive statistics for Mn, Zn, V, Cr, Cu, Ni, As, Pb, Co, Sb, Se and Cd in soil samples are listed in Table 3, which includes minimum, maximum, median, mean, standard deviation, skewness, and results of Kolmogorov–Smirnov test (K–S). The maximum concentrations of all PTEs, except V, Co, and As, were below to those established by soil quality standard. Moreover, the kurtosis of the Cu and Pb distributions were relatively high. Therefore, this condition indicates the presence of unusually high values, which may have been caused by distinct anthropogenic sources of Cu and Pb.

Coherently with the obtained results, the Italian PGI-soils exhibit the following order of metals: $Mn > Zn > V > Cr > Cu > Ni > As > Pb > Co > Sb > Se > Cd$ (see Table 3). The Turkish soils have a different order which is: $Mn > Ni > V > Zn > Cr > Cu > Pb > Co > As > Se > Sb > Cd$. Comparison of the obtained data highlighted a sensitive difference between Ni levels, which are for the Turkish soils seven times greater than the Italian ones.

Conversely, the Italian soils exhibit higher As and Co values (four and two times respectively) than those estimated for the Turkish soils. In any case, except for Ni levels of Turkish soils, the heavy metal contents for all the studied soils do not exceed the reference values established by the 86/278/EEC (for agricultural soils with a $pH > 7$).

Cu and Pb contents are lower than the only values available in literature ($Cu = 76.8$ mg/kg and $Pb = 101$ mg/kg, after Micò et al. 2006a, b), which have been detected in some Spanish soils. Conversely, they are higher than the background values enforced in European countries (Kabata-Pendias and Pendias 2001).

The K–S confirms the normal-distribution of inorganic elements, with the exception of pH, electrical conductivity, organic matter and sand content (see Table 1).

Table 1 Statistical parameters relative to PTEs contents (mg/kg) and some agricultural features in the analyzed soils

Variable	Symbol	Unit	Statistical parameters						SKW	K-S Test		
			Italian soils			Turkish soils						
			Range	Mean	SD	CV (%)	Range	Mean			SD	CV (%)
Cadmium	Cd	mg/kg	0.26–0.84	0.45	0.11	24.4	0.27–0.76	0.49	0.13	26.5	0.73	0.16
Cobalt	Co	mg/kg	7.10–11.57	8.94	1.36	15.2	10.79–25.95	18.10	2.27	12.54	0.78	0.94
Chromium	Cr	mg/kg	33.53–110.49	52.41	17.38	33.16	34.14–69.23	49.07	7.92	16.14	1.98	1.00
Copper	Cu	mg/kg	20.22–40.19	29.99	5.13	17.10	33.00–91.26	56.40	17.46	30.90	1.18	1.00
Manganese	Mn	mg/kg	394.64–767.50	548.04	94.64	17.26	360.81–600.00	476.53	72.41	15.91	0.57	0.58
Nickel	Ni	mg/kg	21.14–38.57	29.94	4.62	15.43	163.91–301.53	210.99	36.66	17.37	0.41	0.30
Lead	Pb	mg/kg	12.68–37.85	23.58	6.24	26.43	7.00–108.20	37.85	36.14	95.48	1.90	1.00
Zinc	Zn	mg/kg	66.66–126.25	86.52	14.95	17.2	40.89–122.92	67.98	14.76	21.71	0.12	0.35
Antimony	Sb	mg/kg	1.98–16.59	7.48	4.11	54.94	0.39–0.91	0.64	0.08	12.51	1.09	0.57
Selenium	Se	mg/kg	2.63–3.61	3.04	0.24	7.89	2.17–5.52	3.76	0.76	20.21	1.27	0.53
Vanadium	V	mg/kg	47.73–76.25	62.72	8.15	12.99	46.16–104.02	77.41	12.08	15.60	0.68	1.00
Arsenic	As	mg/kg	13.12–55.25	24.78	5.61	22.63	3.00–8.99	6.41	1.09	17.00	1.34	0.58
pH	pH	–	6.30–8.06	7.43	0.48	6.41	6.73–8.82	7.89	0.97	12.29	0.03	0.06
Electrical conductivity	EC	mS/cm	0.49–0.89	0.22	0.22	100	2.71–3.10	2.86	0.26	9.09	0.20	0.00
Clay content	Clay	%	2.12–4.98	3.76	0.76	20.21	24.14–33.10	28.14	6.39	22.70	0.37	0.00
Organic Matter	OM	%	1.60–2.99	2.32	0.42	18.10	3.19–5.98	4.77	0.63	13.20	0.49	0.00
Carbonates	CaCO ₃	%	2.12–4.98	3.76	0.40	10.61	24.10–33.10	28.14	2.65	9.41	0.37	1.00

Range minimum value–maximum value, mean mean value, SD standard deviation, CV coefficient of variation, SKW skewness, K–S Test Kolmogorov–Smirnov test

In this respect, different studies suggested the strong relationships between the presence of clay and carbonates in calcareous soils contribute to increase the PTEs content (e.g., Sdiri et al. 2012).

Multivariate analysis

Cluster analysis (CA)

In the present research, the CA was applied to raw ICP-MS data using the Euclidean distance for measuring the extent of dissimilarity among samples, whereas the Ward’s method (agglomerative algorithm) was applied to define the rules able to group samples according to their similarities.

The CA results are mapped in a dedicated graphical interface, which was obtained after assigning their own cluster to each sample and, then, pairs of clusters are repeatedly merged until the whole tree is formed (Kozak and Scaman 2008).

Results of cluster analyses, performed on the two groups of soils, are reported in dendrograms (see Fig. 3). The dendrogram representing the Italian soils displayed three main clusters/groups formed by some sub-groups (Fig. 3a).

Specifically, Cr, V and Zn fall into the first group (Fig. 3a). Instead, the second group includes Co, Sb, Cd, Se and some soil properties (clay and CaCO₃). The aforementioned elements were grouped in the second cluster.

Finally, the third cluster contains As, Pb, Ni and Cu, whereas Mn is out of all groupings (Fig. 3a).

Concerning the Turkish soils, two main clusters are observable in the related dendrogram (Fig. 3b). In particular, Pb, Cr, Cu, V and Zn are grouped together. Cd, Sb, As and Se are well linked, while Co form a sub-group with clay and CaCO₃ (Fig. 3b). Ni and Mn are out of all groupings.

Principal component analysis (PCA) and correlation matrix (CM)

With the aim to evaluate the relationships among the original variables, the Principal components analysis (PCA) was carried out. The PCA algorithm is able to explain the contribution of the estimated variance, however before proceeding the data matrix underwent several propaedeutic statistical treatments, respectively:

- (a) The Kaiser–Meyer–Olkin (KMO) method was used to measure the sampling adequacy for the considered variables. It restituted a value of 0.800, which is indicative of an adequate sampling. In agreement with the recommended cut-off threshold of 0.5, the obtained value, suggesting compact correlations and good reliability of the PCA factors (Field 2009);
- (b) The Bartlett test confirmed the robustness of sampling adequacy, thanks to the obtained Chi square value of 182.865, which is greater than the Chi Square critical value of 9.488 (at *p* value < 0.0001).

The Chi square values demonstrate a significant difference in the variances, which is also confirmed by highly

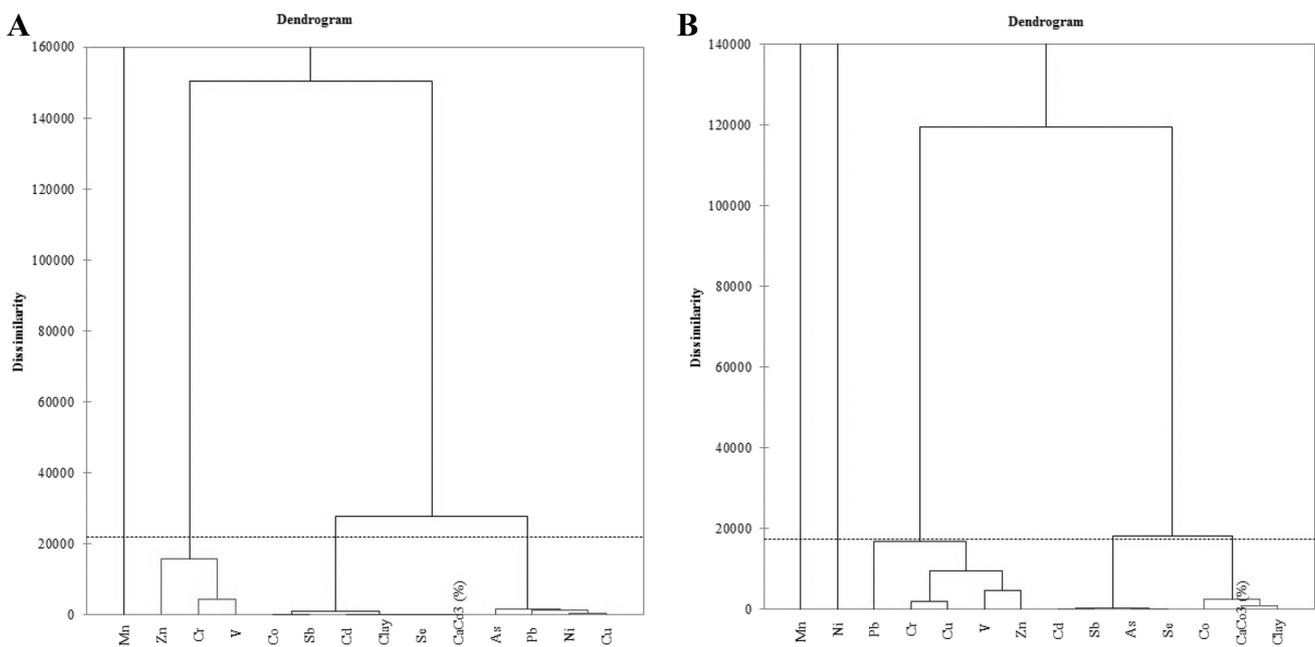


Fig. 3 Cluster Analysis based on mineral contents relatively to Italian (a) and Turkish soils (b)

significant (p value < 0.0001) differences among all elements.

The starting matrix ($N \times P$) includes 40 rows (number of samples) and 17 columns, (12 inorganic elements and 5 agronomic parameters), which represent all the investigated variables.

The covariance between Mn, Zn, V, Cr, Cu, Ni, As, Pb, Co, Sb, Se and Cd levels and the agronomic parameters (clay, CaCO_3 , organic matter, pH and electrical conductivity) was evaluated.

Moreover, coherently with the Kaiser criterion, four principal components with eigenvalues exceeding one (9.53, 2.57, 1.34 and 1.10) were extracted, which together explain the 80.88% of the total variance (52.95%, 14.31%, 7.47% and

6.14, respectively) (see Table 2). Therefore, the correlation matrix was factored, before the PCA chemometric treatment. The PCA showed two groups, clearly distinguished in the projection on the plane, defined by the first two principal components that explain the 67.26% of the total variance for the investigated soil samples (see Fig. 4).

The PGI samples were separated from the Turkish ones on the first component, which explains 51.15% of the total variance, whereas the PC2 justified the 16.11% of the variance.

Both clusters are characterized by several positive correlation degree with inorganic and agronomic parameters. In this regard, the Italian samples exhibit a positive correlation with Sb, As and Mn, whereas the Turkish ones showed a positive correlation with Se, V, Cu, Co and Pb and all agronomic parameters.

To make an easier individuation and interpretation of the contamination inputs, we realize models using a new 3D graphical interface.

Before building up a 3D PCA model, different origins were attributed to each PC, to define the probable sources of PTEs (PC1 = lithogenic source; PC2 = anthropogenic source; PC3 = lithogenic and anthropogenic mixed contribute).

Specifically, the graphical evidences suggest, for the Italian soils (Fig. 5a), the lithogenic input as a main source for

Table 2 Statistical parameters for PCA analysis (eigenvalues, variability and cumulative spatial variations of variables)

	PC1	PC2	PC3	PC4
Eigenvalue	9.531	2.576	1.345	1.106
Variability (%)	52.952	14.313	7.474	6.144
Cumulative (%)	52.952	67.264	74.738	80.882

PCA extracted four principal components with eigenvalues exceeding 1

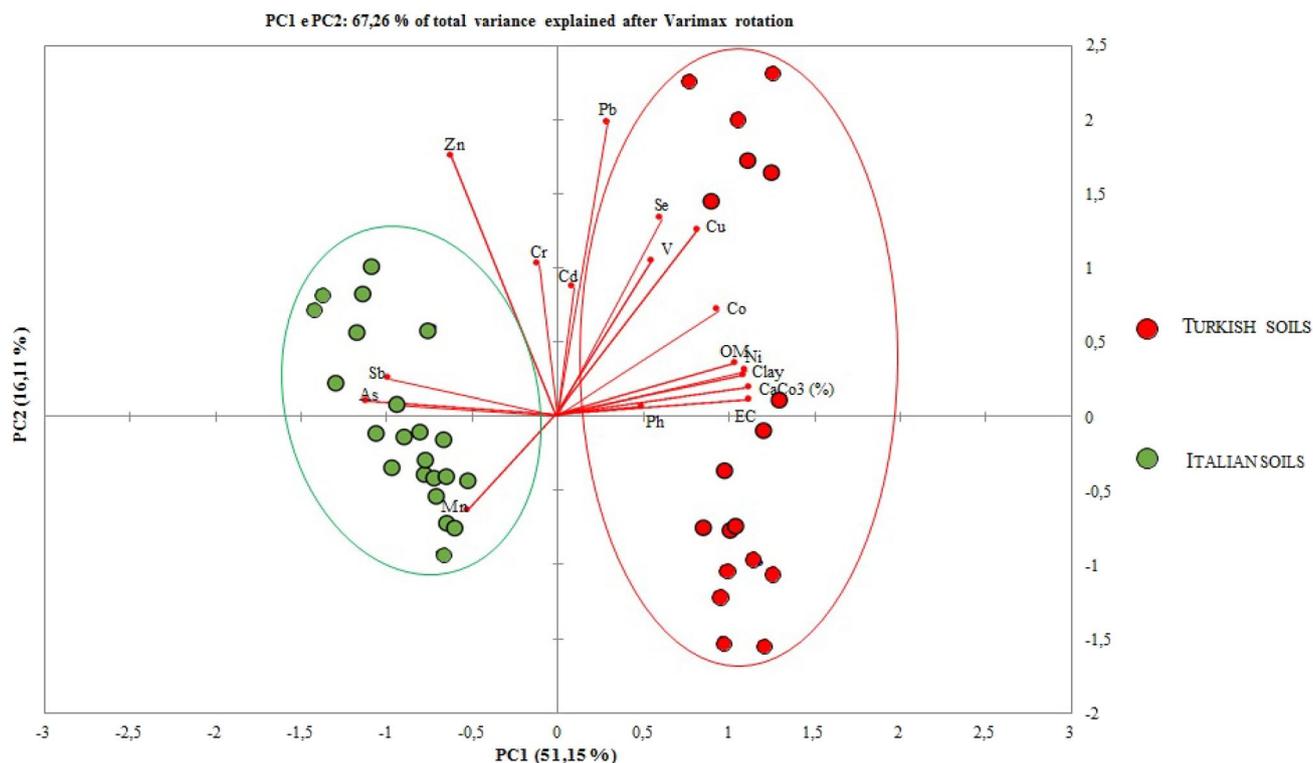


Fig. 4 Two-dimensional PCA biplots of inorganic elements and agricultural parameters of Italian and Turkish soils. Drawn ellipses suggest the natural grouping of samples according to their proveniences

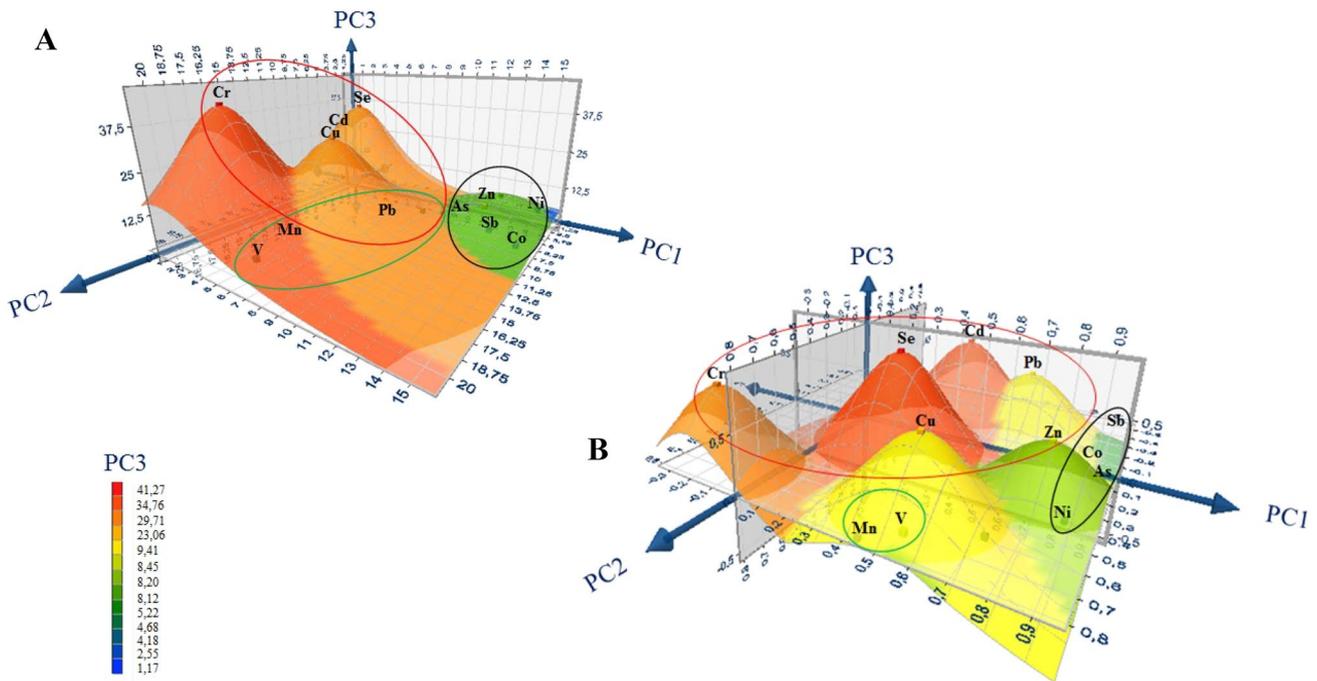


Fig. 5 3D loading plot elaborations for Italian (a) and Turkish soils (b). (PC1 associated to parent rock alterations, PC2 associated to anthropogenic components, PC3 mix of anthropogenic and lithogenic sources, PC1-PC2)

Table 3 Pearson correlation matrix between inorganic mineral levels and pedological soils parameters

Elements	pH	CaCO ₃ (%)	OM	EC	Clay (%)
Cr	0.123 ^a	-0.098 ^a	-0.021 ^a	-0.115 ^a	-0.096 ^a
Co	0.464	0.826	0.750	0.830	0.788
Ni	0.362	0.965	0.860	0.961	0.917
As	-0.322 ^a	-0.735 ^a	-0.720 ^a	-0.735 ^a	-0.705 ^a
Se	0.312	0.560	0.477	0.502	0.515
Cd	0.045 ^a	0.133 ^a	0.163 ^a	0.108	0.152 ^a
Sb	-0.411 ^a	-0.746 ^a	-0.719 ^a	-0.750 ^a	-0.725
Pb	0.109 ^a	0.301	0.378	0.064 ^a	0.049 ^a
V	0.056 ^a	0.491	0.536	0.519	0.498
Mn	-0.181 ^a	-0.418 ^a	-0.386 ^a	-0.397 ^a	-0.393 ^a
B	-0.373 ^a	-0.928 ^a	-0.845 ^a	-0.940 ^a	-0.906
Cu	0.326	0.743	0.693	0.720	0.769
Zn	-0.238 ^a	-0.428 ^a	-0.322 ^a	-0.453 ^a	-0.374 ^a

OM organic matter, EC electrical conductivity, CaCO₃ % of carbonate, Clay (%) clay contents

^aSpearman's coefficient

Se, Cd, Cu, Pb, Co, As, Ni, Sb and Zn elements, due to their spatial distribution near the positive side of the PC1 axis. About Cr, V and Mn a mixed lithogenic and anthropogenic components can be assumed.

Likewise, for the Turkish soils (Fig. 5b), the levels of Se, Cd, Pb, Zn, Co, As and Sb are linked to a lithogenic

source. On the other hand, Cr, Ni, V, Cu and V could be associated to a mix of lithogenic and anthropogenic inputs.

Concerning to the existence of strongly positive/negative interactions among organic matter, carbonates, clay content and PTE availability, several studies have confirmed their strictly correlations (Micò et al. 2006a, b). Thus, the agricultural properties of soils play a key role about the mineral elements availability.

Complementary to PCA approach, and to evaluate the coefficients of correlation (*r*), between PTE contents and pedological soils properties, the Pearson matrix was used. Specifically, the Pearson's correlation coefficient (*r*) is a measure of the strength of the association between the two variables. It can take a range of values from +1 to -1 (+1 indicate a total positive linear correlation, 0 is no linear correlation, and -1 represents a total negative linear correlation). The results of the Pearson correlation matrix do not show a positive linear relationship with the major parts of the dataset (see Table 3). In particular, clay content showed a significant relationship with most of the considered elements except for As and Sb. It was also identified a good relation among CaCO₃ (%) soil content and Co, Cu and Ni levels.

On the contrary, the correlation matrix exhibits a low relationship with most of the considered elements and pH. The results might suggest a higher Cu bioavailability, probably, due to the soil salinity (Micò et al. 2006a, b). Specifically, for all matrices coming from Italy and Turkey, the Cd

and Pb levels showed a weak correlation with soil properties potentially due to their available form in the studied soils.

Conversely, the Cu levels showed a positive correlation with soil properties. In general, the Pearson elaboration put in evidence that some agronomic features may influence the absorption and retention of inorganic elements in the investigated soils.

Natural and anthropogenic sources of PTEs

Sources of heavy metal pollution include natural processes and anthropogenic activities. A natural PTE source is represented by bedrock alteration. In soils used for agricultural purposes, variable amounts of metals can be also introduced together with fertilizers, both organic and mineral. PTEs from natural sources may have lower bioavailability, because they are naturally contained in soils and subjected to weathering and rainfall leaching for thousands to millions of years. This implies that only the metals which are highly stable on the geochemical point of view remain in soils (Jing et al. 2019). Naturally, the PTEs are affected by several kinds of soil features (physical–chemical factors), such as mineral composition, particle size, and organic carbon level (Dung et al. 2013; Jing et al. 2019). The heavy metal sources can be represented by magmatic, sedimentary and metamorphic rocks, which weathering and dismantling processes formed soils. The rock cycle contributed also in the diffusion of PTE in surface and groundwater as well as in the atmosphere. Furthermore, the human activities also represent a considerable cause of PTEs metals injection into the environment. The main anthropogenic inputs are associated with industrialization and, in this respect, the atmospheric deposition, the waste disposal, the waste incineration, urban effluents, traffic emissions, the long-term application of wastewater in agricultural lands (fertilizer) represent the consequence of the irrational industrial development (e.g., Roozbahani et al. 2015).

The results of the present work evidenced that the chemical composition of soils is mainly controlled by lithogenic and pedogenic weathering, although some anthropogenic contribution may be involved, as reported in literature, especially for Turkish soils. Moreover, the obtained results are coherent and similar to those performed by other scientists (e.g., Facchinelli et al. 2001; Abollino et al. 2002) in different parts of the European Mediterranean region.

Italian soils

The chemistry of Italian soils is closely related to the geochemical features of the parent sedimentary (limestones, dolomites) and metamorphic (phyllites, metarenites, quartzites, marble and amphibolite schists) rocks of the Mandanici metamorphic Unit and to the well-known correlated

polymetallic mineralization spread over the Peloritani Mountains (Cosenza et al. 2015). Here, several types of mineralization have been recognized as a result of distinct geologic events. Both of them are located in the low-grade phyllite. The first one is associated with pre-Hercynian strata-bound ores of Fe–Pb–Zn sulphides while the second one is related to hydrothermal discordant-vein ore bodies, with intense thermal activity connected with late metamorphic phases and characterized by complex sulphides of Cu, Pb, Sb and Bi (Saccà et al. 2003; Dongarrà et al. 2009; Cosenza et al. 2015). Specifically, sulphide and sulphosalt rock-forming minerals, such as pyrite, galena, chalcopyrite and arsenopyrite, reported in the Northern Peloritani Mountains, are all carriers of the metallic elements detected for the studied soils (e.g., Saccà et al. 2003; Cosenza et al. 2015). Results of isotopic studies on galena minerals ($^{206}\text{Pb}/^{207}\text{Pb}$ v. $^{208}\text{Pb}/^{207}\text{Pb}$ ratios) by Cosenza et al. (2015), for selected samples of soils in the investigated area, suggest a geogenic contamination related to the presence of sulphide and sulphosalt rock-forming minerals outcropping in the area. As far as some heavy metal contents are concerned, which are relevant in the investigated environmental context and which have been detected in Italian soils, geochemical literature has already reported their mean concentration values. In detail, (Cosenza et al. 2015) have evaluated the levels of the main metals and metalloids elements in soils. The Italian samples were characterized by the following mean concentration values: 84 mg/kg (As), 0.48 mg/kg (Cd), 24.9 mg/kg (Co), 42.9 mg/kg (Cr), 62.8 mg/kg (Cu), 924 mg/kg (Mn), 65.8 mg/kg (Pb), 7.62 mg/kg (Sb), 0.75 mg/kg (Se), 241 mg/kg (Zn) and 54.6 mg/kg (V). These literature data are consistent with the concentrations values of the PTEs determined in this study. On the other hand, results of CA and the similarities in the identified clusters and subgroups on dendrogram allow to confirm the geogenic/lithogenic origin of the detected metals. Only the very high level of Zn could be considered as dependent also by specific human agricultural activities, which at local level can be relevant. For instance, in the investigated area, the anthropic (long term) activity connected with grape-growing can contribute to increase the Zn levels due to an intensive use of fertilizers (Facchinelli et al. 2001). The obtained results allow to hypothesize a main lithogenic source also for Cr, V and Mn, although on the 3D loading plot of PCA they seem to turn out by mixed lithogenic and anthropogenic sources. These metallic elements are also enriched in the iron oxides and polymetallic mineralization of the studied area.

Turkish soils

The Turkish soils, as the Italian ones, show a composition, in terms of inorganic elements, compatible with the geochemical and mineralogical features of the ophiolitic

and carbonatic rocks, from which the investigated soils originated. Most of the detected PTEs generally derive from ophiolitic rocks. Literature on metals soils concentration, collected in the investigated area (Hatay region), reports the following values: 8 ppm V, 80 ppm Cr, 20 ppm Co, 320 ppm Ni, 53 ppm Cu, 70 ppm Zn, 10 ppm As and 40 ppm of Pb (data from TUBITAK-COST Research Project No: 111Y090, 2012–2015). These concentration values are comparable with the metal concentration values obtained in the present study. The measured high values can be attributed to the parent rocks, since the origin of the soil layers are magmatic, metamorphic, and sedimentary rocks. Feldspars, micas, olivines, pyroxene and quartz minerals are the main constituents of those kinds of rocks and are very abundant in the investigated area as component of ophiolitic and volcanic rocks. In Hatay region, the high Ni, Zn, Cr and Cu levels are probably correlated to the presence of anthropogenic inputs (due to intense use of pesticides in the agricultural fields) and to natural sources (i.e., from ophiolites). Typically, the Ni and Cr contents are very high in magmatic and sedimentary rocks (e.g., Sengör and Yılmaz 1981; Karaoglan et al. 2013) and, coherently with these geological settings, the statistical results confirm these scenarios.

The area taken into account in the present study is one of the most rapidly industrializing regions of Turkey. A rather rapid industrialization process took place in this region during the period between 1950 and 1980 (Odabasi et al. 2010; Agca and Özdel 2013). Previous studies carried out in soils of the Hatay-Iskenderun areas evidenced significantly higher Cr, Ni, Cu and Zn concentration values in soils, which are similar to those measured in the nearby industrial sites (e.g., Odabasi et al. 2010). Ni contents in the soils are very high in almost the entire study area and can reach values higher than those recommended by Directive 86/278/EEC. As reported by Agca and Özdel (2013) the Ni presence in the area is strongly linked to fertilization procedures, as an antiparasitic defense treatment, but also owing to industry and vehicle emissions (Agca and Özdel 2013). In the same way, the high Cu concentration values in soils could be due to the use of pesticides (Cu-based) applied to the trees by the growers (Gürel and Başar 2014). The anthropogenic input is the major source of Cu, and the most important sources are attributable to the use of Cu-based anti-parasitic substances or zoo-technical dejections. The high levels of Cr reported in the literature for the investigated area have been attributed primarily to industrial activities and, secondly, to vehicular traffic (Agca and Özdel 2013). On the other hand, the main sources of Zn pollution are due to industries, fertilizers and pesticides.

Conclusions

The results obtained in the present study increase the knowledge of PTE background levels in soils and could be effectively employed for the identification of pollution sources, with a specific reference to those employed in agricultural fields.

On that score, a dataset, composed by 12 inorganic elements and by 5 soil properties has been taken into account. The dataset has been analyzed by means of a statistical approach to estimate the PTEs variability in some important Mediterranean cultivation fields. Furthermore, with the aim to evaluate the background levels of contaminants, in each considered fields, the analysis of PTEs was carried out after fertilizer digestion (3 months).

The results of multivariate statistical approaches in all investigated soil samples show that the natural lithogenic control can justify the presence of the 66.6% of PTEs detected in Sicilian fields and of the 50% in the Turkish ones.

More specifically, the results of the chemometric treatments for PGI soils show that the elements Se, Cd, Cu, Pb, Co, As, Ni, Sb and Zn can be linked to bedrock alteration. This consideration appears coherent with the geological framework, as confirmed by several mineralizations identified herein.

The analytical results provided by Turkish samples suggest that Se, Cd, Pb, Zn, Co, As and Sb levels could be related to lithogenic source, whereas Cr, Ni, V, Cu and V seem to be associated with a mix of lithogenic and anthropogenic components. Probably, it is reasonable to assume that the Cr, Ni, V, Cu and V levels also depend by an anthropogenic contributions since, in the recent past (1950–1980), the area near to Amik plain has been subjected to a rapidly industrializing process.

In effect, for the aforementioned elements, similar PTEs concentrations have been detected also in the nearby industrial sites and this could confirm the previous environmental framework.

Concerning the As levels estimated in all soils, a mean value of 24.78 mg/kg was recorded in PGI site, whereas the obtained Turkish value is approximately equal to 6.41 mg/kg. The As levels, in both sites, appear related to lithogenic control. The difference among PGI and Not-PGI soils can be attributed to the volcanic ash fallout that has interested the PGI samples enriching the level of As. Effectively, in the sampling period (2015), several eruptions have been documented by INGV (Istituto Nazionale Geofisica e Vulcanologia) where Etna ash, transported by the wind, has reached the PGI areas several times (<http://www2.ct.ingv.it/it/banca-dati-delle-eruzioni/eruzioni-etna.html>). However, the registered worldwide soil value for

the As content lies within the range from 1 to 40 mg/kg (WHO 2001) and the values obtained for all the investigated soils fall inside this range. Although this paper shows that the Zn concentration values mostly depend on lithogenic causes, unfortunately, a percentage of the Zn could be connected with the use of some pesticides, based on Zn compounds (Ravindran et al. 2016).

In conclusion, the results obtained in the present work describe an environmental screening of PTEs pollution in agricultural fields, which represent a global concern for the potential ecological risk related to toxic elements in the environment. To improve the interpretative framework of the obtained results, we have planned for the future to evaluate the inorganic mineral levels also in different soil portions. On this purpose, a sequential Tessier extraction could improve the results obtained by this investigation because it could allow to detect some inorganic elements (e.g., heavy metals) into five different soil fractions (exchangeable, linked to carbonates, linked to iron and manganese oxides, associated with organic matter and remaining) (Abollino et al. 2002).

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