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Translocation of potential toxic elements from soil to blackcabbage (*Brassica oleracea* L.) growing in an abandoned mining district area of the Apuan Alps (Tuscany, Italy)

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Abstract

In the Apuan Alps (Tuscany, Italy), long- lasting mining activities have favored the mobilization of numerous metals present in sulfosalts originated from low-grade metamorphism mineralization. Such materials, rich in potentially toxic elements such as antimony, arsenic, barium, copper, lead, thallium, tin and zinc, represent the substrate on which soils of different thicknesses have been formed and are currently used for agricultural activities. High concern is particularly arising about food safety due to traditional horticultural practices, since it is very common in this area to cultivate vegetables in private gardens for both self-consuming and/or local market. In this context, a monitoring survey on both soil and vegetables was performed over the area, with particular attention to *Brassica oleracea* L. as traditional food crop, to assess the degree of contamination of the area, the possible translocation to vegetables and the potential human risk linked to vegetable ingestion. This analysis reveals a different degree of soil contamination in the area and a general high human risk linked to cabbage cultivation and ingestion in the whole area.

Introduction

Heavy metals contamination of soils has been largely studied, but this issue is still a pressing concern in the debate about environmental and food security and safety in Europe (CEC 2006) and globally (Kong 2014). Tóth et al. (2016) estimated that in Europe, 137.000 km^2 of agricultural soils are affected by high potential toxic elements (PTEs) concentration, with consequent risk of PTEs contamination into the food chain. Despite the severity of soil contamination, the authors

stated that there are no sufficient data to provide a reliable view on the exact extent of the problem in Europe and worldwide due to the extreme diffusion and site specificity of the problem (Bini 2019). Generally, many efforts have been taken by public authorities and research centers to establish the background values of soils and to recognize different risk levels according to the origin of PTEs (Amorosi et al. 2014; Varol 2011; Audry et al. 2004). Different databases on PTEs concentration in soils are available all over the world, and in Italy many regions have already published a pedogeochemical map of regional soils (Amorosi et al. 2014). However, due to the extreme heterogeneity of the study cases, a clear overview of the risk associated with PTEs diffusion is still lacking in many parts of the world. PTEs can have a geogenic origin due to the presence of metalliferous rocks, or they can be spread into the soil as result of human activities (Su et al. 2014). Depending on their speciation, they can be presented in stable and immobilized forms (e.g., in the mineral soil fraction), or in available forms (e.g., weakly bound to carbonates, exchangeable and soluble), leading to a different level of risk alarm (Bacon and Davidson 2008). Moreover, a change of both pH or redox condition in soil may lead to a modification in PTEs equilibrium in soil (Ferronato et al. 2015), inducing a shift of the level of PTEs toxicity. For these reasons, studies on bioaccumulation of PTEs on specific vegetable species are incentivized, in order to understand the actual risk associated with their cultivation in polluted soils (Feng et al. 2005). In addition, to evaluate the human risk like to vegetable ingestion, some indexes have been developed by the US Environmental Protection Agency (US- EPA IRIS 2006) in order to detect reference dose levels.

In the Apuan Alps (Tuscany, Italy), sulfosalts mineralization originated by low-grade metamorphism of previous sedimentary rocks (Biagioni et al. 2013) is present in many sites. Weathering processes and mining activities have favored the mobilization of several trace elements contained in the sulfosalts (Ag, As, Ba, Cu, Hg, Pb, Sb, Sn Tl, Zn). As a result, these elements are now largely diffused in both water and soils of the area. Soil has developed materials enriched by potentially toxic elements (PTEs) such as Ag, As, Ba, Cu, Hg, Pb, Sb, Sn, Tl, Zn, and in the Baccatoio River Valley many vegetable gardens are cultivated. In particular, in winter, some varieties of *Brassica oleracea* L. (*acephala, botrytis, capitata, caulorapa*) are traditionally grown in this area for self-consumption. In the last decade, research showed that some varieties of the genus *Brassica* have the ability to accumulate PTEs in the epigeal organs and to tolerate high metal concentrations in soils (Marchiol et al. 2004; Grispen et al. 2006). *Brassica* spp. is known to

accumulate relatively large amounts of toxic metals, and for this reason various studies investigated the possibility to use these species for phytoextraction operations on contaminated soils (Van Ginneken et al. 2007; Gall and Rajakaruna 2013). Even if phytoextraction by *Brassica* spp. can be considered an interesting practice for environmental protection, it is important to consider the high risk linked to those *Brassica* species used for animal and human consumption. In the Apuan Alps area, *B. oleracea* is part of the human diet and is one of the typical products of the area. Thus, the concern of food contamination is high and the rise of the population awareness led to the necessity to assess the actual risk of its health. To answer to people concerns, a monitoring survey was performed on soil–black cabbage system in the Baccatoio Valley. PTEs contamination assessment was performed in both soil and black cabbages, with the aims to ascertain soil vulnerability associated with different contamination degrees and to define the health risk linked to the possible translocation of heavy metals from soil to black cabbage.

Materials and methods

Study area and sampling survey

The study area is located in Pietrasanta (Lucca, Italy), a town of 25,000 inhabitants c.a., and it extends along the Baccatoio Valley next to the mines of Monte Arsiccio and Pollone, highly used for decades and abandoned during the 1980s. The Baccatoio River originates from the drainage tunnels of the abandoned mines and flows from the upper part of the area (Valdicastello-Carducci), to the plain part of the Pietrasanta municipality. The study area constitutes a land strip along the Baccatoio River, spanning from the hamlet of Valdicastello-Carducci Village to Pollino one (Fig. 1). In this land, 63 vegetable gardens have been chosen for the monitoring survey and georeferenced by GPS Garmin in geographic and kilometric coordinates in the UTM- WGS84 system (Fig. 1). In each site, soil of vegetable gardens has been collected in a proper bag and transported in laboratory for analysis. When *Brassica oleracea* L. (*acephala* and *caulorapa* varieties) was present in the selected site, the whole plant was also collected for analysis ($n = 35$).

Figure 1 Study area and monitoring sites location

Heavy metals characterization in soil

Soil samples ($n = 63$) were air-dried, sieved at \2 mm and ultrafine powder milled. The

macro-(Fe, Mn, S) and microelements (As, Ba, Cu, Pb, Sb, Sn, Tl, Zn) content was determined according to Vittori Antisari et al. (2013). Soil samples (0.25 g) were treated with aqua regia (2 mL 65% HNO_3?6 mL 37% HCl, Suprapur grade; Carlo Erba, MI, Italy) in a microwave oven (Milestone 2100, Sorisone, BG, Italy). After digestion, the solutions were made up to 20 mL with Milli-Q water and filtered with a What- man 42 filter paper; the elements concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Ametek, MI, Italy). The analysis of each sample was replicated three times and compared with the analyses of the International Reference Materials (BCR 141) and laboratory internal standards (MO and ML) (Vittori Antisari et al. 2014), which was run after every ten samples to check changes in sensitivity. Controls with only reagents were also determined.

PTEs characterization in vegetable

Roots and leaves of *B. oleracea* ($n = 35$) were separated and treated separately. Each subsample was weighed soon after the collection and after drying (60 °C per 72 h). Dry samples were grounded in a blender with blades made of pure titanium, carefully avoiding introducing any further metal contamination to the samples (Vittori Antisari et al. 2012). Both roots and leaves samples (0.25 g) were treated with 6 mL of HNO_3 (Suprapur, Merck, Kenilworth, NJ, USA) and 2 mL of H_2O_2 (Carlo Erba, MI, Italy) using a microwave oven (Milestone 2100, Sorisone, BG, Italy).

$$TI ¼ MeP \ mg \ kg^1 = MeR \ mg \ kg^1 * 100 \qquad [1]$$

After digestion, the solutions were made up to 20 mL with Milli-Q water and then filtered with a Whatman 42 filter paper and the trace elements were determined by ICP-OES (Spectro Ametek, MI, Italy). The ICP-OES setting followed multi-standard solutions (CPI International, Amsterdam, The Nether- lands) that reproduce the matrix effect present in samples and allow the lowering of detection limits. Instrument response was assessed by measuring a standard sample (CRM 482, Community Bureau of Reference, BCR).

Statistical analysis and GIS elaboration

The spatial distribution of the areas affected by different degrees of soil contamination was carried out creating Voronoi polygons (Drysdale 1993; Okabe et al. 2008) using QGIS 3.6 and having previously assigned to each investigated point a value from 0 to 8. This value was derived from the sum of the soil PTEs (As, Ba, Cu, Pb, Sb, Sn, Tl, Zn) that present concentrations higher than the limit established by Italian legislation for agricultural and residential soil (Legislative Decree No.

152/2006). The analysis of the variance for nonparametric variables (Kruskal– Wallis test) and boxplot representations was per- formed with Statistica 10 (Statsoft).

Contamination indexes

The bioaccumulation factor (BCF) was calculated to evaluate the ability of the plant to accumulate metals, according to the following equation (Zayed et al. 1998):

$$BCF_T \frac{1}{4} MeP \ mg \ kg^{-1} = MeS \ mg \ kg^{-1} \qquad [2]$$

where MeP is the concentration of metals in the plants tissue (mg kg^{-1}) and MeS is the metals concentration in the soil.

The translocation index (TI) was also calculated in order to explore the capacity of each plant to uptake metals in the aerial parts, and it was calculated as follows (Ghosh and Singh 2005): where MeP is the metal concentration in the leaves and MeR is its concentration in the roots. This index is used to assess the ability of the roots to transfer the element through its tissues. The daily metal intake and health risk index are indexes related to daily estimated consumption as well as health risks from the consumption of contaminated food. The US Environmental Protection Agency's reference doses (US-EPA IRIS 2006) were used as reference points. The daily metal intake (DMI) through vegeta- bles (mg/day) was estimated as follows:

$$DMI \frac{1}{4} \eth C_{ML} * 0:085 * DPC\THORN=BW \qquad [3]$$

where C_{ML} is the concentration of microelements in the edible part of the plant (mg kg^{-1} dry weight) multiplied by a conversion factor of 0.085 to convert dry weight vegetable metal content to fresh weight (Rattan et al. 2005; Arora et al. 2008; Harmanescu et al. 2011).

The daily plants consumption (DPC) can be calculated as a function of body weight (BW); for body weights of 70, 56, 33 and 26 kg, daily consumption is estimated to be 35, 24, 22 and 13 g, respectively (Wang et al. 2005; Arora et al. 2008, Leclercq et al. 2009; Seid-Mohammadi et al. 2014); the average body weight used for this study was 46 kg, with a corresponding daily vegetable intake of 23.5 g/day. Based on the daily metal intake, it was possible to calculate the health risk index, as follows:

$$HRI \frac{1}{4} DMI = RfD \qquad [4]$$

where RfD is the reference dose; for As, Cu, Pb and Zn, the value is, respectively, 0.0003, 0.04, 0.0035 and 0.30 mg kg - 1 BW day - 1) (US-EPA IRIS 2006; Jan et al. 2010). HRI values >1 are considered to pose health risks (Cui et al. 2004; Rattan et al. 2005; Pennisi et al. 2016).

Results and discussion

PTEs in soils

The concentration of both macroelements (Fe, Mn, S) and PTEs (As, Ba, Cu, Pb, Sb, Sn, Tl, Zn) in soils of each investigated family garden is reported in Table 1S. In most of the sites, soils presented PTEs concentration above the threshold limits established by Italian legislation (Legislative Decree No. 152/2006). In particular, the Cu concentration exceeded the limits in 44% of soil samples, as well as Pb in 47%, Zn in 65%, As in 60%, Sn in 65%, Ba in 30%, Sb in 33% and Tl in 7%, respectively. Even if some PTEs, as Cu and Zn, are essential microelements for life, in this study we chose to consider them as PTEs, because their high concentration could bring to deep toxic effect to plants and to the food chain. In order to explore the spatial distribution of soil contamination, samples were classified according to the number of PTEs exceeding the legislative thresh- old (e.g., 0, 1–2, 3–4, 5–6, 7–8 exceeded PTEs, building five classes). Data were interpolated using Voronoi polygons method in Qgis, in order to display the distribution of the soil classes within the area (Fig.2). Figure 2 shows the distribution of PTEs within the investigated area according to soil contamination classes, highlighting that the most contaminated area was located in the upper part of the Baccatoio River Valley and just downstream the Sarzanese road. In order to better understand the map, Table 1 shows the PTEs mean concentration in the five classes of soil contamination and their standard deviation. According to the Kruskal–Wallis test, classes 1 and 2 (0–2 PTEs exceeding the legislative threshold) did not result statistically different and their location were mainly in the areas farer from the Baccatoio River. In these samples, Zn and Sn were the metals that exceeded more frequently the law limits, but, in general, this area represented the non-contaminated/ low-contaminated zone, where probably the effect of mining activity was not consistent.

Fig. 2 Soil contamination classes referred to the PTEs number with concentrations exceeding the law limits (Legislative Decree 152/2006 of Italy, Annex 4/14)

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Table 1 Mean and standard deviation (SD) of the different groups classified according to the number of PTEs exceeding the legislative threshold

Class 3 (3–4 PTEs exceeding the legislative threshold) can be considered a medium-contaminated area, where As, Cu, Pb and Zn were the most critical elements. These samples mostly correspond to the areas located along the Baccatoio River, in the conoid area and downstream of the Sarzanese road, probably due to the overlapping of two causes of impact occurred in the past: the presence of sludge deposits deriving from the floatation tanks of mining products and the spreading of pollutants from the nearby municipal waste incinerator plant.

Classes 4 and 5 (5–8 PTEs exceeding the legislative threshold) were not statistically different, except for As concentration that was higher in Class 5. These samples resulted highly contaminated and represent the highly risky areas, located in the upper part of the Baccatoio River. PTEs concentrations in these soils are ascribed generally to a geogenic origin, linked to the soil recent formation on mine debris, localized next to the old mine and transported downstream by the Baccatoio waters.

Generally, the study area presented high contamination level if compared with other studies in other Italian regions (Rascio and Navari-Izzo 2011; Wahsha et al. 2014; Wahsha et al. 2015). Moreover, the soil of horticultural sites had higher PTEs concentration if compared with soils natural background of the Tus- cany Region. From a geochemical point of view, this result was quite expected, since this land is an old mining area, and the presence of tailing in the area deeply impacts the surrounding soils (Liu et al. 2016; Yun et al. 2017). However, we think that the role of human activities has been crucial in spreading the pollution in the area. In addition, the lack of mitigation of acid drainage water of abandoned mine flowing into Baccatoio River has largely contributed enlarging the contamination problem.

PTEs in plant tissues

Mean PTEs concentration in leaves and roots of *B. oleracea* varieties sampled in the five different areas is reported in Tables 2S and 3S, respectively. Multi-PTE accumulation by cabbage leaves is evident in many sites, but no statistical differences were noted among vegetables, grouped according to the five contaminated areas Fig. 2. In our study, PTEs mean concentration in the leaves of cabbage that is generally lower than those recorded in plants from Western Europe (Angelone and Bini 1992; Kabata-Pendias and Mukherjce 2007). Very high concentration (mean 7013 mg kg^{-1}) of sulfur in all samples was detected. Yet, sulfur substitutes oxygen in the composition of

chemical compounds of cabbage, and this substitution is responsible for the high S levels and the resulting typical fragrance (Chin and Lindsay 2006). To evaluate the PTEs risk related to the cabbages consumption as prevalent food in the local diet in this highly contaminated area, bioaccumulation index (BCF) and translocation factor (TF) are considered useful tools that can predict the potential mobility of PTEs from soil to food crops, linked to plant-specific defense mechanisms or site-specific phenomena (Ferronato et al. 2016; Zacchini et al. 2009). Bioaccumulation factor (BCF) represents the ratio between the PTEs concentrations in the *Brassica* roots and that in soil, and it is used to assess the capacity of plants to adsorb nutrients or pollutants from soil. The higher is the BCF, the higher is the ability of the elements to be accumulated in plant roots; consequently, the higher is the BCF, the higher is the probability to be translocated in the edible parts of the plant (Zacchini et al. 2009). Figure 3 displays the mean BCF calculated in the different areas, and its low values, with exception of Sn, indicate that PTEs accumulation in cabbage roots was quite low. Interestingly, to note that BCF was higher in cabbages collected from the group 1 area (not- contaminated soils) than in group 5 (the most contaminated area), with exception of Sn, where BCF increased with an increase in soil contamination (group 1 to group 5). Arsenic, Ba, Pb, Sb and Zn BCF in group 1 was significantly higher than that calculated in samples of the group 5 area. These results suggest that in the less contaminated areas, these PTEs are more available for plant uptake, probably due to a higher degree of soil development or due to the use of contaminated water for irrigation. These results confirm that the only data of soil total concentration is often not sufficient to assess the metal availability and the risk of human health (Ferronato et al. 2015; Farkas et al. 2007) and hat environmental or human risk assessment should always approach with a multidisciplinary approach.

Fig. 3   Boxplot distribution of BCF of PTEs in the cabbage collected in the different areas. Data expressed in mg kg^{-1}

The same trend was noted when applying the translocation factor (TF), that is the ratio between the metal concentrations in the *Brassica* roots and leaves (Fig. 4). Also in this case, higher TF values were detected in the vegetables of group 1 than that of group 5, highlighting a high mobility of the metals in the vegetables of group 1, where the translocation in the edible parts of the cabbages is generally higher. Notably, very high TF was detected for Pb and As, followed by Cu and Zn.

PTEs risk of human health

The US Environmental Protection Agency (US-EPA IRIS 2006) has defined the reference dose for different PTEs. Based on these indications, DMI and HRI were calculated in our study case, assuming body weight for adult men = 70 kg, adult women = 56 kg, kid = 26 kg. Table 2 shows the mean values of DMI and HRI found in the different areas (1 to 5 groups) for As, Cu, Pb and Zn. Since no significant difference was noted for the different reference body weight, data were reported mediated values. All the other investigated PTEs were not considered because of lack of reference dose.

Fig. 4   Boxplot distribution of TF of PTEs in the cabbage roots collected in the different areas. Data expressed in mg kg^{-1}

Table 2 Mean and standard deviation of DMI and HRJ calculated on the collected Brassica plants, grouped according to the different groups.

DMI values indicate that considering the daily intake, the cabbage characteristics and the site where vegetables are cultivated, people ingest quite low concentrations of PTEs (Zn>Cu >Pb>As). Since soils presented significant differences in terms of PTEs concentration but no significant differences were detected among groups of cabbages, we can assume that the DMI is not depending on the degree of soil contamination where vegetables are cultivated. However, a serious health risk is recorded when applying the HRI. HRIs were always for the PTEs considered, indicating a very high human health risk linked to the toxic effects of these PTEs. Cu and Zn (average HRI 8.24 and 4.81, respectively) are well-known essential microelements for life, but at high levels they can induce different toxicity effects (Sandstead 1995). Arsenic (average HRI 10.79) and Pb (average HRI 9.71) are extremely high, and our data reveal a serious alarm for human health. The toxicity of As and Pb is also well documented (Bissen and Frimmel 2003; Flora et al. 2012) and in this area our data reveal a serious health risk that has to be considered by public authorities. This data also confirms that to assess the human risk linked to vegetable cultivation in contaminated soils, the study of PTEs distribution in soils or in plants tissues is not sufficient alone. In fact, this study shows that even if the soils of the area are differently contaminated, cabbages counteract the adverse effect of the environment with self-defense mechanisms that generally

avoid metals adsorption (Ebbs and Kochian 1997), showing relatively low BCF. However, this study shows that when metals are present in soil in more available forms (e.g., linked to soil organic matter or sulfides), plants defense mechanisms can be less strong, thus absorbing higher quantity of contaminants that can be translocated in the edible parts (see TF).

Conclusions

In this study, a monitoring of the spatial distribution of toxic elements was conducted to assess major and PTEs content in soils and edible plants of an abandoned mining area. In addition, health risks were investigated. The results indicate that in various cases, PTEs exceed the corresponding limits of the Italian regulations for green and residential soil areas, and geospatial analysis identified the most critical areas: (a) in proximity of the abandoned mines and (b) in the nearby Baccatoio River, indicating that the lack of maintenance of the old mining area is probably the main cause of the spread of soil contamination. Considering the relationship between soil and plants, the highest concern regards the translocation of As, Cu, Pb and Zn, and their consequent ingestion through cabbage leaves. Concerning the problem of PTEs contamination, these results highlight the complexity of the topic that cannot be evaluated by only the study of soil contamination, or simple analysis on the edible plants tissues. The deep interconnection between soil, plants and site-specific mechanisms has to be evaluated in order to correctly understand the state of the problem. Considering the very high heterogeneity of metal contamination in this area, and the lack of reference dose values for most of the heavy metals considered in this study, we strongly support the research on the definition of reference parameters to evaluate the HRI for other heavy metals. The results of this survey indicated that human activities and land uses have increased the potential health risk in the study area, and that greater attention needs to be focused on this issue.

References

Amorosi, A., Guermandi, M., Marchi, N., & Sammartino, I. (2014). Fingerprinting sedimentary and soil units by their natural metal contents: a new approach to assess metal contamination. Science of the Total Environment, 500–501, 361–372. https://doi.org/10.1016/j.scitotenv. 2014.08.078.

Angelone, M., & Bini, C. (1992). Trace element concentrations in soils and plants of western Europe. In D. Adriano (Ed.), Biogeochemistry of trace metals (pp. 19–60). Boca Raton: Lewis.

Arora, M., Kiranb, B., Rania, S., Rania, A., Kaura, B., & Mittala, N. (2008). Heavy metal-accumulation in vegetables irrigated with water from different sources. Food Chemistry, 111(4), 811–815. https://doi.org/10.1016/ j.foodchem.2008.04.049.

Audry, S., Scha¨fer, J., Blanc, G., & Jouanneau, J. M. (2004). Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environmental Pollution, 132(3), 413–426. https://doi.org/10. 1016/j.envpol.2004.05.025.

Bacon, J. R., & Davidson, C. M. (2008). Is there a future for sequential chemical extraction? Analyst, 133, 25–46. https://doi.org/10.1039/B711896A.

Biagioni, C., D'Orazio, M., Vezzoni, S., Dini, A., & Orlandi, P. (2013). Mobilization of Tl–Hg–As–Sb–(Ag, Cu)–Pb sulfosalt melts during low-grade metamorphism in the Alpi Apuane (Tuscany, Italy). Geology, 41, 747–750. https:// doi.org/10.1130/G34211.1.

Bini, C. (2019). Urban soils and human health. EQA International Journal of Environmental Quality, 33, 1–10.

Bissen, M., & Frimmel, F. H. (2003). Arsenic — a Review. part i: occurrence, toxicity, speciation, mobility. Acta hydrochimica et hydrobiologica, 31, 9–18. https://doi.org/ 10.1002/aheh.200390025.

Chin, H. W., & Lindsay, R. C. (2006). Volatile sulfur com- pounds formed in disrupted tissues of different cabbage cultivars. Journal of Food Science, 58(4), 835–839. https:// doi.org/10.1111/j.1365-2621.1993.tb09370.x.

Cui, Y. J., Zhu, Y. G., Zhai, R. H., Chen, D. Y., Huang, Y. Z., Qiu, Y., et al. (2004). Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. Environment International, 30, 785–791. https://doi.org/ 10.1016/j.envint.2004.01.003.

Drysdale, S. (1993). Voronoi diagrams: applications from Archaeology to Zoology. Northampton: Regional Geometry Institute, Smith College.

Ebbs, S. D., & Kochian, L. V. (1997). Toxicity of zinc to Brassica species: implication for phytoremediation. Journal of Environmental Quality, 26(3), 776–781. https:// doi.org/10.2134/jeq1997.00472425002600030026x.

Farkas, A., Erratico, C., & Vigano, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. Chemosphere, 68(4), 761–768. https://doi.org/10.1016/j.chemosphere.2006.12.099.

Feng, M. H., Shan, X. Q., Zhang, S. Z., & Wen, B. (2005). Comparison of a rhizosphere-based method with other one- step extraction methods for assessing the bioavailability of soil metals to wheat. Chemosphere, 59(7), 939–949. https://doi.org/10.1016/j.chemosphere.2004.11.056.

Ferronato, C., Falsone, G., Natale, M., Zannoni, D., Buscaroli, A., Vianello, G., et al. (2016). Chemical and pedological features of subaqueous and hydromorphic soils along a hydrosequence within a coastal system (San Vitale Park, Northern Italy). Geoderma, 265, 141–151.

https://doi.org/ 10.1016/j.geoderma.2015.11.0186.

Ferronato, C., Vianello, G., & Vittori, Antisari L. (2015). Heavy metal risk assessment after oxidation of dredged sediments through speciation and availability studies in the Reno River basin, Northern Italy. Journal of Soils and Sediments, 15, 1235–1245. https://doi.org/10.1007/s11368-015-1096-4.

Flora, G., Gupta, D., & Tiwari, A. (2012). Toxicity of lead: a review with recent updates. Interdisciplinary Toxicology, 5(2), 47–58. https://doi.org/10.2478/v10102-012-0009-2.

Gall, J. E., & Rajakaruna, N. (2013). (2013) The physiology, functional genomics, and applied ecology of heavy metal-tolerant Brassicaceae. In M. Lang (Ed.), Brassicaceae: characterization, functional genomics and health benefits (pp. 121–148). Hauppauge: Nova Science Publishers.

Ghosh, M., & Singh, S. P. (2005). A comparative study of cadmium phytoextraction by accumulator and weed species. Environmental Pollution, 133(2), 365–371. https://doi.org/10.1016/j.envpol.2004.05.015.

Grispen, V. M. J., Nelissen, H. J. M., & Verkleij, J. A. C. (2006). Phytoextraction with Brassica napus L.: a tool for sustainable management of heavy metal contaminated soils. Environmental Pollution, 144, 77–83. https://doi.org/10. 1016/j.envpol.2006.01.007.

Harmanescu, M., Alda, L., Bordean, D., Gogoasa, I., & Gergen, I. (2011). Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area: a case study: Banat County, Romania. Chemistry Central Journal, 5, 64.

Jan, F. A., Ishaq, M., Khan, S., Ihsanullah, I., Ahmad, I., & Shakirullah, M. (2010). A comparative study of human health risks via consumption of food crops grown on wastewater irrigated soil (Peshawar) and relatively clean water irrigated soil (lower Dir). Journal of Hazardous Materials, 179, 612–621. https://doi.org/10.1016/j. jhazmat.2010.03.047.

Kabata-Pendias, A., & Mukherjce, A. B. (2007). Trace elements from soil to human. Berlin: Springer.

Kong, X. B. (2014). China must protect high-quality arable land. Nature, 506(7). https://doi.org/10.1038/506007a.

Leclercq, C., Arcella, D., Piccinelli, R., Sette, S., Le Donne, C., & Turrini, A. (2009). The Italian national food consumption survey INRANSCAI 2005–2006: main results in terms of food consumption. Public Health Nutrition, 12, 2504–2532. https://doi.org/10.1017/S1368980009005035.

Liu, H., Xiong, Z., Jiang, X., Liu, G., & Liu, W. (2016). Heavy metal concentrations in riparian soils along the Han River, China: the importance of soil properties, topography and upland land use. Ecological Engineering, 97, 545–552. https://doi.org/10.1016/j.ecoleng,2016.10.060.

Marchiol, L., Assolari, S., Sacco, P., & Zerbi, G. (2004). Phytoextraction of heavy metals by canola (Brassica napus) and radish (Raphanus sativus) grown on multi-contaminated soil. Environmental Pollution, 132, 21–27. https:// doi.org/10.1016/j.envpol.2004.04.001.

Okabe, A., Satoh, T., Furuta, T., Suzuki, A., & Okano, K. (2008). Generalized network Voronoi diagrams: Concepts, computational methods, and applications. International Journal of Geographical Information Science, 22(9), 965–994. https://doi.org/10.1080/13658810701587891.

Pennisi, G., Orsini, F., Gasperi, D., Mancarella, S., Sanoubar, R., Vittori, Antisari L., et al. (2016). Soilless system on peat reduce trace metals in urban-grown food: unexpected evidence for a soil origin of plant contamination. Agronomy for Sustainable Development, 36, 56. https://doi.org/

10.1007/s13593-016-0391-9.

Rascio, N., & Navari-Izzo, F. (2011). Heavy metal hyperaccumulating plants: how and why do they do it? and what makes them so interesting? Plant Science, 180, 169–181. https://doi.org/10.1016/j.plantsci.2010.08.016.

Rattan, R. K., Datta, S. P., Chhonkar, P. K., Suribabu, K., & Singh, A. K. (2005). Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. Agriculture, Ecosystems & Environment, 109, 310–322. https://doi.org/10.1016/j. agee.2005.02.025.

Sandstead, H. H. (1995). Requirements and toxicity of essential trace elements, illustrated by zinc and copper. American Journal of Clinical Nutrition, 61–62, 1S–4S.

Seid-Mohammadi, A., Roshanaei, G., & Asgari, G. (2014). Heavy metal concentration in vegetables irrigated with contaminated and fresh water and estimation of their daily intakes in suburb areas of Hamadan, Iran. Journal of Research in Health Sciences, 14(1), 70–75.

Su C., Juand L., Zhang W. (2014). A review on heavy metal contamination in the soil worldwide: situation, impact and remediation techniques. Environmental Skeptics and Critics, 3(2), 24–38. ISSN 2224-4263.

To´th, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. Environment International, 88, 299–309. https://doi.org/10.1016/j. envint.2015.12.017.

US-EPA IRIS (2006) United States, environmental protection agency, integrated risk information system. http://www. epa.gov/iris/substS.

Van Ginneken, L., Meers, E., Guisson, R., Ruttens, A., Elst, K., Tack, F. M. G., et al. (2007). Phytoremediation for heavy metal-contaminated soils combined with bioenergy production. Journal of Environmental Engineering and Landscape Management, 15, 227–236.

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. Journal of Hazardous Materials, 195, 355–364. https://doi.org/10. 1016/j.jhazmat.2011.08.051.

Vittori, Antisari L., Bianchini, G., Dinelli, E., Falsone, G., Gardini, A., Simoni, A., et al. (2014). Critical evaluation of an intercalibration project focused on the definition of new multi-element soil reference materials (AMS-MO1 and AMS-ML1), EQA. EQA International Journal of Environmental Quality, 15, 41–64. https://doi.org/10.6092/issn. 2281-4485/4553.

Vittori, Antisari L., Carbone, S., Ferronato, C., Simoni, A., & Vianello, G. (2012). Leaf washing as an assessment tool to characterize dry atmospheric deposition. EQA International Journal of Environmental Quality, 9, 37–50. https://doi.org/10.6092/issn.2281-4485/3737.

Vittori, Antisari L., Ventura, F., Simoni, A., Piana, S., Rossi, Pisa P., & Vianello, G. (2013). Assessment of pollutants in wet and dry deposition in a suburban area around a waste- to-energy plants (WEP) in Northern Italy. Journal of Environmental Protection, 4, 16–25. https://doi.org/10. 4236/jep.2013.45A003.

Wahsha, M., Bini, C., Zilioli, D., Spiandorello, M., & Gallo, M. (2014). Potentially harmful elements in terraced agroecosystems of NE Italy: geogenic vs anthropogenic enrichment. Journal of Geochemical Exploration, 144(B), 355–362. https://doi.org/10.1016/j.gexplo.2014.01.012.

Wahsha, M., Nadimi-Goki, M., & Bini, C. (2015). Land contamination by toxic elements in abandoned mine areas in Italy. Journal of Soils and Sediments, 16(4), 1300–1305.

https://doi.org/10.1007/s11368-015-1151-1.

Wang, X., Sato, T., Xing, B., & Tao, S. (2005). Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. Science of the Total Environment, 350(1–3), 28–37. https://doi.org/10.1016/j. scitotenv.2004.09.044.

Yun, S. W., Kim, D. H., Kang, D. H., Son, J., Lee, S. Y., Lee, C. K., et al. (2017). Effect of farmland type on the transport and spatial distribution of metal(loid)s in agricultural lands near an abandoned gold mine site: confirmation of previous observations. Journal of Geochemical Exploration, 181, 129–137. https://doi.org/10.1016/j.gexplo.2017.07.004.

Zacchini, M., Pietrini, F., Scarascia-Mugnozza, G., Iori, V., Pietrosanti, L., & Massacci, A. (2009). Metal tolerance, accumulation and translocation in poplar and willow clones treated with cadmium in hydroponics. Water, Air, and Soil Pollution, 197, 23–34. https://doi.org/10.1007/s11270-008-9788-7.

Zayed, A., Gowthaman, S., & Terry, N. (1998). Phytoaccumulation of trace elements by wetland plants: I. Duckweed. Journal of Environmental Quality, 27(3), 715–721. https://doi.org/10.2134/jeq1998. 00472425002700030032x.

Zhang, W. H., Cai, Y., Tu, C., & Ma, Q. L. (2002). Arsenic speciation and distribution in an arsenic hyperaccumulat- ing plant. Science of the Total Environment, 300, 167–177. https://doi.org/10.1016/S0048-9697(02)00165-1.
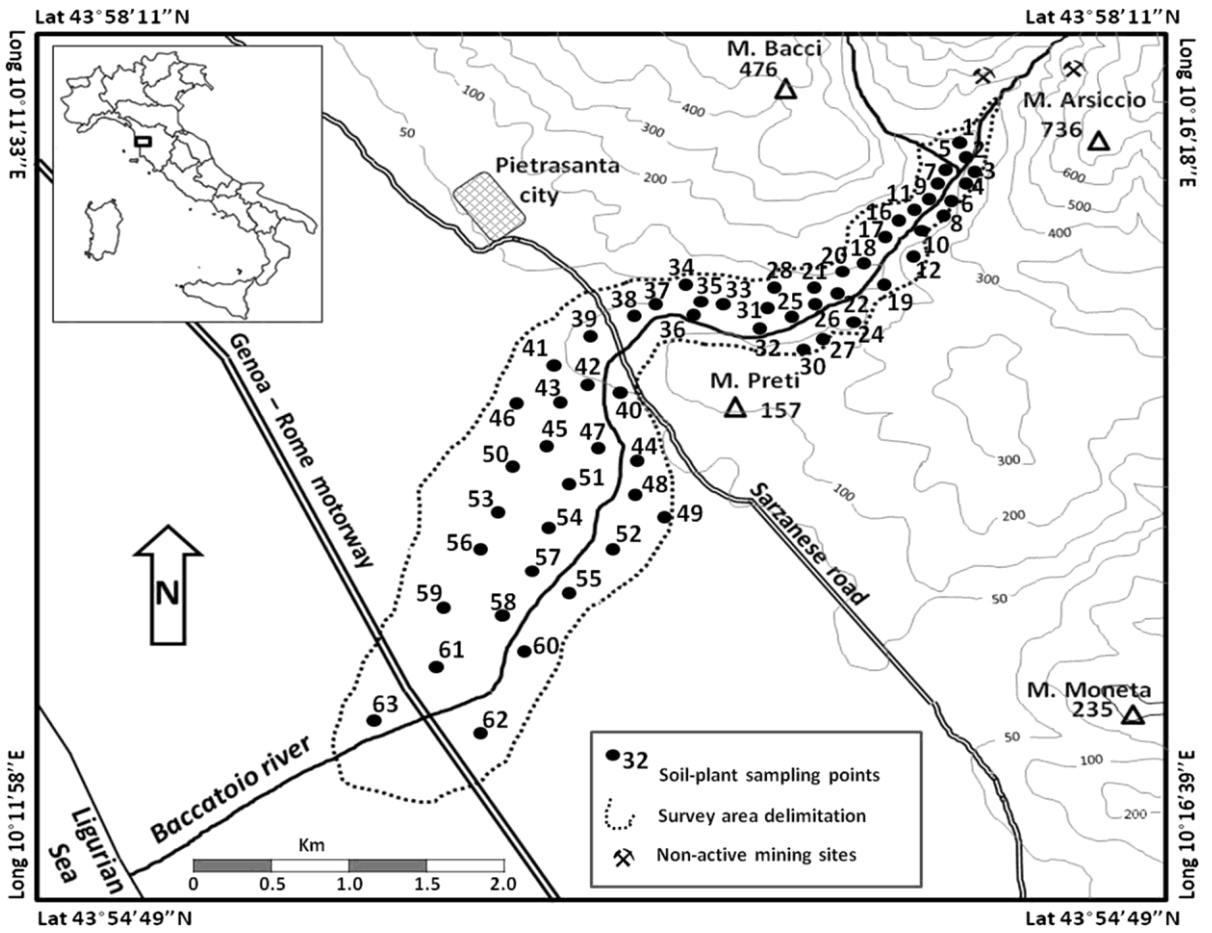
Fig. 1 Study area and monitoring sites location

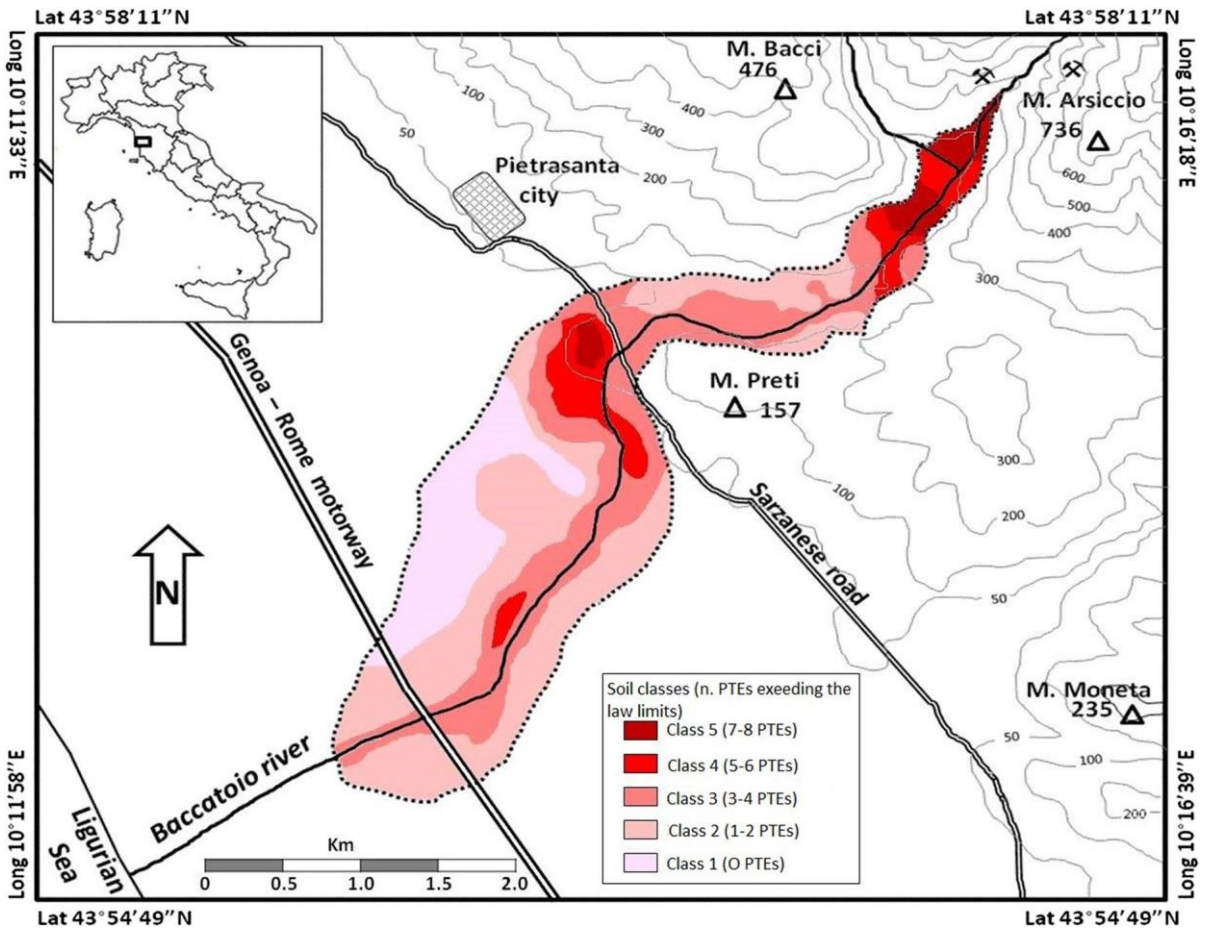Fig. 2 Soil contamination classes referred to the PTEs number with concentrations exceeding the law limits (Legislative Decree 152/2006 of Italy, Annex 4/14)
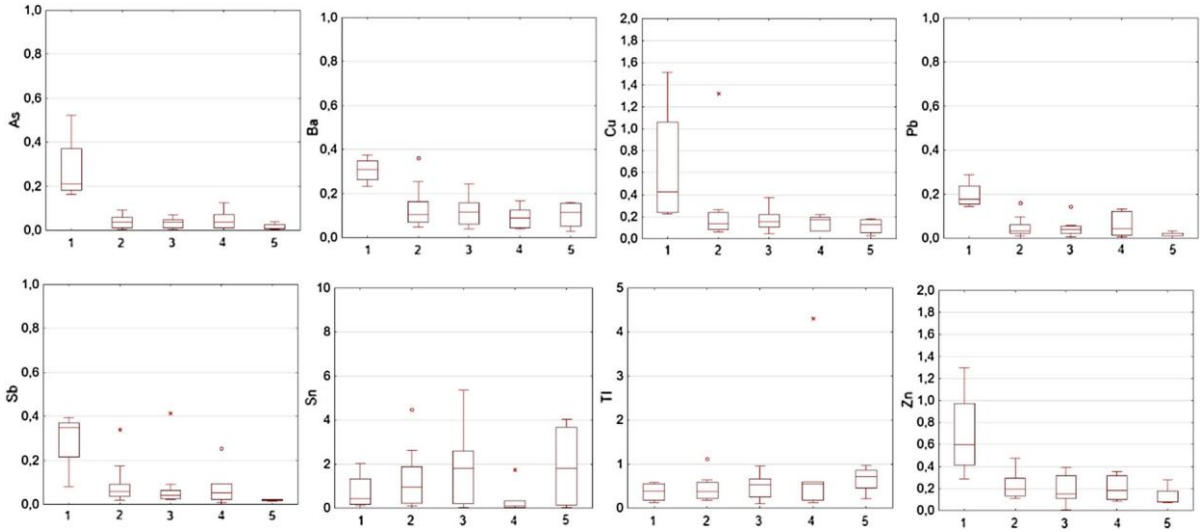
Fig. 3 Boxplot distribution of BCF of PTEs in the cabbage collected in the different areas. Data expressed in mg kg^{-1}
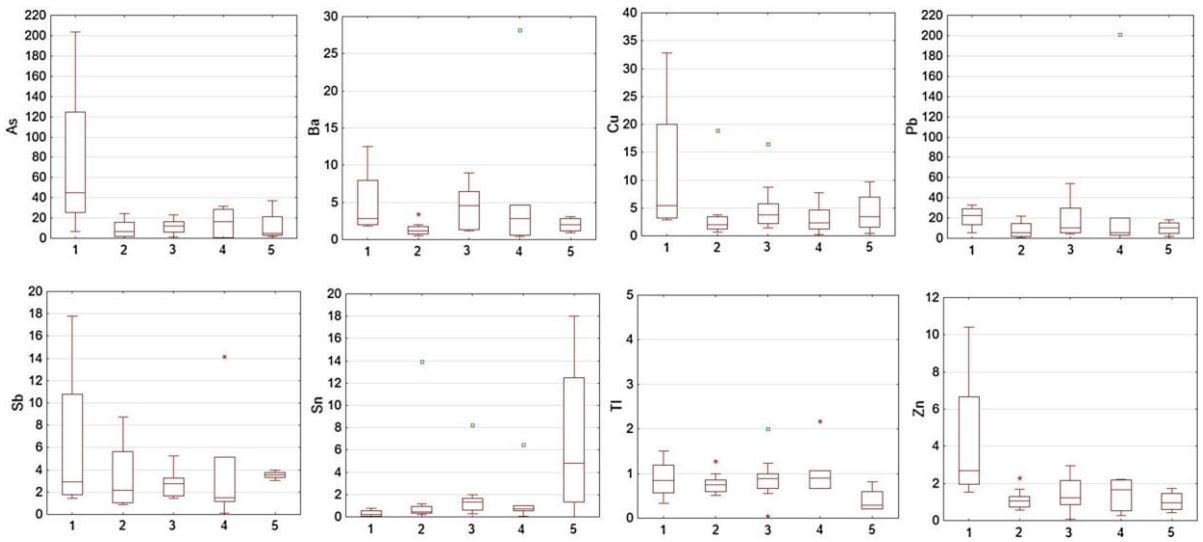

Fig. 4 Boxplot distribution of TF of PTEs in the cabbage roots collected in the different areas. Data expressed in mg kg^{-1}

Table 1 Mean and standard deviation (SD) of the different groups classified according to the number of PTEs exceeding the legislative threshold

Group		Fe mg kg^{-1}	Sig.	Mn	Sig.	S	Sig.	As	Sig.	Ba	Sig.	Cu	Sig.
1 ($n = 6$)	Mean	18246	c	297.3	c	412.8	b	16.8	c	558.7	c	94.8	b
	SD	5088.8		70.6		102.4		2.4		306.6		73.7	
2 ($n = 19$)	Mean	18262.8	c	435.8	c	487.9	b	18	c	535.2	c	92.2	b
	SD	3891.7		121.9		264.2		7.8		377.3		56.5	
3 ($n = 14$)	Mean	19508.3	bc	476.6	bc	900.6	ab	22.4	b	1281.9	ab	149	ab
	SD	3381.5		158.3		423.4		8.9		574.3		108.4	
4 ($n = 11$)	Mean	23511.5	ab	703.9	ab	1275.4	a	37	b	2094.5	ab	151.1	a
	SD	4172.5		203.5		391.5		12.2		541.6		106.7	
5 ($n = 9$)	Mean	27216.9	a	1092.3	a	1455.9	a	50.2	a	2357.6	a	215.8	a
	SD	5128		755.5		701.9		13.8		662.7		110.8	

Group		Pb mg kg^{-1}	Sig.	Sb	Sig.	Sn	Sig.	Tl	Sig.	Zn	Sig.
1 ($n = 6$)	Mean	67.3	c	4.5	c	1.6	c	0.2	b	102.6	c
	SD	17.6		0.5		0.4		0.1		10.5	
2 ($n = 19$)	Mean	81.9	c	4.7	c	2.1	c	0.1	b	142.5	c
	SD	27.6		2.1		0.5		0.1		48.9	
3 ($n = 14$)	Mean	141.5	ab	8.1	ab	2.4	b	0.3	a	190.2	ab
	SD	106.6		4.6		0.9		0.3		43.6	
4 ($n = 11$)	Mean	235.9	ab	15.3	ab	4.1	a	0.3	a	309.2	ab
	SD	142.1		8.5		2.4		0.4		61.9	
5 ($n = 9$)	Mean	299.2	a	15	a	3.8	a	0.3	a	396.9	a
	SD	151.6		5.2		1		0.4		91.4	

Significant differences (Sig.) are marked by different letters

Group		Cu		As		Pb		Zn	
		DMI	HRI	DMI	HRI	DMI	HRI	DMI	HRI
1	Mean	0.20	5.04	0.01	25.26	0.03	9.48	0.81	2.71
	SD	0.1	1.7	0.0	30.4	0.0	7.3	0.4	1.3
2	Mean	0.30	7.55	0.01	16.82	0.03	9.79	1.22	4.08
	SD	0.1	3.1	0.0	15.7	0.0	10.7	0.6	2.0
3	Mean	0.20	4.95	0.00	11.18	0.02	6.19	1.02	3.39
	SD	0.1	3.3	0.0	16.3	0.0	11.2	0.6	2.0
4	Mean	0.71	17.66	0.01	19.62	0.10	28.48	2.08	6.93
	SD	0.1	1.5	0.0	8.5	0.0	5.5	0.3	1.0
5	Mean	0.24	5.98	0.00	10.79	0.03	9.71	2.08	6.92
	SD	0.1	2.7	0.0	1.3	0.0	7.9	1.6	5.4
Average	Mean	0.33	8.24	0.01	16.74	0.04	12.73	1.44	4.81
	SD	0.10	2.46	0.00	14.44	0.03	8.51	0.70	2.32

Table 2 Mean and standard deviation of DMI and HRI calculated on the collected Brassica plants, grouped according to the different groups

1
2