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Thallium uptake and risk in vegetables grown in pyrite past-mining contaminated soil amended with organic fertilizer (compost): A potential method for Tl contamination remediation

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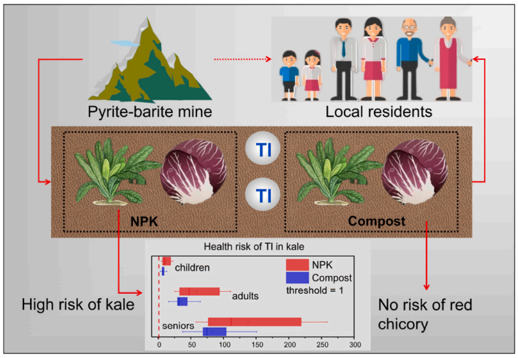
HIGHLIGHTS

- Tl, Ba, As and Pb contamination was unveiled in courtyard soil from a pyrite past-mining area.
- Hyper-accumulation of Tl (up to 17.1 mg kg^{-1}) was evident in Tuscany kale leaves.
- Tl in kale leaves displayed conspicuously high intake risk while red chicory was safe.
- Compost possessed better remediation ability compared with mineral fertilizer (NPK).
- Agricultural practice using compost suggested its possibility for Tl remediation in agro-system.

GRAPHICAL ABSTRACT



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ABSTRACT

Thallium (Tl) is a highly toxic trace metal that can cause severe pollution and damage to the ecological system. In this study, a field trial was conducted in a Tl-rich pyrite-barite past-mining area to unveil the fate of Tl in agricultural practice. Tuscany kale and red chicory cultivated in soil impacted by the dismissed mine of Valdicastello Carducci (Northern Tuscany, Italy) displayed significantly different uptake behaviors of Tl. Hyper-accumulation of Tl was observed in kale leaves and its content reached up to 17.1 mg kg^{-1} whereas only $<$0.70 mg kg^{-1} of Tl was found in leaves of red chicory. Due to the regionally polymetallic pollution, Tuscany kale grown in this area possessed a great Tl intake risk for the residents. As for the fertilization treatment, Tl in Tuscany kale leaves fertilized with mineral fertilizer (NPK) and compost were 21.4 and 12.8 mg kg^{-1}. The results suggested a potential remediation ability of compost in diminishing Tl in the vegetable leaves and thus may reduce its risk in the soil-crop system. Since Tl poisoning emergency may occur in agricultural fields near past-mining zones, it is critical to establish possible remediation measures to ensure food safety surrounding former mining areas likewise.

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1. Introduction

Persistent attentions have been received from the environmental pollution caused by toxic elements (Antoniadis et al., 2019; Beiyuan et al., 2023; Wang et al., 2023; Yin et al., 2019; Zeng et al., 2022; Zhou et al., 2020). Thallium is naturally present in soil at concentrations below the safety concentration threshold of 1 mg kg^{-1} set for arable soils of countries with advanced legislation on environmental protection. Enrichment of Tl in soil can be due to natural phenomena such as volcanic emissions or anthropogenic associated coal combustion and sulphide-involving mining/smelting activities (Liu et al., 2023; She et al., 2022; Wei et al., 2020a; Yin et al., 2021). Uncontrolled emissions from anthropogenic sources cause regional pollution and long distance diffusion induce significant thallium exposure to plants, animals and humans (Ouyang et al., 2023; Vaněk et al., 2012; Wang et al., 2021). Accumulation of Tl in soil over the safe concentration limits has been reported from several areas polluted by mining activities in various countries such as Poland, Spain, Greece, Italy, the United States, China and India, due to past and current emissions associated to natural sources and anthropogenic activities (e.g. Biagioni et al., 2013; Karbowska, 2016; Perotti et al., 2017; Zhou et al., 2020; Ghezzi et al., 2021; Wei et al., 2021). In polluted areas where soils are used for crop production, Tl poses significant risks to human health due to the well documented uptake by plant roots and storage in plant edible parts, which represent the entry pathway of Tl into the food chain (Zhang et al., 2023). In dismissed mining areas, Tl concentration in soil is receiving increasing public and governmental concerns as it acts as neurotoxin, and prolonged human exposure cause gastroenteritis and even death (Queirolo et al., 2009; Xiao et al., 2012).

For above-mentioned facts and reasons it is listed as one of the 13 priority potentially toxic elements (PTEs) by the U.S. Environmental Protection Agency (USEPA), European Commission (EC) and World Health Organization (WHO). Thallium in the environment assumes redox states of Tl(I) and Tl(III), and owing to its geochemical sulfophilic characteristics similar to other elements such as Hg, As, Cu, Pb and Zn, it is generally found in S-containing minerals such as lorandite (TlAsS), hutchinsonite ($PbTlAs_5S$), crookesite ($(Cu, Tl, Ag)_2Se$) and other sulphides (Kabata-Pendias and Pendias, 1999). Insoluble Tl-sulfides can be also present in galena (PbS), pyrite (FeS_2), sphalerite (ZnS), stibnite (Sb_2S_3), chalcopyrite ($CuFeS_2$), realgar (AsS) and orpiment (As_2S_3), or associated to clay minerals and Mn/Fe-oxides (Peter and Viraraghavan, 2005; Xiao et al., 2012). Thallium release in the environment is mainly due to mining activities and ore processing (Karbowska et al., 2014), or uncontrolled smelting emissions (Liu et al., 2022), and its fate in the environment is mainly controlled by water, in which Tl(I) salts are readily dissolved, whereas insoluble Tl(III) species are partitioned into sediments (Gomez-Gonzalez et al., 2015). From these secondary sources, Tl can spread into the food chain accumulation into soil and use of polluted waters for irrigation followed by uptake and concentration in crop plants and animals (Wang et al., 2022).

The southern sector of the Apuan Alps in North-West Italy is characterized by the occurrence of a series of pyrite–barite–Fe oxide orebodies, whose Tl-rich characteristic was only recently recognized. In particular, fine-grained pyrite is characterized by Tl concentrations up to 1100 mg kg^{-1} coupled with high contents of several other PTEs (D'Orazio et al., 2017; Wang et al., 2023). Uncontrolled mining waste released from acid drainage of mining areas and from mine spoil heaps after decommissioning resulted in high environmental Tl pollution in aqueous bodies (Biagioni et al., 2013; Perotti et al., 2017), and in streambed sediments (Ghezzi et al., 2021). In the same area high levels of Tl were found in tap water (Campanella et al., 2016, 2019), and Tl contamination in upland rhizospheric soils of horticultural crops in the Baccatoio watershed was also reported by Campanella et al. (2019). However, toxic effects of Tl arisen by soil-crops system are still rarely studied.

Production of high yields and high quality horticultural crops rely on tillage and fertilizing activities which can change the total concentration and potential phytoavailability of Tl and other PTEs by modifying the physical and chemical properties of the soil. In polluted areas, reworking of the soil surface prior to planting and organic fertilization can modify the Tl phytoavailability by modifying the Tl oxidation state due to the generation of acidic products of Tl-pyrite oxidation that control the Tl solubility and mobility, with Tl(I) being generally considered as less toxic than Tl(III), the first is more mobile in the aqueous phases than the most oxidated Tl, which forms stable covalent inorganic complexes or organic Tl compounds (Ralph and Twiss, 2002). The horticultural practice can also influence the uptake of Tl from horticultural plants. Also mineral fertilization with N, P and K may quench the uptake of Tl(I) by ionic competition with K^+, soils fertilized with organic amendments may reduce the Tl uptake by the formation of stable Tl-organic complexes, but to our knowledge information is still limited on Tl uptake by agrifood plants in arable soils. Such horticultural practices also influence the phytoavailability of other PTEs including such as As, Cd, Hg, Pb, Sb, and Zn, which are generally associated to Tl in mining tailing. However, dynamics of Tl and associated PTEs in relation to agricultural practices have been still poorly studied (Migaszewski and Gałuszka, 2021).

The objectives of the present work were (i) to investigate uptake and accumulation of Tl, Ba, Pb, Cr, As, Cd, Mn, Ni, Sb and Zn in vegetables grown in an Tl-polluted area contaminated by decommissioned mine, (ii) to evaluate the effects of different mineral or organic fertilization on crop uptake of PTEs, and (iii) to assess the potential health risk posed by PTEs ingested by the consumption of vegetables grown on polluted soils, with particular reference to Tl. Comparison between mineral and organic fertilization can bring new knowledge on Tl impact because Tl in soil is present as monovalent hydrated cation (Tl^+) which has a similar ionic radius to K^+, and NPK fertilization may quench Tl uptake by plants (Vaněk et al., 2011). Moreover, our experimental setup mimicked current smallholder horticultural own production in this polluted area, therefore the calculated health risks related to soil pollution and food intake can provide indications for more effective health protection measures in areas impacted by abandoned mines.

2. Materials and methods

2.1. Study area, cultivation trail and sampling

A small-scale cultivation trial was established in a Tl-contaminated area located in Valdicastello Carducci Village (Pietrasanta Municipality, Northern Tuscany, Italy), an area impacted by mining activities ceased in the 1990s. The cultivation trial was established in a private orchard of 6 m × 5 m area on July 2021, with Lacinato kale (*Brassica oleracea* L. *Viridis* Group 'Laciniato') and red chicory (*Cichorium intybus* L. var. *foliosum* Hegi) as leafy horticultural species typically grown in the area. Crops were fertilized either with compost or NPK mineral fertilizer, with two blocks for each species treated with the same fertilization type (Fig. 1). All fertilization methods were managed so as to provide the macronutrient requirement to the vegetable during the growing cycle. Specifically, reference was made to the following nutritional needs: 150 kg/ha of nitrogen (N), 100 kg/ha of phosphorus (P) and 200 kg/ha of potassium (K), respectively. Chemical characteristics of the compost used are reported in Table 1. All plots were irrigated using unpolluted water from the town water supply network.

2.2. Elemental analysis of soils and plants

Soil samples, taken before crop plantation, were dried in an oven at 65^{o} C to constant weight, ground and sieved (2 mm mesh). For elemental concentration analysis in plants, seedlings, intermediate leaves of two-month-old plants and leaves of plants at full maturity (six months after planting) were collected. Detailed information for sampling and plant growth capacity analysis are reported in Table S1. All vegetable samples were cleaned and dried in an oven at 65 °C to constant weight, ground (Retsch, GM 200), sieved (2 mm mesh) and stored prior to analysis. Quantification of elements was conducted by microwave-assisted mineralization using Suprapur® quality reagents (Merck, Germany). A quantity of 0.35 g of soil or leaves sample was transferred into a TFM closed vessel for the microwave digestion process (Ethos 1600 Milestone S.r.l. Sorisole, Bergamo, Italy). The microwave digestion was conducted by adding 6 mL of concentrated hydrochloric acid (30 %) and 3 mL of concentrated nitric acid (65 %), both of Suprapur® quality (Merck Chemicals GmbH, Darmstadt, Germany). Elemental concentrations were then quantified by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Ametek, Germany). The percentage of recovery for the analyzed elements was 95.25 %. For soil bulk concentrations were reported on a dry weight (dw) basis, whereas for plant tissues elemental concentrations were converted to fresh weight (fw) concentrations using the moisture contents of kale and red chicory to calculate their intake risk.

2.3. Risk assessment of PTEs in soil and vegetable based on geochemical and health risk indices

The geochemical enrichment factor (EF) was calculated according to Eq. (1) (Chester and Stoner, 1973), the geoaccumulation index (I_{geo}) according to Eq. (2) (Loska et al., 2003) and risk index (RI) according to Eq. (3) (Håkanson, 1980). Details of contamination levels for these three factors were reported in Table S2.

$$EF = \frac{(C_i/C_{Al})_{sample}}{(B_i/B_{Al})_{background}} \quad (1)$$

$$I_{geo} = log_2(C_i/1.5 \times B_i) \quad (2)$$

$$RI^i = Tr^i \times C_i/B_i \quad (3)$$

Table 1
Chemical profile of the compost used in the test.

Chemical compound	Value	Unit measure
N	1.65	% dw
P	0.53	
K	1.98	
Ca	79.9	g/kg dw
Fe	8.74	
Mg	13.2	
Na	10.1	
S	18.7	
Al	7797	mg kg^{-1} dw
As	3.59	
B	42.7	
Ba	132	
Be	0.15	
Cd	0.62	
Co	3.34	
Cr tot	27.1	
Cu	94.4	
Li	10.9	
Mn	309	
Mo	2.19	
Ni	13.2	
Pb	31.4	
Si	601	
Sr	293	
Ti	208	
Zn	179	
Hg	<0.10	

The EF value was calculated by normalizing element/Al ratios in sample to the background value. In this study, Al is considered as the reference element, and Ci and B_i refer to the element content (mg kg^{-1}) in soil sample and background. C_{Al} and B_{Al} are Al contents (mg kg^{-1}) in sample and background. The RI value of target element was calculated

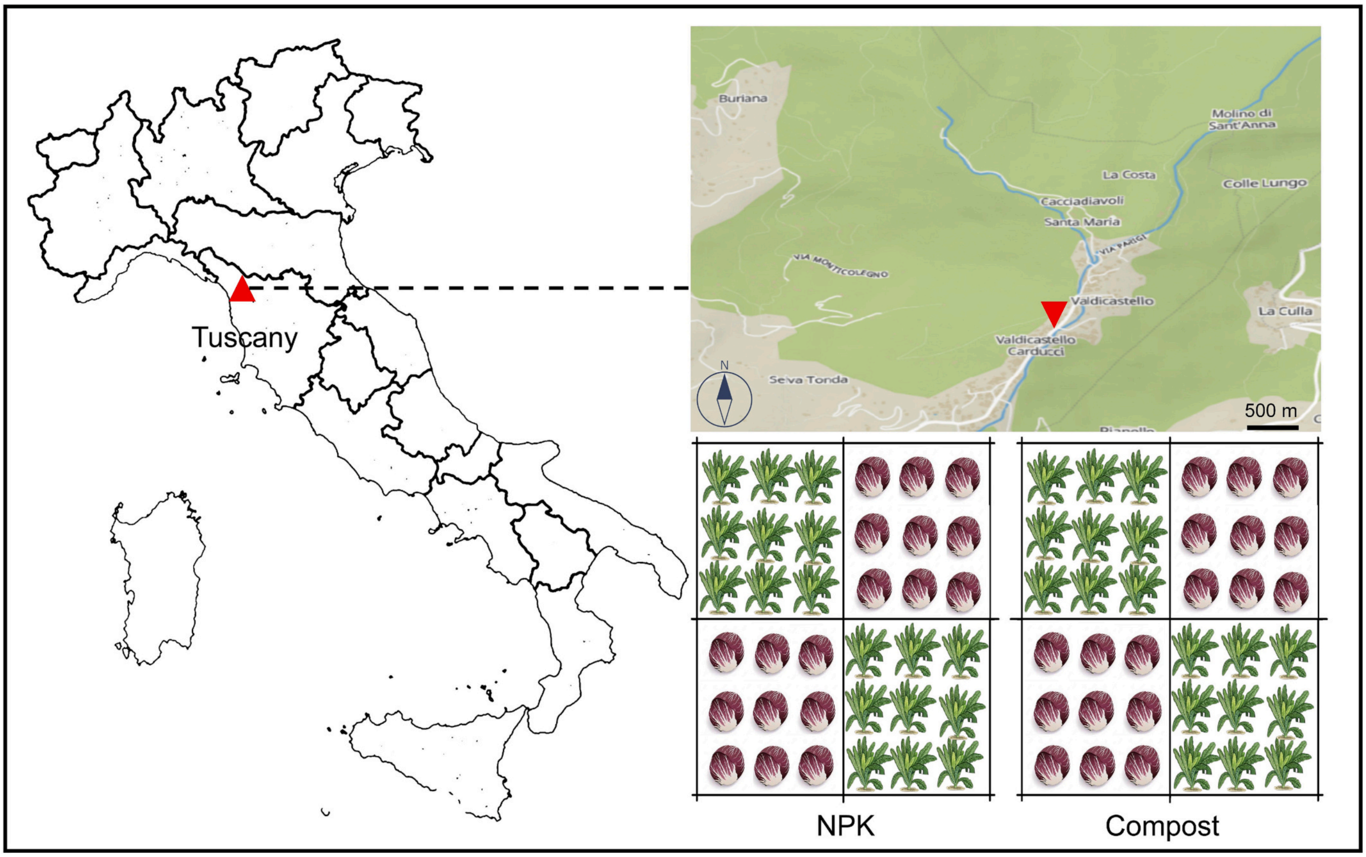

Fig. 1. Schematic display of the study area and cultivation trail.

by multiplying element toxicity coefficient by its sample/background content ratio. The toxicity coefficient (Tr^i) for Tl, As, Pb, Zn, Cd, Cr, Sb, Mn and Ni were 40, 10, 5, 1, 30, 2, 7, 1 and 5 (Håkanson, 1980; Ren et al., 2022).

The bioconcentration factor (BCF) was calculated by Eq. (4) to assess the correlation between element content in the soil and in the crop tissue (Samsøe-Petersen et al., 2002):

$$BCF_{leaves} = \frac{C_{leaves}}{C_{soil}} \tag{4}$$

where C_{leaves} and C_{soil} are the PTE contents in the leaves and soil, respectively. The hazard quotient (HQ) and chronic daily intake (CDI, mg/(kg/d)) values were calculated by Eq. (5) (Wang et al., 2005):

$$HQ = \frac{CDI}{R_fD} = \frac{C_i \times IR \times ED \times EF}{BW \times AT} \Big/ R_fD \tag{5}$$

where C_i (mg kg^{-1}), IR (kg/d), ED (a), EF (d/a), BW (kg) and AT (d) are: the PTE concentration converted into fresh weight in edible part (leaves), the daily ‘intake rate’ of kale and red chicory, the ‘exposure duration’, the ‘exposure frequency’, the consumer's “body weight” and the “averaging exposure time”, respectively. The IRs for children, adults and seniors in Italy are 0.0163, 0.0431 and 0.0431 kg/d, respectively, according to the Italian dietary consumption (Leclercq et al., 2009). The ED and BW values for children, adults, and seniors are 6, 30 and 70 a, and 26, 70 and 70 kg. The oral reference doses (RfD, mg·$(kg·d)^{-1}$) in food are 0.00001 for Tl, 0.02 for Ba, 15.1 for As, 0.024 for Mn, 0.02 for Sb and 0.30 for Zn (US EPA (United States Environmental Protection Agency), 2008; SCHER, 2012; US EPA (United States Environmental Protection Agency), 2018). Risk levels of HQ were set into three levels: $HQ < 1$, low risk or no risk, $HQ = 1.1–10$, moderate risk, and $HQ > 10$, high risk. Calculation of HQ values for potential carcinogenic elements Pb, Cd and Cr is multiplying their CDI values by their corresponding slope factors (mg·$(kg·d)^{-1}$) were 0.0085 (Pb), 42.0 (Cr), and 6.1 (Cd) (US EPA (United States Environmental Protection Agency), 2018). The HQ indices for Pb, Cd and Cr within $1·10^{-6}–1·10^{-4}$ represent low or no risk.

3. Results and discussion

3.1. Concentrations of Tl and other PTEs in soil and risk assessment

Thallium concentration in soil was 6.5 mg kg^{-1} (Table 2), higher than the soil threshold concentration value of 2 mg kg^{-1} of the Italian Legislation (Presidente della Repubblica, 2006, 2010). D'Orazio et al. (2020) reported that Tl concentrations in soils of the area were in the range 25–184.6 mg kg^{-1}. Concerning the Tl background concentration, for our specific case study it is hard to refer to values of local non managed areas because the past and ongoing domestic horticultural practice has conditioned the concentrations of Tl in the topsoil, with non-quantifiable Tl translocation to plants and soil biota, nor of its movement down the soil profile. Compared to other Tl contaminated agricultural soils from mining area in southwest China (Xiao et al., 2004a, 2004b) or forest soils from Olkusz district in southern Poland

Table 2

Contents of elements (mg kg^{-1}, dw) in soils, seedlings and leaves of kale and red chicory.

	Tl	Ba	Pb	Cr	As	Cd	Mn	Ni	Sb	Zn
Cultivated soil (n = 2)	6.72 ± 0.36	18,318 ± 335	555 ± 4.00	41.8 ± 0.65	106 ± 9.28	3.60 ± 0.02	849 ± 9.55	27.9 ± 1.45	30.5 ± 7.40	1115 ± 240
Earth crust[a]	0.45	425	15.0	35.0	1.80	0.20	950	20.0	0.20	20.0
Concentration limit in soil, Italy[b]	2.00	/	100	150	20.0	2.00	/	120	10.0	120
Seedling of kale (*n* = 1)	<0.50	12.84	<0.50	0.44	<0.50	0.15	85.07	<0.30	<0.50	28.02
Seedling of red chicory (n = 1)	0.59	19.23	<0.50	0.60	0.89	0.42	198.08	84.88	<0.50	65.81
Maximum permissible limit in food[c]	0.50	200	0.30	0.50	0.20	0.20	500	1.00	1.00	20.0
Element concentrations in leaves of 2 months (based on factors “treatment” and “species”)										
Treatment										
NPK (n = 8)	27.8 ± 10.5	701 ± 197 *a*	8.90 ± 3.03	2.28 ± 0.83	1.05 ± 0.33	0.79 ± 0.16	52.4 ± 4.97	83.4 ± 21.2	0.42 ± 0.21	79.4 ± 12.6
Compost (*n* = 8)	20.9 ± 8.33	402 ± 66.1 *b*	7.26 ± 1.91	1.02 ± 0.17	1.10 ± 0.37	0.78 ± 0.12	58.5 ± 6.86	67.9 ± 8.99	0.28 ± 0.19	106 ± 15.1
Species										
Kale (n = 8)	48.2 ± 4.62 *a*	394 ± 65.3 b	6.31 ± 2.07	1.00 ± 0.18	1.08 ± 0.34	0.44 ± 0.04 *b*	63.1 ± 5.40	54.4 ± 12.1	0.40 ± 0.20	72.0 ± 14.5 *b*
Red chicory (n = 8)	0.52 ± 0.17 *b*	709 ± 196 a	9.86 ± 2.80	2.31 ± 0.82	1.06 ± 0.36	1.13 ± 0.08 *a*	47.8 ± 5.35	96.9 ± 16.4	0.30 ± 0.19	114 ± 10.3 *a*
Interaction	*	NS	NS	NS	NS	NS	NS	NS	NS	NS
Element concentrations in leaves of 6 months (based on factors “treatment” and “species”)										
Treatment										
NPK (n = 20)	21.4 ± 3.85 *a*	195 ± 34.2	2.58 ± 0.43	0.68 ± 0.10	<0.70	0.24 ± 0.02	33.6 ± 3.33	0.62 ± 0.05	<0.70	50.5 ± 3.68
Compost (*n* = 20)	12.8 ± 1.65 *b*	206 ± 43.8	3.55 ± 1.20	0.66 ± 0.09	<0.70	0.21 ± 0.02	37.7 ± 3.33	0.65 ± 0.05	<0.70	60.1 ± 3.39
Species										
Kale (n = 20)	17.1 ± 1.43 *a*	292 ± 23.1 *a*	3.86 ± 0.45	0.95 ± 0.05 *a*	<0.70	0.15 ± 0.01 *b*	47.7 ± 1.40	0.66 ± 0.04	<0.70	48.2 ± 2.06 *b*
Red chicory (n = 20)	<0.70 *b*	109 ± 22.7 *b*	1.50 ± 0.26	0.40 ± 0.03 *b*	<0.70	0.30 ± 0.02 *a*	23.6 ± 1.05	0.60 ± 0.03	<0.70	62.3 ± 2.97 *a*
Interaction	*	NS	NS	NS	NS	NS	NS	NS	NS	NS

Note: *$P < 0.05$; NS no significance; / value not given.

[a] Data taken from Hamilton (2000).

[b] Maximum contents established for soils of public, residential and private areas by the Italian Ministry of Environment.

[c] Value taken from Umweltqualität (1998), European Commission (EC, 2006) and FAO/WHO (2011).

(Vaněk et al., 2013), Tl concentration in the studied soil was lower and was similar to those reported for paddy soils (~3 mg kg^{-1}) from a pyrite mining area in China (Jiang et al., 2021), and for farmland soils (2.00 mg kg^{-1}) from southern Italy (Duri et al., 2020). Among the other determined PTEs such as Pb, As, Cd, Sb, and Zn showed higher concentrations than the threshold limits of the Italian environmental legislation (Table 2). These results paralleled those by Resongles et al. (2014). Excessive Pb, As and Zn accumulation into edible parts of plants can impact human health by altering the functions of central nervous system, liver and kidneys (Kalia and Flora, 2005). Concentrations of Ba in the studied soil were also high (Table 2). Though the Italian environmental legislation shares no threshold concentration limits for Ba, natural Ba concentrations in unpolluted soil range from 100 to 3000 mg kg^{-1}, with mean value of 425 mg kg^{-1} in the Earth crust (Nogueira et al., 2010). A Ba concentration limit for sludge used as amendment of agricultural soils was set at 1300 mg kg^{-1} (dw) by the Brazilian National Environment Council (CONAMA, 2006). These data confirm that in the studied soil the Ba concentration was unusually high, due to the presence of Barite in the released mine waste material. High Ba concentrations in a paddy soil of a Ba mining area in South-West China, ranging from 518 to 65,760 mg kg^{-1} was also reported (Lu et al., 2019). Excessive Ba concentrations in soil may cause high accumulation into edible plants and impact human health because Ba may interfere with the Ca metabolism and cause bone diseases (Standen and Stanfield, 1978; Kravchenko et al., 2014).

Values of EF and I_{geo} indices of PTEs Tl, Ba, As, Pb, Zn, Cd and Sb were over 20, indicating that they were of very high contamination in soil (Table S3). The RI value of single target elements showed significant values for Tl, As, Pb, Cd and Sb. These geochemical enrichment and risk indices confirmed potential high risk of PTEs in the studied soil because of their possible accumulation or hyper-accumulation in crops.

3.2. *Contents of Tl and other PTEs in vegetable leaves, and uptake mechanism*

Concentrations of Tl, Ba and the other measured PTEs in the original of kale and red chicory seedlings were acceptable for various food qualitative standards (Umweltqualität, 1998; EC, 2006; FAO/WHO, 2011; Wei et al., 2020b) (Table 2). After 2 months of growth, kale leaf concentrations of Tl, Ba, Pb, As, Cr and Ni exceeded the safety threshold limits for kale, whereas red chicory leaves presented comparatively lower concentrations of these PTEs, Tl but Ba, Cd and Zn concentrations above the safety thresholds limits (Table 2). At the end of the growth cycle, Tl, Ba, Cr, Cd, Mn, Ni and Sb concentrations in leaves of red chicory were all below the safety thresholds, whereas kale leaves accumulated high concentrations of Tl and other PTEs (Table 2). Reduction of PTEs concentrations during plant growth was growth-related dilution (calculated by dividing decreased element concentration to the original element concentration) effect, which varied across the PTEs and plant species with the magnitude shown in Table S4. Though for kale leaves Tl concentration decreased from 48.2 mg kg^{-1} of 2 months leaves to 17.0 mg kg^{-1} of 6 months leaves, its concentration at maturity harvest still exceeded the safety thresholds for foodstuff (Table S4). In addition, compared with Tl concentration in edible parts of vegetables such as chard (0.01 mg kg^{-1}), onion (0.18 mg kg^{-1}) and chili pepper (0.17 mg kg^{-1}) from the same mining area in Tuscany (D'Orazio et al., 2020). A similar growth-related dilution degree of PTEs for old leaves as compared to young leaves was reported for *Arabidopsis halleri* (*Brassicaceae* family) grown on a metal amended soil (Stolpe et al., 2017), and higher As concentrations in young than in old plant leaves was reported by Bondada et al. (2004).

Plant elemental analysis confirmed the capability of *Brassicaceae* species to accumulate higher concentrations of various PTEs in the edible parts compared to *Asteraceae* family species (red chicory) or *Solanaceae* family species such as tomato, potato, eggplant and pepper (Liu et al., 2017; Liu et al., 2019a,b; Pearson and Ashmore, 2020; Bawwab et al., 2022). The Tl accumulation by kale at the end of its growth cycle was at a similar level reported by Liu et al. (2020) for oilseed rape grown in pyrite mining affected soils of southern China (Liu et al., 2020) or grown on Tl-contaminated soil near a cement plant in Leimen, Germany (Kurz et al., 1999). The Tl concentrations detected after 2 months of growth were similar to those of young leaves of green cabbage growing in Tl-As-Hg mining contaminated soils in southwest China (Jia et al., 2013). For plant leaves, the BCF value was >1 only for Tl in kale plants with values of 7.2 after 2 months and 2.5 at full maturity, indicating accumulative behavior towards Tl (Table S4). Previous studies on horticultural crops such as basil, mint, and strawberry grown on Tl polluted soils showed BCF (leaves) values as 0.40, <0.01 and 0.30, respectively (Ferronato et al., 2016).

High Ba concentrations were observed in leaves of both kale (394) and red chicory (709) either after 2 months or at the end of the growth cycle. Typical Ba contents in foodstuff ranges from 2 to 13 mg kg^{-1}, with median values lower than 2.0 mg kg^{-1} (Gormican, 1970; IRIS, 2006). Previous studies have shown that rice from Ba mining impacted areas of southern and southwest China ranged from 0.06–1.20 and 0.10–3.50 mg kg^{-1} (Ma et al., 2017; Lu et al., 2019), and that Ba concentration on maize grains grown in soils treated with sewage sludge were in the range of 0.06 to 1.05 mg kg^{-1} (Nogueira et al., 2010). A Ba content of 200 mg kg^{-1} in food is moderately toxic, whereas a concentration of 500 mg kg^{-1} is considered toxic (Pais and Jones Jr, 2000). Meanwhile, Ba concentrations in the studied vegetable leaves were far below the internal toxicity threshold values established for trifoliated bush bean leaves (2000 mg kg^{-1}) according to Llugany et al. (2000). Unusually high Ba concentrations in the order of 45 mg kg^{-1} were reported for leafy vegetables grown in urban environment (McBride et al., 2014) and in Brazilian nut, a known Ba hyper-accumulator concentrations in the range 3000–4000 mg kg^{-1} have been reported (Beliles, 1979). In the present study, even if for Ba the growth-related dilution was relatively high (Table S4) for both red chicory and kale, the health risks arisen by final Ba concentrations in the edible parts were of concern. Similar results were reported various plants such as *Jatropha curcas*, *Dodonea viscosa* and *Cassia auriculata* growing in Barite rich soils from the Nellore mica belt, Andhra Pradesh, India (Nagaraju and Karimulla, 2002), and Ba concentrations up to 3550 mg kg^{-1} were reported for shoots of *Indigofera cordifolia* grown on barite-rich mine dumps of the Vemula area, India (Raghu, 2001).

As displayed in Fig. 2a, thallium concentrations in two months kale leaves showed significant negative correlation with As and Mn, while Ba showed significant positive correlation with Pb, Cd, Cr, and Ni ($P < 0.01$) (Fig. 2a). At full maturity no significant correlation between Tl and other PTEs was observed whereas Ba was positively and significantly correlated with Pb, Cr, and Ni (Fig. 2b). As for red chicory, in 2 months leaves no significant correlation was observed in Tl and other PTEs (Fig. 2c) whereas Ba was positively and significantly correlated with Pb, Cd, Cr and Ni, but only with Pb and Cr in leaves of plants at full maturity (Fig. 2d). Globally, the correlation analysis showed that kale and red chicory displayed similar PTEs uptake behaviors of elements, indicating that Tl may be adsorbed by these two crops via different pathways compared to other PTEs. In particular, the competitive accumulation trend observed between Tl and K in leaves confirmed a potential common uptake route of these two elements, e.g. using the K^+-ATPase2 system (Xiao et al., 2004a, 2004b). Differently, the other studied PTEs such as Ba, Pb, Cd, Cr and Ni showing positive correlations, could be accumulated and transferred to leaves through the same metabolic pathways (Fig. 2).

3.3. *Effects of different fertilization on Tl uptake in vegetables*

Plants fertilized with compost absorbed significantly less Ba after 2 months and significantly less Tl at full maturity as compared to plants fertilized with NPK (Table 2). Thallium concentration in 2 months' kale leaves fertilized with NPK and compost were 55.0 and 41.4 mg kg^{-1},

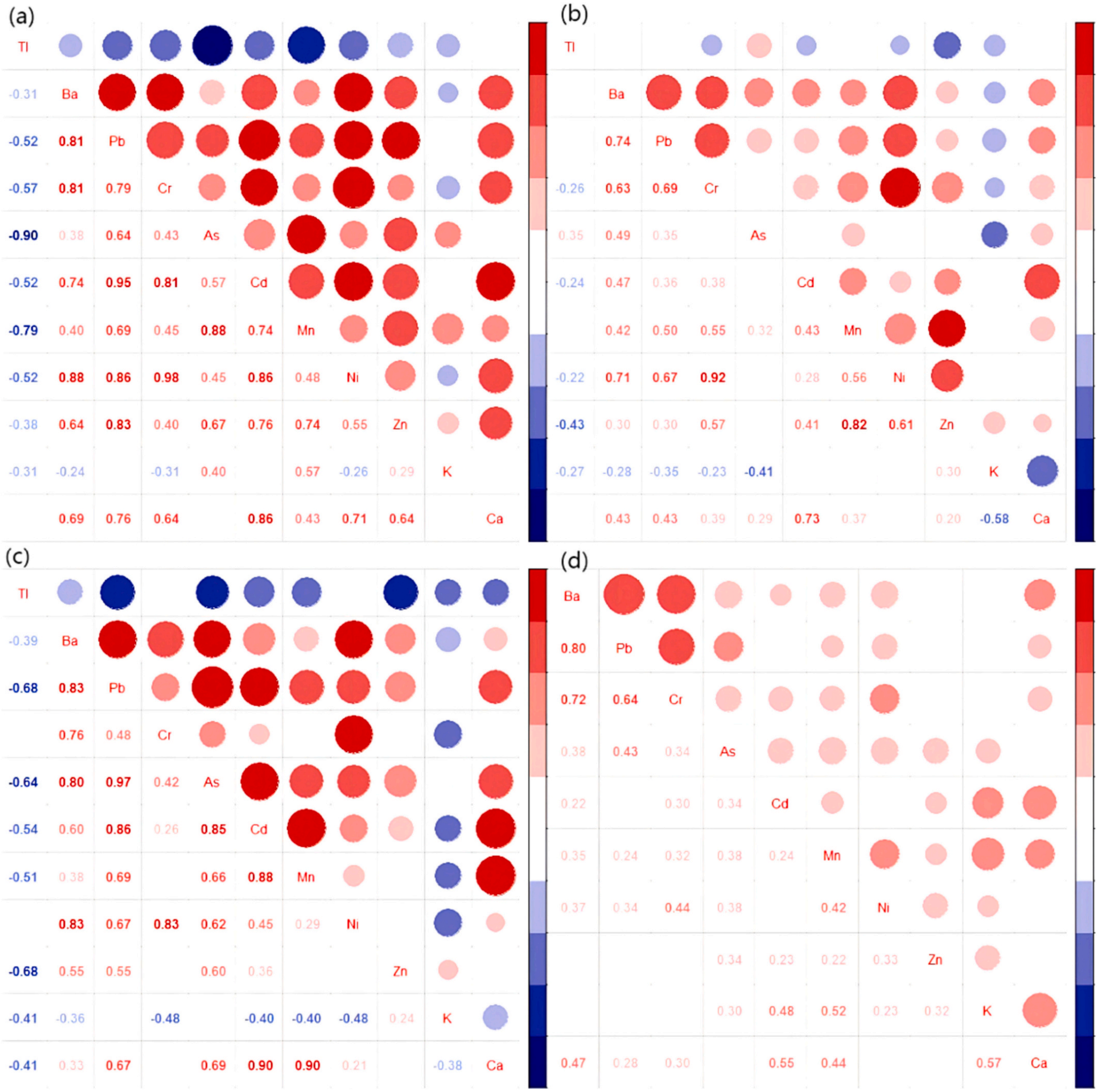

Fig. 2. Correlation between Tl and other PTEs in leaves: (a)/(b): 2/6 months kale; (c)/(d): 2/6 months red chicory (circle in red: positively correlated; circle in blue: negatively correlated).

respectively, whereas in red chicory leaves Tl concentrations were 0.71 and 0.34 mg kg^{-1} (Table 2, Fig. 3). These results indicate that the hypothesis that NPK fertilization could quench Tl uptake by plants was not verified. However, 6 months kale fertilized with compost accumulated less Tl in leaves (12.8 mg kg^{-1}) as compared to that of NPK (21.4 mg kg^{-1}). Although this result is in line with previous studies which suggested that compost can reduce plant uptake of PTEs in polluted soils (Vaněk et al., 2010; Luo et al., 2020) as PTEs can be bound to organic matter (OM) by complexation (Clemente and Bernal, 2006; Hu et al., 2010; Gustafsson et al., 2014) reducing its bioavailability (Liu et al., 2011), we ascribe these results to the lower plant vigor and growth in soils of NPK than compost plots (Fig. 4). This hypothesis is supported by the significant correlation between plant biomass production and PTEs uptake (Table S1).

3.4. Risk assessment based on chronic intake

Hazard quotients for adults, seniors and children calculated based on the chronic intake of PTEs from their concentrations in kale and red chicory leaves at full maturity (Figs. 5, 6; Tables S5–S7). The HQ values of As, Mn, Ni, Sb and Zn in kale and red chicory were <1, indicating no health risks posed by these PTEs for adults and seniors for both plant species (Fig. 5). The HQ values of Ba for children and adults were <1, while those in kale for seniors ranged from 0.18 to 2.27 (with average of 0.94), therefore generally there is no risk (or slight risk) of Ba in vegetables grown in the studied area. Concerning the potential carcinogenic

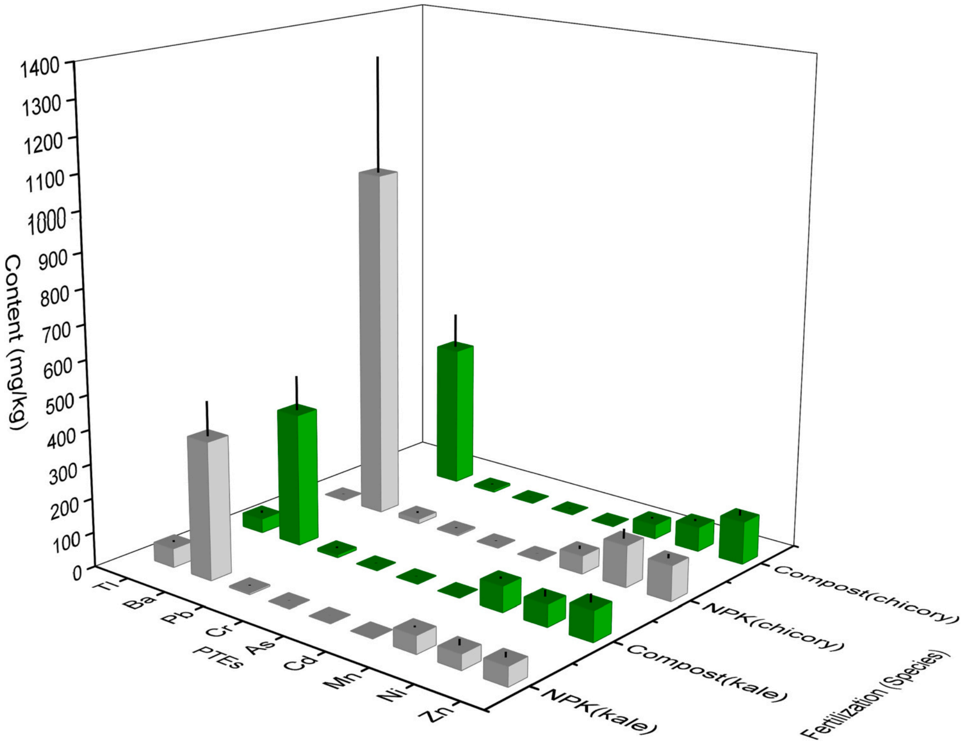

Fig. 3. Concentration of Tl and other PTEs in 2 months leaves of kale and red chicory fertilized by NPK and compost.

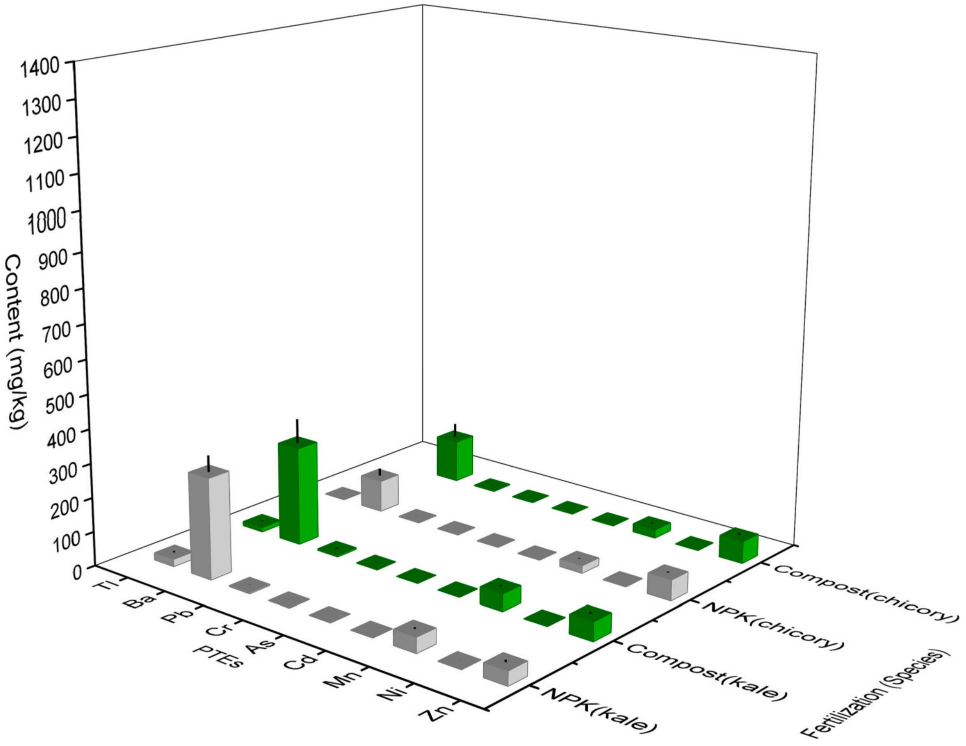

Fig. 4. Concentration of Tl and other PTEs in 6 months leaves of kale and red chicory fertilized by NPK and compost.

HQ values of Pb and Cd were $<10^{-4}$ except for Cr, suggesting that Cr could pose carcinogenic risks to adults and seniors through consumption of both kale and red chicory (Fig. 5). According to the dietary estimated intake risk of trace elements in an Italian population, average HQ values for Tl was 0.744 (lower than 1) (Filippini et al., 2020). The HQ values in Tuscany kale leaves for Tl ranged from 16.0 to 110 for adults and 37–259 for seniors, much higher than the threshold value of 10, indicating high health risk for kale (Fig. 5). Considering other researches also focusing on health risk in environmental samples, Queirolo et al. (2009) found that HQ values for Tl in potatoes from mining areas were in the range of 75 to 138, for adults. The average HQ value of 9.65 for Tl in kale also indicated moderate risks for children (Fig. S1). Calculation

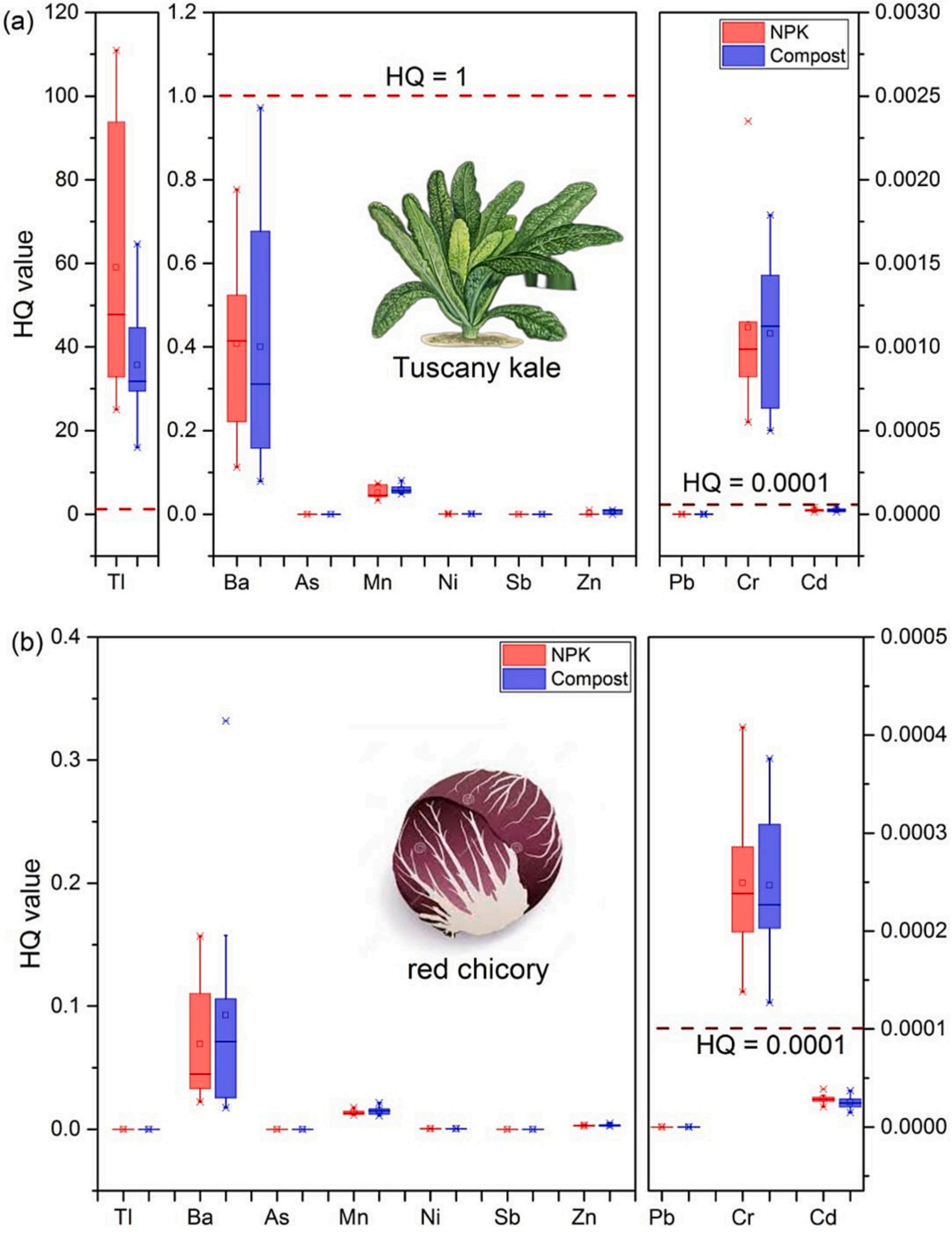

Fig. 5. Hazard quotients of Tl and other PTEs in (a) Tuscany kale and (b) red chicory leaves for adults.

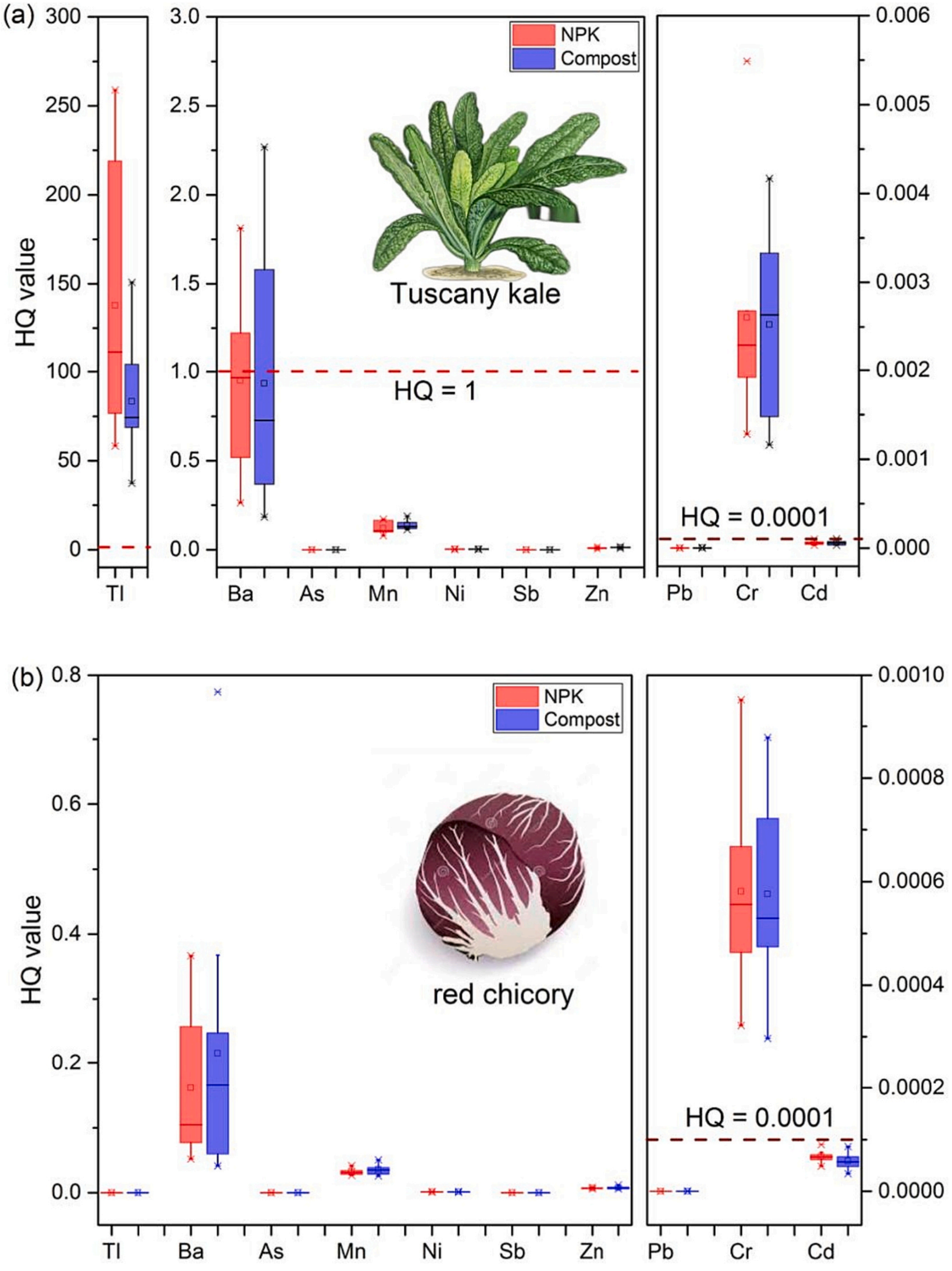

Fig. 6. Hazard quotients of Tl and other PTEs in (a) Tuscany kale and (b) red chicory leaves for seniors.

of HQ values for red chicory indicated no risks posed by Tl nor by other determined PTEs.

Globally, risk assessment of vegetables grown on these studied soil showed possible high risk of Tl for the local residents by daily intake of Tuscany kale, higher for seniors than adults or children owing to their long-term consumption. These findings are in line with previous risk assessment studies of cultivation of agricultural plants on soils polluted by PTEs (Zukowska and Biziuk, 2008).

4. Conclusion

This study confirmed that improper waste management of thalliferous pyrite-barite mining can release Tl, Ba and other PTEs into regional soils. Investigation of courtyard soil from historical mining zone in Tuscany unveiled definite pollution of Tl and Ba. Although different vegetables at full maturity stage accumulate Tl, Ba and various PTEs at different concentrations, home cultivation and consumption of horticultural plants on soils polluted by Tl and various PTEs pose risks to health of residents due to high concentrations of PTEs in the edible parts. While for red chicory all PTEs concentrations were below the safety thresholds, Tuscany kale presented Tl concentrations above safety thresholds and imposed hazards due to hyper-accumulation of Tl and other PTEs. Mineral NPK fertilization was not effective in reducing Tl plant uptake, whereas soil amendment with compost significantly reduced Tl and Ba uptake by both red chicory and kale plants, which can be considered as a applicable Tl immobilization in mining affected agro-system. Crop safety within Tl-bearing minerals mining area should be concerned in order to avoid potential public poisoning incidents. The presented results indicated that residential soils polluted by PTEs should not be used for home horticulture, and remediation interventions in such areas should be valued.

CRediT authorship contribution statement

Xudong Wei: Writing - Original draft, Experiment, Formal analysis. **Carlo Nicoletto**: Supervision, Project administration, Methodology, Review & Editing. **Paolo Sambo**: Review & Editing. **Juan Liu**: Supervision, Project administration, Review & Editing. **Jin Wang**: Review & Editing. **Riccardo Petrini**: Review & Editing. **Giancarlo Renella**: Methodology, Review & Editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.168002.

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