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Potentially Toxic Elements (PTEs) in Soils and Bulbs of Elephant Garlic (*Allium ampeloprasum* L.) Grown in Valdichiana, a Traditional Cultivation Area of Tuscany, Italy

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Featured Application: Evaluation of the ecological and health risk associated with the cultivation and consumption of the typical product "Aglione della Valdichiana" (elephant garlic).

Abstract: The aim of this study was to provide, for the first time, data on the concentration of potentially toxic elements (PTEs) in soils and bulbs of elephant garlic (*Allium ampeloprasum* L.) cultivated in Valdichiana, a traditional agricultural area of Tuscany, Italy. Bulbs of elephant garlic and soil samples were collected in four cultivation fields and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U, V, Zn. The concentrations of these PTEs in bulbs and cultivation soils were used to calculate geochemical, ecological and health risk indices. The results of this study suggest that, although bulbs of elephant garlic from the Valdichiana area may present slightly high concentrations of Cd, Ni and Pb, the associated health risk based on the daily intake is absolutely negligible. Cultivation soils had somewhat high Cu concentrations probably due to the diffuse use of Cu-based products in agriculture, but showed overall a very low ecological risk.

Keywords: *Allium ampeloprasum*; elephant garlic; environmental risk; health risk; heavy metals

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1. Introduction

Tuscany is home to some of the most typical Italian food products [1], which are particularly appreciated for their gastronomic quality. Among them is elephant garlic (*Allium ampeloprasum* L.) cultivated in the Valdichiana area, locally known as "Aglione della Valdichiana" (hereafter, AdV). The AdV is currently deeply investigated with the aim of promoting its particular nutraceutical features [2], which are quite different from those of common garlic (*Allium sativum* L.) [3]. The most important feature of elephant garlic is a much lower content of fibers and alliin, the sulfur-containing compound responsible for the aggressive taste of garlic, giving to this plant a greater digestibility and a much more delicate taste.

Bulbs of common garlic are known to accumulate potentially toxic elements (PTEs) such as Cd, Cu, Ni, Pb [4–7]; therefore, this plant is of questionable edibility when cultivated in contaminated soils with uncertain safety [8,9]. Allicin, an organosulfur compound originated from alliin, has been suggested to be involved in the accumulation process of PTEs in common garlic as a metal-binding molecule [10]. Due to its lower alliin content compared to common garlic, elephant garlic may show a lower capacity to accumulate

PTEs in the bulbs [11], thus ensuring greater safety for its consumption. Nevertheless, to the best of our knowledge, data on the concentration of PTEs in the Tuscan traditional product AdV are completely missing, and there is thus the need of a quick investigation of this chemical feature of AdV, especially as its notoriety is increasing and it is being preferred over common garlic in many traditional recipes.

Similarly, data on the concentration of PTEs in soils where AdV is cultivated are also missing. From an environmental point of view, soils of the Valdichiana area are generally not at risk of contamination from polluted air and waters since their main use is as arable land and industrial activities are only marginally present. However, this area is classified as vulnerable to nitrates [12], and agricultural practices could alter the geochemical profile of Valdichiana soils, due to the release of chemical elements from fertilizers and pesticides which can affect soil quality as well as crop edibility [13–15].

In this view, the concentrations of several PTEs (namely As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U, V, Zn) were determined in bulbs of AdV and soils from cultivation fields in the Valdichiana area. The aim of this study is to fill the gap of knowledge about the inorganic chemical composition of AdV, by providing, for the first time, data on the concentration of PTEs in bulbs and cultivation soils, with the final purpose to assess the uptake and accumulation of these chemicals in bulbs and the potential risk associated with AdV consumption.

2. Materials and Methods

2.1. Study Area

Valdichiana (the Chiana plain) is an almost flat geographic area of ca. 2000 km^2 located in SE Tuscany. From the geological point of view, Valdichiana is a NW–SE oriented tectonic basin filled by marine, lacustrine and continental deposits (Miocene-Pleistocene) mainly consisting of sandy, silty-clayey and clayey sediments. The climate is sub-Mediterranean, with rainfall in the range of 700–900 mm/year and mean temperatures from 5.4 °C in January to 23.5 °C in July–August. The local economy is based on agriculture, and industrial activities are scanty [16]. The Valdichiana area is crossed by important routes of communication such as the highway 1, the main highway of Italy, and the important railway line connecting Rome with Florence.

2.2. Experimental Design and Sample Treatment

To realize this study, four cultivation fields in the Valdichiana area were selected among the farms producing the AdV, members of the local "Association for the Protection and Promotion of the "*Aglione della Valdichiana*". From each cultivation field, 50 cloves of AdV used as seeds and 10 surface soil samples (0–20 cm) were randomly collected during October 2019 at the time of sowing. AdV cloves derived from the harvesting campaign of June 2019.

In the laboratory, 10 cloves from each cultivation field were randomly selected, coupled two by two, and divided in five separated stocks. Then, the cloves were peeled, cut in pieces of ca. 1 cm^3, freeze-dried for 12 h, then powdered using a ceramic mortar.

Soil samples were air dried at room temperature and then processed as follows. Five soil samples were randomly selected from each cultivation field, and dried for two days at 40 °C in a ventilated oven; the dried soil samples were then crushed using a rubber hammer and sieved at 2 mm. The soil fraction < 2 mm was homogenized by quartering and pulverization using an agate mortar and a mechanical pulverizer for 40 min.

2.3. Chemical Analysis

The AdV samples were solubilized by the following procedure: 3 mL of nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2) (ultrapure reagents) were added to about 250 mg of powdered AdV sample. Soil samples were solubilized by acid digestion adding 2 mL of HNO_3, 2 mL of hydrofluoric acid (HF) and 1 mL H_2O_2 (ultrapure reagents) to 250 mg of pulverized soil sample. Digestion of AdV and soil samples was carried out in Teflon bombs in a Milestone Ethos 900 microwave lab station. Concentrations of PTEs in AdV and soil samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin Elmer NexION 350 spectrometer. Analytical accuracy was evaluated analyzing the standard reference materials GBW 07604 (Poplar Leaves) and SRM 2709 (San Joaquin Soil; see Table S1 of "Supplementary Files"). Recoveries ranged from 91% (Cr) to 114% (Cd) for GBW 07604, and from 90.4% (Ni) to 105.5% (Cu) for SRM 2709 (see Table S1 of "Supplementary Files" for details).

2.4. Data Analysis

Since concentrations of each analyzed PTE in AdV and soil samples approached normal distribution (Shapiro–Wilk test, $p < 0.05$), their descriptive statistics are given as min, max, mean, standard deviation and coefficients of variation. To appreciate selective uptake of PTEs by AdV from the soil, a soil–plant rank-ordered plot of these chemical elements was arranged.

Soil contamination, ecological risk and health risk were evaluated using the following specific indices.

2.4.1. Health Risk

The risk associated with the consumption of the AdV bulbs was evaluated by means of the Health Risk Index (HRI) as the ratio between the Daily Intake of PTE (DIPTE) and its reference dose (R_{fd}), expressed as mg/kg/day:

$$\text{Health Risk Index (HRI)} = \text{DIPTE}/R_{fd},$$

The DIPTE for the inhabitants of the Valdichiana area was calculated following the formula proposed by Khan et al. [17]:

$$\text{DIPTE} = C_{plant} \times D_{food\ intake}/B_{average\ weight},$$

where C_{plant} is the average concentration of the chemical element (PTE) in the AdV bulbs expressed as mg/g dw, $D_{food\ intake}$ is the daily dose of food (AdV) expressed as grams, and $B_{average}$ weight is the average body weight expressed in kg. An average body weight of 70 kg was selected for the DIPTE calculation.

The R_{fd} values (mg/kg/day) were taken from the IRIS (Integrated Risk Information System) of the US EPA [18] and were as follows: As = 0.0003, Cd = 0.005, Co = 0.0055, Cr = 1.5, Cu = 0.040, Ni = 0.020, Pb = 0.0035, Sb = 0.004, Tl = 0.0003, U = 0.003, V = 0.009, Zn = 0.3.

Therefore, HRI values > 1 are indicative of a potential risk for human health [19].

2.4.2. Soil Contamination

To identify contamination by PTEs in cultivation soils of the Valdichiana area, the following geochemical indices were used: contamination factor (CF) and geo-accumulation index (I_{geo}). The CF is a rough indicator of the soil contamination, calculated as the ratio between the concentration of a chemical element in the investigated soil and its reference soil background level [20]; the I_{geo} is a slightly more refined contamination index, based on the use of CF index corrected by a value (1.5) for background concentration in the soil [21],

$$\text{Contamination Factor (CF)} = C_{element}/C_{background}$$

$$\text{Geo-accumulation index } (I_{geo}) = \log_2 (C_{element}/(1.5 \cdot C_{background}))$$

where $C_{element}$ is the element concentration in the investigated soil and $C_{background}$ is its soil background level.

To calculate the CF and I_{geo} indices for the cultivation soils of the Valdichiana area, the regional (Southern Tuscany) and national (Italy) soil background of PTEs were used as reference values. The background of PTEs in soils of Southern Tuscany was assessed from the element concentrations in uncontaminated surface soils (0–20 cm) formed by the most common metamorphic and sedimentary rocks of this sector of the Tuscan region [22,23]. The data of Bini et al. [24] were used as representative of soil background of PTEs in the Italian territory.

The values of CF and I_{geo} obtained in this study were interpreted according to the scales reported in Table 1.

Table 1. Categories of the Contamination Factor (CF) and Geo-accumulation Index (I_{geo}) according to Mmolawa et al. [25] and Barbieri et al. [26], respectively.

Contamination Factor (CF)		Geo-Accumulation Index (I_{geo})	
CF < 1	Low contamination	$0 < I_{geo}$	Uncontaminated
1 < CF < 3	Moderate contamination	$0 \leq I_{geo} < 1$	Low to moderately contaminated
		$1 \leq I_{geo} < 2$	Moderately contaminated
3 < CF < 6	Considerable contamination	$2 \leq I_{geo} < 3$	Moderately to heavily contaminated
		$3 \leq I_{geo} < 4$	Heavily contaminated
		$4 \leq I_{geo} < 5$	Heavily to extremely contaminated
CF > 6	Very high contamination	$I_{geo} \geq 5$	Extremely contaminated

2.4.3. Ecological Risk

The Potential Ecological Risk Index (PERI) is widely used to assess if a certain degree of soil contamination can pose a potential risk for the environment, through the integration of both chemical and ecotoxicological data [20]. In this study, PERI was calculated according to the formula:

$$PERI = \Sigma ERF = \Sigma T \cdot (CF)$$

where ERF is the Ecological Risk Factor, CF is the contamination factor of each PTE and T is the respective toxic-response factor for As (10), Cd (30), Co (5), Cr (2), Cu (5), Ni (5) Pb (5), Sb (7), Tl (10), U (5), V (2), Zn (3) [27]. The ERF and PERI values can be expressed following the interpretative scales reported in Table 2.

Table 2. Categories of the Ecological Risk Factor (ERF) and Potential Ecological Risk Index (PERI) according to Amuno et al. [28].

Ecological Risk Factor (ERF)		Potential Ecological Risk Index (PERI)	
ERi < 40	Low ecological risk	RI < 65	Low risk
40 < ERi < 80	Moderate ecological risk	65 < RI < 130	Moderate risk
80 < ERi < 160	Considerable ecological risk	130 < RI < 260	Considerable risk
160 < ERi < 320	High considerable ecological risk	130 < RI < 260	Considerable risk
ERi > 320	Significant high ecological risk	RI > 260	Very high risk

3. Results and Discussions

Among the analyzed potentially toxic elements (PTEs), Zn, Cu and Ni showed the highest concentrations in AdV bulbs: 12.9–44.2, 2.4–6.6 and 0.72–8.76 mg/kg dw, respectively (Table 3). Chromium and Pb had levels normally in the range 0.1–0.5 mg/kg dw, while Co, U, V showed lower concentrations from 0.02 to 0.12 mg/kg dw. Levels of Cd and Sb in AdV bulbs were in the wide range <0.001–0.29 and <0.001–0.06 mg/kg dw respectively, with values below the limit of detection (LOD) in 50% of samples for Cd and 15% for Sb. Arsenic and Tl had very low concentrations, always below the LOD of 0.001 mg/kg dw.

Table 3. Concentrations (mg/kg dw) of PTEs in bulbs of elephant garlic from the Valdichiana area (AdV). For the calculation of mean and standard deviation of Cd and Sb concentrations, the values <LOD (0.001 mg/kg) were considered equal to the limit of detection. For comparison, concentrations of PTEs in bulbs of elephant garlic grown in uncontaminated soils [11,29,30] are also reported.

Elements	Valdichiana Elephant Garlic (AdV)			Elephant Garlic from Uncontaminated Soils
	Min	Max	Mean ± std. dev.	
As	<0.001	<0.001	–	0.07
Cd	<0.001	0.29	0.07 ± 0.09	0.02
Co	0.02	0.07	0.04 ± 0.02	—
Cr	0.01	0.46	0.17 ± 0.13	2.2
Cu	2.41	6.62	4.34 ±1.18	1.1–10
Ni	0.72	8.76	3.65 ± 2.30	0.2
Pb	0.22	0.41	0.27 ± 0.05	0.1
Sb	<0.001	0.06	0.01 ± 0.01	–
Tl	<0.001	<0.001	–	–
U	0.06	0.09	0.07 ± 0.01	–
V	0.04	0.12	0.07 ± 0.02	–
Zn	12.94	44.20	23.92 ± 8.18	6.5–40

The concentrations of PTEs in AdV bulbs are comparable with those reported for elephant garlic grown in uncontaminated sites [11,30], and much lower than those measured in this garlic species cultivated in contaminated soils [31]. In particular, the comparison with the few data available for PTEs in elephant garlic grown in uncontaminated soils, showed that AdV has very lower concentrations of As and Cr, similar levels of Cu and Zn and slightly higher concentrations of Cd and Pb. Nickel contents in AdV bulbs are one order of magnitude higher than in elephant garlic from uncontaminated sites, but still 10 times lower than in plants grown in contaminated soils (Table 3).

Extending the comparison to common garlic for the problematic PTEs (Cd, Pb, Ni) [8,11,17,32–34], it emerged that Ni and Pb contents in AdV bulbs are within the respective range in common garlic cultivated in uncontaminated sites (0.03–6.3 mg/kg dw for Ni; 0.08–0.54 mg/kg dw for Pb). Cadmium concentrations in AdV are both lower than and similar to the usual levels (0.02–0.07 mg/kg dw) reported for common garlic, except for the highest contents (0.12–0.29 mg/kg dw) measured in AdV bulbs from one of the investigated cultivation fields. Furthermore, the concentrations of PTEs in AdV are comparable with those reported for the "reference plant" [35], with the exceptions of Cd, Ni and U which had concentrations 1.4, 2.5 and 7 times higher, respectively, based on the average value, and 5.8, 9 and 6 times higher, respectively, considering the maximum concentration measured.

The European Legislation [36] and the FAO/WHO Codex Alimentarius [37] indicate a maximum permissible content in vegetables such as elephant garlic, of 0.1 and 0.05 mg/kg fw, respectively, for Cd and 0.1 mg/kg fw for Pb. Concentrations of Cd and Pb in AdV were calculated on a fresh weight basis considering an average water content of 61.8% measured in our cloves, and resulted, on average, 0.03 mg/kg fw for Cd and 0.1 mg/kg fw for Pb; thus, within the legal limits. However, the highest Cd and Pb concentrations in AdV (0.11 mg/kg fw for Cd and 0.16 mg/kg fw for Pb) were higher than the legal limit. As far as Ni is concerned, although garlic has been included by Picarelli et al. [38] in the list of food that contain high amounts of this PTE, values of tolerable daily intake for Ni (considering one clove of ca. 25 g of elephant garlic and a body weight of 70 kg) are well within the 13 μg/kg of body weight suggested by the European Food Safety Authority [39], even considering the highest concentration measured (8.7 mg/kg dw).

DIPTE values of each PTE in elephant garlic from the Valdichiana area (Table 4) were several times below those calculated for onion, common garlic and leek plants cultivated in unsafe situations, e.g., using untreated contaminated waters or in the surroundings of polluted cities [17,40,41], and comparable with those calculated for these plant species sold in the market [42].

Table 4. Values of the Daily Intake (DIPTE, mg/kg/day), reference dose (R_{fd}, mg/kg/day), and Health Risk Index (HRI) for each PTE in bulbs of elephant garlic from the Valdichiana area.

Elements	DIPTE	R_{fd}	HRI
As	6×10^{-8}	3×10^{-4}	2×10^{-4}
Cd	4×10^{-6}	5×10^{-3}	8×10^{-4}
Co	2×10^{-6}	5×10^{-3}	5×10^{-4}
Cr	1×10^{-5}	2×10^{-0}	1×10^{-5}
Cu	3×10^{-4}	4×10^{-2}	7×10^{-3}
Ni	2×10^{-4}	2×10^{-2}	1×10^{-2}
Pb	2×10^{-5}	4×10^{-3}	4×10^{-3}
Sb	6×10^{-7}	4×10^{-3}	1×10^{-4}
Tl	6×10^{-6}	3×10^{-4}	2×10^{-4}
U	4×10^{-6}	3×10^{-3}	1×10^{-3}
V	4×10^{-6}	9×10^{-3}	5×10^{-4}
Zn	1×10^{-3}	3×10^{-1}	5×10^{-3}

In more detail, DIPTE values for PTEs showed the following order (mg/kg/day): Zn > Cu > Ni > Pb > Cr > U > V > Cd > Co > Sb, from the most to the less relevant element from a biological point of view. Moreover, when DIPTE values are compared with their respective reference dose (R_{fd}; Table 4), the consumption of AdV cloves resulted in an uptake of PTEs several orders of magnitude lower than the maximal oral reference dose which guarantees acceptable human exposure limits [43]. In addition, the HRI values of all the investigated PTEs (Table 4) were at least 100 times lower than the threshold of 1 (HRI << 1), indicative of no risk for human health as well as the complete improbability to develop carcinogenic effects [44]. This is further confirmed by the fact that even using maximum concentrations, HRI values were all >35 times below 1. For comparison, garlic plants cultivated using questionable techniques or irrigated with wastewaters showed HRI values several times beyond the threshold of 1 (HRI > 1), indicating possible adverse effects for human health [17].

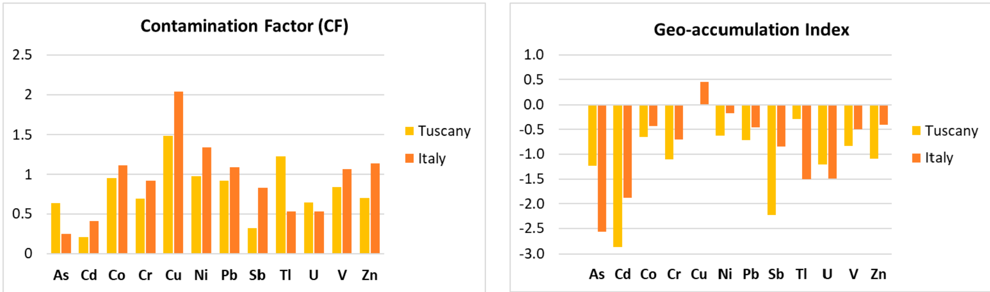
Concentrations of PTEs in AdV cultivation soils in the Valdichiana area (Table 5) are overall comparable with the respective background level in soils of Southern Tuscany [22,23] and Italy [24].

Table 5. Concentrations (mg/kg dw) of PTEs in AdV cultivation soils in the Valdichiana area, along with their background levels in soils of Southern Tuscany [22,23] and Italy [24]. Values in bold were calculated from the concentrations of PTEs in 51 surface soil samples collected in Italy [45].

Elements	Valdichiana Soils			Soil Background Southern Tuscany	Soil Background Italy
	Min	Max	Mean ± std. dev.		
As	5.4	24.2	10.9 ± 6.8	18.0	41
Cd	0.12	0.23	0.18 ± 0.04	0.87	0.44
Co	9.0	25.7	15.8 ± 5.5	17.3	14
Cr	46.3	124.8	87.6 ± 29.8	132.5	95
Cu	29.8	90.1	50.2 ± 18.8	36.3	24
Ni	39.0	92.5	66.8 ± 17.1	74.6	50
Pb	20.8	51.4	29.2 ± 9.7	32.0	26
Sb	0.49	1.07	0.66 ± 0.21	2.1	**0.77**
Tl	0.26	0.63	0.44 ± 0.13	0.34	**0.83**
U	1.3	2.04	1.68 ± 0.26	2.4	3.17
V	62.6	110.7	81.7 ± 16.2	96.5	76
Zn	55.0	120.5	78.5 ± 18.9	116.7	68

The Contamination Factor (CF) of PTEs calculated using their background levels in soils from Southern Tuscany (Figure 1a) indicated the absence of contamination or low contamination for most of the analyzed PTEs, as CF values were normally <1 in the investigated AdV cultivation soils [46]. Copper and Tl were the only exceptions since both elements frequently showed CF values between 1 and 3 (on average 1.5 and 1.2, respectively), suggesting a moderate soil contamination. The geo-accumulation index (I_{geo})

clearly indicated the absence of soil contamination by PTEs as all values were below the threshold of 0 (Figure 1b) [47].



(**a**) (**b**)

Figure 1. Contamination factor (**a**) and Geo-accumulation Index (**b**) of PTEs (average values) in the AdV cultivation soils in the Valdichiana area, calculated using their background levels in soils of Southern Tuscany [22,23] and Italy [24].

Using as reference the PTE background levels in soils of Italy (Figure 1a,b), several PTEs such as Co, Cu, Ni, Pb, V, Zn, showed CF average values in the range 1–2 in the AdV cultivation soils in the Valdichiana area, indicating a moderate contamination [46]. Conversely, the results of I_{geo} confirmed the absence of soil contamination for all PTEs (I_{geo} < 0; absent contamination), except for Cu which showed an average value of 0.4, indicating a low to moderate contamination [47].

The above-reported results for the CF and I_{geo} indices suggested that Cu is the only PTE for which there is some concern about its levels in agricultural soils of the Valdichiana area. On the other hand, it is well-known that Cu is present in somewhat high concentrations in agricultural soils of Tuscany, being Cu-based products such as the Bordeaux mixture, widely used in agriculture [48,49].

According to soil concentrations of PTEs, the Ecological Risk Factor (ERF) and the Potential Ecological Risk Index (PERI) for the Valdichiana soils had average values below their respective lowest thresholds of 40 and 65 (Table 2; Figure 2), suggesting therefore a very low ecological risk [28].

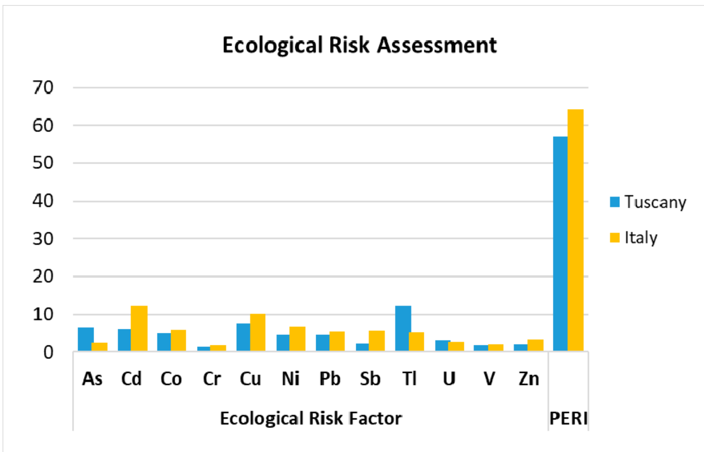


Figure 2. Average values of the Ecological Risk Factor (ERF) and Potential Ecological Risk Index (PERI) related to the concentrations of PTEs in AdV cultivation soils in the Valdichiana area and PTE background levels in soils of Southern Tuscany and Italy.

The rank-ordered concentration of PTEs in elephant garlic from the Valdichiana area was quite different from that in cultivation soils (Figure 3), indicating that AdV accumulates preferentially Cd, but also Cu and U as well as Pb, Zn, Ni. Cadmium is a non-essential element that can be easily translocated from roots to cloves of garlic following a dilution process from roots to shoots [4]. In addition, Pb can be translocated from roots to shoots but its concentration in the cloves of garlic is usually lower than those measured in other plant parts [6]. Copper and Zn are essential micronutrients in plants and are accumulated following an active process and generally proportionally to their concentration in the soil [50]. Uranium average concentrations in AdV are consistent with those observed in other edible plants [51]. Ni is known to be taken up by several edible plants in proportion to the content in the soil and to be translocated from the roots to the aerial parts [52].

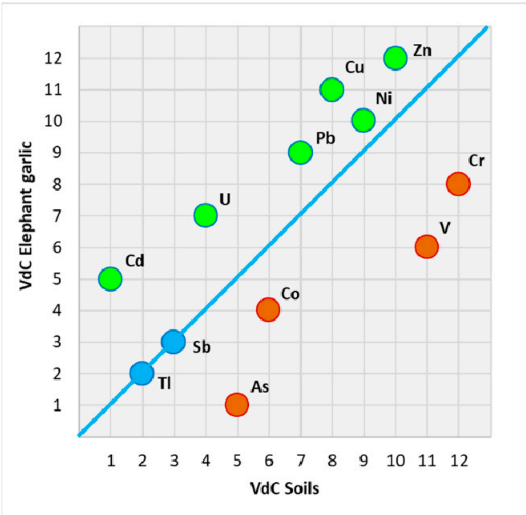


Figure 3. Scatterplot of PTE concentration ranks in elephant garlic vs. soil from the Valdichiana area. Elements in green are preferentially accumulated in elephant garlic; elements in red are found preferentially in the soil.

4. Conclusions

The results of this study indicated that although bulbs of elephant garlic from Valdichiana may present somewhat slightly high concentrations of Cd, Ni, Pb and U, the associated health risk based on the daily intake is absolutely negligible. In fact, calculations of the Health Risk Index (HRI) showed values below the threshold of risk for human health (HRI < 1). On the basis of the results obtained from the contamination factor (CF) and the geo-accumulation index (I_{geo}), cultivation soils showed somewhat high Cu values, probably due to the diffuse use of Cu-based products in agriculture, but presented overall a very low ecological risk (PERI < 65).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11157023/s1, Table S1: Limit of Detection (LOD; mg/kg) of PTEs analyzed by ICP-MS and range of PTE concentrations (mg/kg) and recoveries (%) in the standard reference materials GBW 07604 (*Poplar Leaves*) and SRM 2709 (*San Joaquin Soil*).

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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