








Article

Assessing the Uptake of Toxic Elements by *Brassica rapa* and Associated Health Risks in Soils with Different Natural Background Levels

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Abstract

This research investigates the uptake of potentially toxic elements (PTEs) by *Brassica rapa* L. grown in volcanic and clay soils with high natural background levels of these elements, and assesses related human health risks. The study was conducted in two Italian regions that produce *B. rapa* L. for food use (Campania and Sicily). The results of this exploratory research indicate that the naturally elevated concentrations of PTEs in soils lead to correspondingly high levels of these elements in *B. rapa* L. The investigated soils exhibited marked chemical differences. Volcanic soils had higher Total Organic Carbon (TOC) and PTEs concentrations alongside lower pH and Cation Exchange Capacity (CEC) than clayey soils. In the investigated plants, PTEs accumulated mainly in roots and stems, with notable Hg levels in leaves. While As exceeded safety limits in only one edible sample from volcanic soil, Cd, Hg, and Pb frequently surpassed them. Health risk assessments revealed significant carcinogenic and non-carcinogenic risks from plants grown on volcanic soils, with levels that remain unacceptable even at low consumption rates. In contrast, lower risk levels are associated with the consumption of *Brassica rapa* grown in clay soils, with values that are generally considered tolerable at low consumption rates. The preliminary findings of this study highlight that natural soil enrichment can cause PTE levels in *B. rapa* L. that often exceed safe consumption thresholds. These results provide a foundation for future research aimed at more thoroughly investigating the mechanisms of metal uptake by edible plants in areas naturally enriched with PTEs in order to enhance the safety and sustainability of our food.

Keywords: edible hyperaccumulator plants; potentially toxic elements; volcanic soil; clay soil; health risk



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1. Introduction

Food consumption is the primary pathway for human exposure to Potentially Toxic Elements (PTEs) [1–3]. The toxicity of PTEs is influenced by various factors, including their chemical forms, exposure routes, nutritional imbalances, disruption of intracellular homeostasis, and oxidative damage to biological macromolecules (enzymes, DNA,

lipids, and proteins) due to free radical production [4]. PTE poisoning is associated with severe health consequences such as dementia in adults, intellectual disabilities in children, central nervous system disorders, insomnia, renal and hepatic diseases, and vision impairments [5,6]. Therefore, monitoring PTE concentrations in food and evaluating health risks associated with their consumption is essential for mitigating the intake of hazardous foods. Vegetables constitute a significant portion of the human diet, providing proteins, carbohydrates, vitamins, minerals, antioxidants, and dietary fibres [7]. Consequently, they are a primary focus of health risk assessments related to food consumption. Several plant species tend to accumulate PTEs in their tissues, particularly hyperaccumulator plants that can absorb PTEs in quantities even higher than in the soil [4,8]. Therefore, many studies have concentrated on the uptake of PTEs by hyperaccumulator plants in contaminated soils due to the heightened health risks associated with their consumption.

Among hyperaccumulator plants, members of the *Brassicaceae* family are particularly significant nutritionally and economically. They are extensively cultivated globally for human consumption and oil production. The genus *Brassica* comprises six species derived from three ancestral species (*B. rapa* L., *B. oleracea*, and *B. nigra*) through interbreeding, resulting in three amphidiploid species (*B. napus*, *B. juncea*, and *B. carinata*). *Brassica rapa* is one of the most widely distributed crop species [9], originating from the Mediterranean region (Western race) as turnip and oleiferous forms and from Central Asia (Eastern race) as a vegetable. Alongside domestication efforts, it has also become a weed in Mediterranean regions and across Europe [10]. Within *B. rapa* L., various subspecies are cultivated for distinct purposes: *B. rapa* L. subsp. *rapifera* (turnip), *B. chinensis* (pak choi), *B. rapa* L. subsp. *trilocularis* (yellow sarson), and *B. rapa* L. subsp. *sylvestris* (broccoletto). The latter is prevalent in southern Italy and is cultivated for its edible leaves, buds, and stems; it also grows spontaneously in temperate regions worldwide [11]. The *Brassica* genus comprises over 100 plant species that are distinguished by their remarkable resilience to PTEs and their notable phytoaccumulation potential [12], with substantial evidence supporting their ability to accumulate multiple elements [13–17]. Generally, *Brassica* plants demonstrate high bioaccumulation factors (BAFs), facilitating the transfer of PTEs to aerial parts such as shoots and leaves. This characteristic poses significant health risks when cultivated or wild *B. rapa* L. is consumed as food.

It is well established that soils contaminated by anthropogenic activities promote the accumulation of high concentrations of PTEs in the edible parts of *Brassica rapa* L., often resulting in unacceptable health risks for consumers. However, the role of soils naturally enriched in PTEs as a source of metal uptake by edible crops remains poorly investigated.

This exploratory study aims to address this knowledge gap by examining the accumulation of PTEs in *B. rapa* L. grown on soils characterized by different natural geochemical profiles. In particular, the study focuses on soils with contrasting PTE enrichment patterns, volcanic and clay soils, which are widespread in southern Italy.

The objective of this study is to evaluate the uptake of four critical PTEs (As, Cd, Hg, and Pb) by *B. rapa* L. cultivated on naturally enriched soils and to perform a preliminary assessment of the associated human health risks related to their consumption. By comparing different geochemical environments, this work seeks to clarify how natural soil properties influence PTE accumulation in edible plant tissues and the resulting exposure risks.

2. Materials and Methods

2.1. Study Area

The study encompasses two regions in southern Italy: Campania (Figure 1A) and Sicily (Figure 1B). These areas exhibit distinct geochemical characteristics and host *B. rapa* L. in both wild and cultivated forms. According to the Köppen–Geiger classification [18], both

regions experience a Mediterranean climate, with average annual temperatures ranging from 11 °C to 20 °C in Sicily and from 10 °C to 20 °C in Campania. The total annual precipitation varies significantly, averaging between 385 mm and 1192 mm in Sicily, while Campania's range is from 750 mm to 1450 mm. These regions were selected due to their active volcanic landscapes and diverse sedimentary rock formations, contributing to the natural enrichment of PTEs in the soil [19,20].

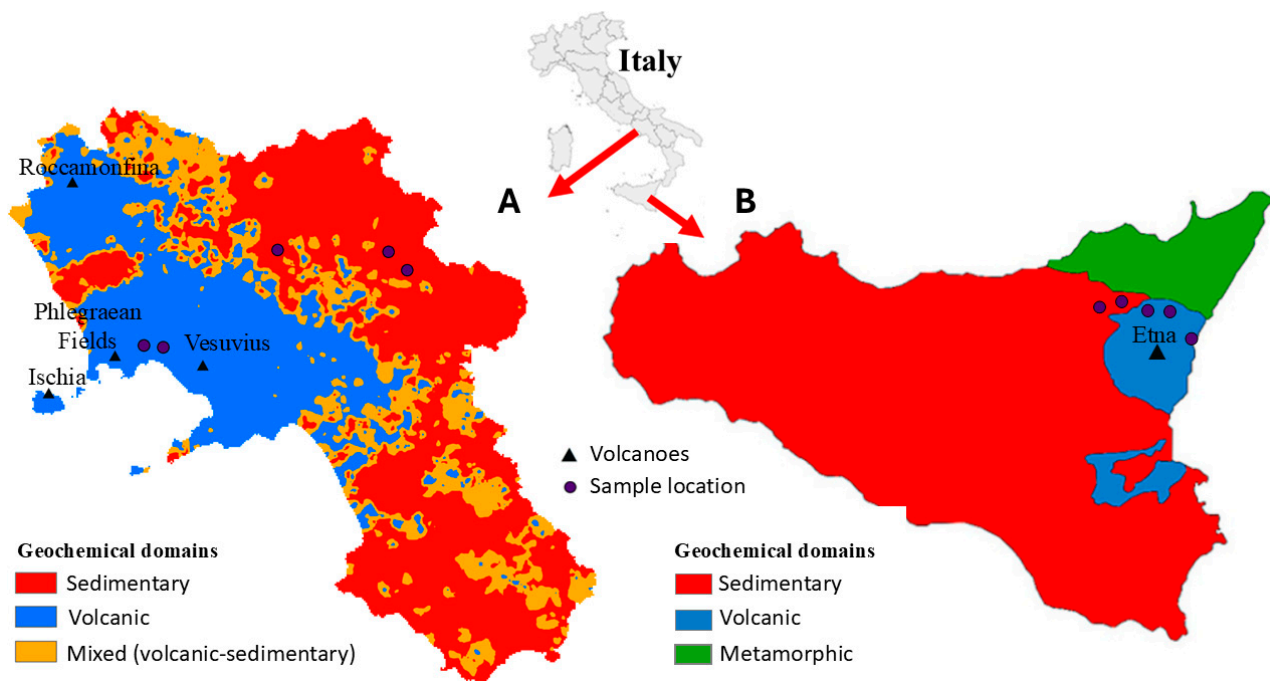


Figure 1. Sampling location in the Campania region (A) and the Sicily region (B).

Notable chemical differences exist between the volcanic products of Sicily's Etna volcano and those of Campania's volcanoes, Vesuvius, Phlegraean Fields, Ischia, and Roccamonfina [21,22]. Etna is characterised by Na-rich rocks with lower Si content but higher Fe and Mg levels [23]. Conversely, Campanian volcanoes produce a broader spectrum of evolved rocks, typically enriched in potassium, ranging from trachybasalts to phonolites. Additionally, sedimentary rocks in these areas display significant compositional variations due to their distinct geological environments and weathering degrees. Recent studies conducted at both regional [24,25] and local scales [26] have shown the spatial distribution and the pronounced compositional differences of soils derived from volcanic and sedimentary parent materials in the Campania region. These investigations demonstrate that volcanic soils are the principal natural source of PTEs, whereas clay soils exhibit enrichment predominantly in a limited subset of PTEs, notably Ni and Co, with minor enrichments of As and Cd. Carbonate soils, in contrast, maintain consistently low concentrations of PTEs. The authors highlighted that these natural enrichments result in background levels of certain PTEs in soils that exceed the intervention limits established by both Italian and European regulations. Consequently, natural processes alone can lead to concentrations of some PTEs (e.g., As, Co, Ni, Pb, Tl) in these soils comparable to those found in contaminated areas. Analogous results have been obtained in the Sicilia region [19,27]. Unlike in Campania, elevated PTE concentrations in Sicily are observed not only in volcanic soils but also in soils derived from sedimentary successions. It is worth noting that Sicilian clay soils display elevated concentrations of As and Cd, occasionally surpassing those measured in volcanic soils. These previous findings, integrated with extensive geochemical knowledge of both

study areas, informed the strategic selection of sampling sites to encompass representative volcanic and clay soil types across the two regions.

2.2. Sampling and Analysis

2.2.1. Sampling

To assess only the natural sources of PTEs the ten locations identified for sampling purposes (5 in Campania and 5 in Sicily) have been selected, ensuring that the sampling sites were far from pollution sources. In each site, a sample of the entire *B. rapa* L. plant and a soil sample were collected (5 volcanic and 5 clayey). Appropriate permission was obtained from the landowners for the study. *Brassica rapa* L. was identified by Giuseppe Diego Puglia, PhD, comparing the collected specimen with the reference sample PAL-72916, housed at the Herbarium Mediterraneum Panormitanum (PAL) in Palermo, Sicily, Italy. The plant samples collected have not been deposited in a public herbarium; however, they are stored at the University of Messina and remain available for future investigations. The soil sampling and preparation adhered to the international guidelines outlined in the GEMAS sampling protocol [28]. At each site, 1.5 kg of soil was obtained from 0 to 20 cm below the surface after removing vegetation cover. Each sample consisted of a composite material collected from the corners of a 1 m square plot and its central point according to the procedure described by [29]. All soil and plant samples were stored in Ziplock plastic bags and transported to the laboratory for analysis. In the laboratory, the collected plants were thoroughly washed with tap water, rinsed three to five times with deionised water, and then air-dried at room temperature. Following drying and assessment of moisture content, the *B. rapa* L. samples were separated into their respective organs and ground into a powder for subsequent chemical analysis.

2.2.2. Sample Preparation

From each *B. rapa* L. plant harvested, a total of 2 g of each partial sample (leaves, stems, and roots) was obtained. Additionally, the soil samples were carefully stored in labelled plastic basins and transported to the laboratory for pre-treatment and analysis. Before treatment, the soil samples were dried at 50 °C for 24 h and then sieved through a 2 mm mesh sieve to remove stones, pebbles, and plant litter. Simultaneously, the individual plant components were meticulously cleaned and placed in an oven set at 50 °C for 24 h, during which they were left to dry. Subsequently, the samples were analysed to determine the concentrations of As, Ca, Cd, Fe, Hg, K, Mg, and Pb.

2.2.3. pH, TOC and CEC Analysis

pH, total organic carbon (TOC), and cation exchange capacity (CEC) were measured on all soil samples. Soil pH was measured potentiometrically in a 1:2.5 soil-to-water suspension using a calibrated pH meter (HANNA HI2002-02, produced in Padova (Italy)). TOC was measured using a carbon/sulfur analyzer based on infrared spectroscopy (ELTRA-Helios). To remove inorganic carbon, 1 g of sample was treated with 4 mol/L HCl for 4 h at room temperature, then dried for 16 h at 70 °C. Subsequently, 100–200 mg of dried sample was combusted in the analyzer's preheated (1350 °C) furnace, with organic carbon quantified by an infrared cell. CEC was measured using the silver-thiourea method. Namely, 1 g of soil was equilibrated with 30 mL of silver-thiourea (AgTU^+ , 0.01 M Ag/0.1 M thiourea) solution for 1–2 h with shaking, and protected from light to prevent Ag reduction. After centrifugation and filtration, AgTU^+ retained on exchange sites was quantified in the supernatant via atomic absorption spectrometry, with CEC calculated as the difference from the initial concentration.

2.2.4. Materials and Reagents

Approximately 0.5 g of each sample was weighed for elemental analysis. Subsequently, acid digestion was conducted in a closed-vessel microwave digestion system (ETHOS easy, Milestone, Bergamo, Italy) utilising a range of reagents, including 1 mL of Re internal standard at 0.5 mg/L, 7 mL of HNO₃ (65% v/v) and 2 mL of H₂O₂ (30% v/v) for the leaf, stem and root samples. The following reagents were used to analyse the soil samples: 1 mL of Re internal standard at 0.5 mg/L, 9 mL of HCl (37% v/v) and 3 mL of HNO₃. Ultrapure water (total organic carbon (TOC) concentration < 5 mg/L) was obtained from a Barnstead Smart2Pure 12 water purification system (Thermo Scientific, Milan, Italy) for sample dilution following acid digestion. The filtration process was successful, with the samples passing through a filter with a pore size of 0.45 µm. The digestion programme was operated under different conditions for the various types of samples. The certified matrices SRM 1570a (Spinach Leaves) and SQC001 (Metals in Soil) from Merck Spa, Sigma-Aldrich, Milan, Italy, were used for accuracy in the analytical validation methods.

2.2.5. ICP-MS Analysis

The analysis was conducted using a single quadrupole inductively coupled plasma-mass spectrometer (ICP-MS, iCAP-Q, Thermo Scientific, Waltham, MA, USA), which enabled the determination of the following elements: As, Ca, Cd, Fe, Hg, K, Mg, and Pb. The operational conditions followed those adopted in previous studies [30,31]. All samples and analytical blanks were analysed in triplicate. The Thermo Scientific Qtegra™ Intelligent Scientific Data System software, version 2.10 (Thermo Scientific, Waltham, MA, USA) was used for data acquisition.

2.2.6. ICP-MS Validation Methods

The method was validated following the European Association for Analytical Chemistry (Eurachem) criteria [32]. This encompassed the determination of linearity (R²), sensitivity (limit of detection (LOD) and limit of quantification (LOQ), and accuracy (% recovery) of the method. LODs and LOQs were calculated as 3.3 σ/S and 10 σ/S, respectively, where σ is the standard deviation of six blanks, and S is the slope of the relative calibration curve. Linearity was determined by linear least squares regression and seven-point calibration curves in the 0.5–100.0 µg/L range. The certified matrix SRM 1570a (spinach leaves) was analysed to assess the accuracy for root, stem and leaf samples, SQC001 (Metals in soil) for soil. If the element was not present in the certified matrix, it was spiked with the known amount of the analyte. The resulting data are shown in Table 1.

Table 1. Analytical value for the ICP-MS validation method.

Element	SRM 1570a (<i>B. rapa</i> . L. Leaves)				SQC001 (Metals in Soil)			
	R ²	LOD (mg kg ⁻¹)	LOQ (mg kg ⁻¹)	Recovery (%)	R ²	LOD (mg kg ⁻¹)	LOQ (mg kg ⁻¹)	Recovery (%)
As	0.9998	0.001	0.003	98.66 ± 3.20	0.9999	0.001	0.003	98.15 ± 1.80
Ca	0.9988	0.320	1.056	90.45 ± 2.98	0.9987	0.471	2.445	91.85 ± 2.10
Cd	0.9998	0.001	0.003	97.73 ± 3.11	0.9999	0.001	0.003	97.20 ± 1.35
Fe	0.9994	0.015	0.050	93.88 ± 2.57	0.9993	0.020	0.066	94.75 ± 1.20
Hg	0.9998	0.001	0.003	99.65 ± 2.44	0.9997	0.001	0.003	98.40 ± 2.05
K	0.9990	0.480	1.584	91.73 ± 1.65	0.9989	0.555	1.832	90.65 ± 1.70
Mg	0.9992	0.132	0.436	93.42 ± 3.09	0.9993	0.115	0.380	94.50 ± 2.10
Pb	0.9998	0.001	0.003	101.03 ± 3.87	0.9999	0.001	0.003	99.52 ± 2.75

2.3. Statistical Analysis and Bioaccumulation Factor (BAF)

To identify the chemical associations present in the analysed soil and plant samples, data were subjected to multivariate statistical analysis within a compositional data analysis (CoDA) framework [33,34]. In addition to the focus on selected PTEs (As, Cd, Hg, Pb), several major elements (e.g., Ca, Fe, K, Mg, Na) were incorporated into the multivariate statistical analysis to achieve a comprehensive geochemical characterisation. The decision to utilise the CoDA approach is based on its effectiveness in extracting meaningful information from compositional data, as demonstrated in previous studies [35–38]. CoDA emphasises the analysis of log-ratios between the elements that comprise the geochemical compositions, which, unlike raw data, are independent of measurement units (scale invariance) and the overall size of the composition (subcompositional coherence). Furthermore, employing log-ratios facilitates the application of standard statistical methods and models. In this study, we expressed the original geochemical compositions in isometric log-ratio (ilr) coordinates before conducting multivariate statistical analyses [39,40]. Principal component analysis (PCA) was subsequently performed on the two databases comprising soil and edible parts of plants using the factextra package [41] available in R software (version 4.4.0). Concurrently, the bioaccumulation factor (BAF) index was calculated using dry weight concentrations according to [17] to assess the capacity of plants to accumulate PTEs from soil. The following equation defines the BAF:

$$\text{BAF} = \frac{C_v}{C_s} \quad (1)$$

where C_v represents the concentration of PTEs in the edible parts of *B. rapa* L. (mg kg^{-1}), and C_s denotes the concentration of PTEs in the soil (mg kg^{-1}).

2.4. Health Risk Assessment

The health risks associated with the consumption of *B. rapa* L. were assessed by evaluating their total PTEs content. Initially, the concentrations of PTEs in the edible portions of *B. rapa* L. (e.g., stems and leaves) were determined based on fresh weight (C_{fresh}), calculated using the following equation [17]:

$$C_{\text{fresh}} = C_{\text{dry}} \cdot (1 - W) \quad (2)$$

where C_{dry} represents the concentration of PTEs in *B. rapa* L. in dry weight, and W denotes the water content in *B. rapa* L., measured according to the following equation:

$$W = \left(\frac{\text{fresh mass} - \text{dry mass}}{\text{fresh mass}} \right) \quad (3)$$

The fresh and dry masses of each *B. rapa* L. sample were recorded during the cleaning and drying procedures. Subsequently, exposure to PTEs via vegetable consumption was assessed for both children and adults, expressed as the estimated daily intake (EDI), calculated using the equation proposed by the US-EPA:

$$\text{EDI} = \frac{EF \cdot ED \cdot C_{\text{fresh}} \cdot IR}{BW \cdot AT} \quad (4)$$

In this equation, EDI is measured in $\text{mg kg}^{-1} \cdot \text{d}^{-1}$, EF is the exposure frequency (day/year), ED is the exposure duration (year), C_{fresh} is defined above, IR is the daily ingestion rate of *B. rapa* L. (g/d), BW is the average body weight (kg), and AT is the average exposure time ($ED \times 365$ day/year). This study utilised an exposure frequency of 180 days/year, reflecting seasonal consumption patterns as *B. rapa* L. is primarily available

during autumn and winter. The exposure duration values of 6 years for children and 70 years for adults were selected following ATSDR guidelines [42]. For ingestion rates, a range was adopted due to individual variability in consumption; values between 50 and 150 g/day for children and 200 to 350 g/day for adults were derived from previous studies [17,43]. The average body weights used were 70.0 kg for adults and 16.0 kg for children [44]. The concentration values used, calculated on a fresh weight basis (C_{fresh}), represent the average concentrations measured in the edible parts of *Brassica rapa* samples collected from each of the four investigated soil groups.

EDI values allow the calculation of Target Hazard Quotients (THQs), as indicated by Equation (5), to assess non-carcinogenic risks associated with individual PTEs for consumers of *B. rapa* L. [45]. Furthermore, Total Target Hazard Quotients (TTHQ) were computed as the aggregate of THQs for individual PTEs using Equation (6). The TTHQ provides an estimate of potential non-carcinogenic risk from the PTEs considered in this study:

$$\text{THQ} = \frac{\text{EDI}}{\text{RfD}} \quad (5)$$

$$\text{TTHQ} = \sum_{i=1}^n \text{THQ}_i \quad (6)$$

where RfD denotes the chronic reference dose of PTEs via ingestion exposure ($\text{mg kg}^{-1} \text{BW} \cdot \text{d}^{-1}$).

The RfD values for As, Cd, Hg, and Pb were 0.0003, 0.001, 0.0003, and 0.0035 $\text{mg kg}^{-1} \text{BW} \cdot \text{d}^{-1}$, respectively [46–48]. A THQ or TTHQ value less than or equal to 1 indicates no significant adverse health effects; conversely, values exceeding 1 suggest potential non-carcinogenic risks. Additionally, EDI values were employed to estimate Target Cancer Risk (TCR), assessing carcinogenic risks associated with individual PTEs among consumers of *B. rapa* L. [42]. Total Target Cancer Risk (TTCR) was calculated as the summation of TCRs for individual PTEs. The equations for estimating TCR and TTCR are presented as follows:

$$\text{TCR} = \text{EDI} \cdot \text{CPSo} \quad (7)$$

$$\text{TTCR} = \sum_{i=1}^n \text{TCR}_i \quad (8)$$

In these equations, CPSo represents the carcinogenic potency slope for oral exposure routes: 1.5 ($\text{mg kg}^{-1} \cdot \text{d}^{-1}$) for As and 0.0085 ($\text{mg kg}^{-1} \cdot \text{d}^{-1}$) for Pb [49]. Due to the absence of a defined CPSo for the ingestion of Cd and Hg, TCR calculations were not performed for this element. Generally, TCR or TTCR values lower than 1.0×10^{-6} are negligible, above 1.0×10^{-4} are unacceptable, and lying between 1.0×10^{-6} and 1.0×10^{-4} is acceptable [45,50].

3. Results and Discussion

3.1. Concentration of PTEs in Soils and Plants

The pH, TOC and CEC values are shown in Table 2. The PTE concentrations in topsoil samples are presented in Table 3, where they are compared with the local baseline values [19,51–53] and European soil quality standards [54]. The findings indicate a broad compositional range for the analysed elements, with Pb concentrations varying from 0.27 to 112 mg kg^{-1} , underscoring the unique geochemical signatures of the soils studied. Among the examined PTEs, volcanic soils generally displayed higher concentrations, except for Cd, which was elevated in Sicilian clay soils. In addition to the pronounced compositional differences between volcanic and clay soils, it is crucial to recognise that the distinct geological contexts of the two studied regions also significantly influence soil pH, CEC and TOC. Campanian volcanic soils show a lower pH, higher TOC, a moderate CEC and are enriched in As, Hg, and Pb due to their highly evolved parent material, which results in

rocks rich in these elements. Notably, one sample from Campanian volcanic soils exceeded the target value for Pb, and both samples surpassed the precautionary limit for Hg.

Table 2. pH, TOC and CEC values measured on the studied soils.

	pH Potentiometric	TOC IR-Cell (wt. %)	CEC Silver Thiourea, AAS (meq/100 g)
SicilyClay N = 2	7.2 7.3	1.5 1.8	22.5 23.8
Sicily Volcanic N = 3	6.8 6.5 6.6	1.1 1.1 1.3	13.4 14.2 16.1
Campania Clay N = 3	7.1 7.2 7.1	1.8 1.9 2.3	25.7 26.1 29.1
Campania volcanic N = 2	5.9 6.3	3.5 4.3	20.2 21.5

Table 3. Soil sample concentrations compared to local baseline values and European Union soil quality standards; values in bold exceed the precautionary limit.

		As (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Hg (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Mg (%)	Ca (%)	Na (%)	K (%)	Fe (%)
Sicily_clay N = 2	Sampled soils	2.1	0.46	0.51	5.97	0.14	0.16	0.09	0.1	0.6
		0.9	0.05	0.43	0.27	0.12	0.13	0.07	0.08	0.25
	Baseline *	19 ^a	1.2 ^a	0.03 ^b	42 ^a	0.54 ^b	4.6 ^b	0.07 ^b	0.29 ^b	3.2 ^c
Sicily_volcanic N = 3	Sampled soils	7.1	0.32	1.05	25.4	0.18	0.27	0.07	0.09	0.4
		6.3	0.27	1.02	21.9	0.17	0.2	0.07	0.08	0.32
	Baseline	4.1	0.22	0.51	18.2	0.15	0.19	0.06	0.06	0.22
		9 ^a	0.6 ^a	0.03 ^b	35 ^a	0.41 ^b	2 ^c	0.12 ^b	0.46 ^b	2.5 ^c
Campania_clay N = 3	Sampled soils	11.6	0.3	0.79	36	0.12	0.2	0.09	0.1	0.57
		9.9	0.23	0.62	30	0.11	0.19	0.08	0.09	0.56
	Baseline	3.6	0.12	0.53	23	0.1	0.18	0.08	0.08	0.55
		9.4	0.5	0.15	30	<0.7 ^d	<3 ^d	<0.1 ^d	<0.6	3 ^d
Campania_volcanic N = 2	Sampled soils	19.7	0.26	1.82	111.9	0.16	0.22	0.09	0.15	0.61
		16.3	0.21	1.67	53.4	0.14	0.2	0.09	0.13	0.59
	Baseline	17.3	0.5	0.32	80	<0.7 ^d	<3 ^d	0.7 ^d	<2 ^d	2.5 ^d
	Target values	20	0.8	0.5	75	NR	NR	NR	NR	NR
EU soil quality standards	Precautionary limit	30	1	1	200	NR	NR	NR	NR	NR
	Critical limit	50	3	3	500	NR	NR	NR	NR	NR

* The baseline values, shown in the table, were calculated by different authors in studies carried out at the national and regional levels. ^a [19]; ^b [51]; ^c [52]; ^d [50]. NR: Not Regulated.

Sicilian volcanic soils show a slightly acidic pH, medium-low TOC and CEC, and a moderate PTEs enrichment, exceeding the target value and precautionary limit for Hg in only one sample. Clay soils from both regions show slightly alkaline pH, high CEC, medium-low TOC, and low PTEs concentrations, which consistently adhered to EU quality standards. However, their compositional differences were evident: Campanian clays were enriched in As and Pb, while Sicilian clays exhibited higher Cd concentrations. Baseline values were exceeded for Pb in only one volcanic soil sample from Campania, while Hg concentrations exceeded baseline values in all analysed samples. The slight Pb enrichment (1.4 times above baseline) may be attributed to natural processes or minor anthropogenic influence. Regarding Hg, further studies are needed to determine whether local enrichment occurs at all sampling sites or if previous baseline values have been underestimated. Nonetheless, the enrichment patterns observed for mercury and other elements reflect the

characteristics of the bedrock from which the soils originated, indicating that the measured concentrations are primarily driven by natural variations.

The fresh weight composition of the three *B. rapa* L. organs (stems, roots, and leaves) is presented in Table 4 and compared with standard values for PTEs in vegetables established by FAO and WHO [55,56]. The fresh weight composition was calculated using Equation (2), applying a water content (W) value of 0.85, estimated using Equation (3). Accordingly, the concentrations reported in Table 3 can be converted to dry weight basis by dividing the fresh weight values by 0.15. The highest concentrations of the investigated PTEs were found in the roots and stems, while Hg exhibited elevated levels in the leaves. Additionally, PTE concentrations in plant organs reflected soil geochemistry patterns, with higher values observed in plants growing on volcanic soils compared to those in clay soils, which generally showed lower PTE levels. This pattern is partly explained by the slightly acidic pH of volcanic soils, which enhances Cd, Hg, and Pb mobility. The slightly alkaline pH of clay soils does not favor mobility of any investigated elements (As is highly mobile only at pH > 8). Thus, the high CEC of clay soils does not significantly influence PTE sorption due to their low mobility. The dry weight concentrations, readily derived as described above, were used to facilitate comparison of the present data with those reported in previous studies. From this comparison, it was found that in 80% of the samples, PTE concentrations in plant organs exceeded the thresholds defined by [57,58] for hyperaccumulator plants (e.g., 0.1 mg kg⁻¹ for Cd and Hg; 1 mg kg⁻¹ for Pb), supporting the classification of *B. rapa* as a metal hyperaccumulator in these settings. Furthermore, the dry weight concentration ranges of the investigated PTEs align with previous studies on *B. chinensis* [17] and *B. rapa* L. [59] from polluted areas, indicating that soils naturally enriched in PTEs can lead to comparable levels in *B. rapa* L. as those found in contaminated environments. Regarding FAO-WHO standards, arsenic concentrations in the edible parts of *B. rapa* L. (leaves and stems) exceeded standards in only one sample from Sicilian volcanic soils. Cadmium concentrations exceeded standards in 3 out of 5 Sicilian samples and in one sample from Campanian volcanic soils. Mercury concentrations exceeded standard values in all samples from volcanic soils and in 3 out of 5 samples from clay soils. Lead levels exceeded standards in all samples from volcanic areas and Sicilian clays, while one sample from Campanian clay soils exceeded standards only in the stems. Among the major elements, notable enrichments include Fe in clay and Na-K in volcanic environments, both in soils and plants.

Table 4. Concentration of the elements analysed in the different plant organs compared with FAO-WHO standards; the values in bold correspond to the samples that exceed the FAO-WHO thresholds.

Elements (mg kg ⁻¹) *		As	Cd	Hg	Pb	Mg	Ca	Na	K	Fe
Sicily_clay N = 2	Roots	0.4	0.13	0.08	1.76	53.6	94.9	53.9	130	6.12
		0.05	0.06	0.02	0.68	42.8	82.6	52.6	103	4.48
	Stem	0.2	0.23	0.06	1.89	14.1	61.5	24.2	84.6	1.56
		0.08	0.12	0.01	0.45	12.5	58.9	13.5	56.7	1.32
	Leaves	0.015	0.05	0.09	0.51	24.2	60.8	42.2	96.3	1.77
		0.008	0.008	0.008	0.26	23.5	58.3	38.4	91.2	1.43
Sicily_volcanic N = 3	Roots	0.9	0.23	0.15	2.8	46	120	52	122	5.77
		0.72	0.18	0.14	2.3	42	112	51	121	5.22
		0.06	0.11	0.1	0.7	40	108	49	118	4.64
	Stem	0.5	0.15	0.11	4.2	29	98	27	77	2.37
		0.1	0.1	0.1	2.3	27	87	25	72	2.22
		0.03	0.09	0.08	1.78	26	77	24	64	1.89
	Leaves	0.42	0.14	0.13	1.84	33	80	41	99	3.12
		0.16	0.08	0.09	0.9	28	54	34	82	2.34
		0.01	0.03	0.08	0.15	22	46	29	78	1.68

Table 4. Cont.

Elements (mg kg ⁻¹) *		As	Cd	Hg	Pb	Mg	Ca	Na	K	Fe
Campania_clay N = 3	Roots	0.72	0.02	0.1	2.2	49	129	58	122	7.96
		0.64	0.02	0.08	1.9	42	111	47	112	6.77
		0.06	0.01	0.04	0.7	36	105	37	90	5.12
	Stem	0.08	0.02	0.03	0.42	25	100	39	88	2.82
		0.05	0.01	0.03	0.38	18	89	37	73	1.87
		0.01	0.008	0.01	0.21	15	77	32	69	1.52
		0.05	0.03	0.05	0.16	28	86	48	89	2.19
Leaves	0.03	0.01	0.02	0.11	22	77	44	88	2.08	
	0.01	0.01	0.01	0.05	19	65	40	86	1.71	
Campania_volcanic N = 2	Roots	0.8	0.05	0.29	3.68	40.9	116	56.4	113	4.66
		0.52	0.03	0.13	2.51	32.4	114	54.2	106	3.62
	Stem	0.24	0.06	0.25	0.38	37.1	99.8	33.7	71.8	1.89
		0.05	0.03	0.13	0.26	31.2	83.4	40.7	63.3	1.79
	Leaves	0.05	0.04	0.19	0.48	26.9	87.4	37.8	82.1	2.24
		0.03	0.02	0.07	0.36	22.1	77.3	35.2	76.5	1.92
FAO-WHO standards		0.5	0.05	0.03	0.3	NR	NR	NR	NR	NR

* The element contents in *Brassica rapa* are calculated by fresh weight; the values in bold represent the edible parts that exceed the FAO-WHO standards [49,50]. NR: Not Regulated.

3.2. Soil–Plant Interactions

Principal component analysis (PCA) facilitated a comprehensive chemical characterisation of soil (Figure 2A) and plant samples (Figure 2B). The biplot derived from soil geochemistry accounts for 93.3% of the total variance and effectively distinguishes the four investigated soil groups. Specifically, Dimension 1 (Dim1), which explains 82.5% of the total variance, differentiates volcanic soils, characterised by negative values (enriched in As, Hg and Pb), from Sicilian clay soils, which exhibit positive values (enriched in Cd and Ca). Campanian clay soils show minimal variation along Dim1. Dim2 separates samples enriched in Ca, Cd, Mg, and Pb from those enriched in As, Fe, Hg, and K, providing a preliminary classification between Campanian and Sicilian samples. Clay soils display a broader compositional variation compared to volcanic soils, which form more compact clusters. The biplot based on the composition of the edible parts of *B. rapa* L. (Figure 2B) accounts for 87.9% of the total variance. It exhibits geochemical associations consistent with those obtained from soil geochemistry. Dim1, explaining 73.4% of the total variance, separates samples collected from volcanic soils (characterised by positive values and enriched in PTEs) from those collected in clay soils (characterised by negative values and enriched in major elements). Dim2, which accounts for 14.5% of the total variance, distinctly separates samples from Sicily (enriched in Pb and Mg) from those collected in Campania (enriched in As, Fe, Hg, and Na). The analogous patterns observed in soils and plants as a function of soil geochemistry provide compelling evidence of the strong relationship between soil geochemistry and PTE uptake by *B. rapa* L.

To assess the capability of *B. rapa* L. to uptake the investigated PTEs in its edible parts, we employed the Bio-Accumulation Factor (BAF) index, consistent with the methodology outlined by [17]. The BAF average values obtained were as follows: Hg = 0.44 ± 0.21; Cd = 0.42 ± 0.29; As = 0.07 ± 0.05; Pb = 0.04 ± 0.03. These results agree with those reported by [17] for As, Cd, and Pb in *Brassica chinensis* cultivated in contaminated soils. Additionally, the observed Hg values correspond with findings from [60], who investigated Hg uptake in *B. chinensis* grown under greenhouse conditions.

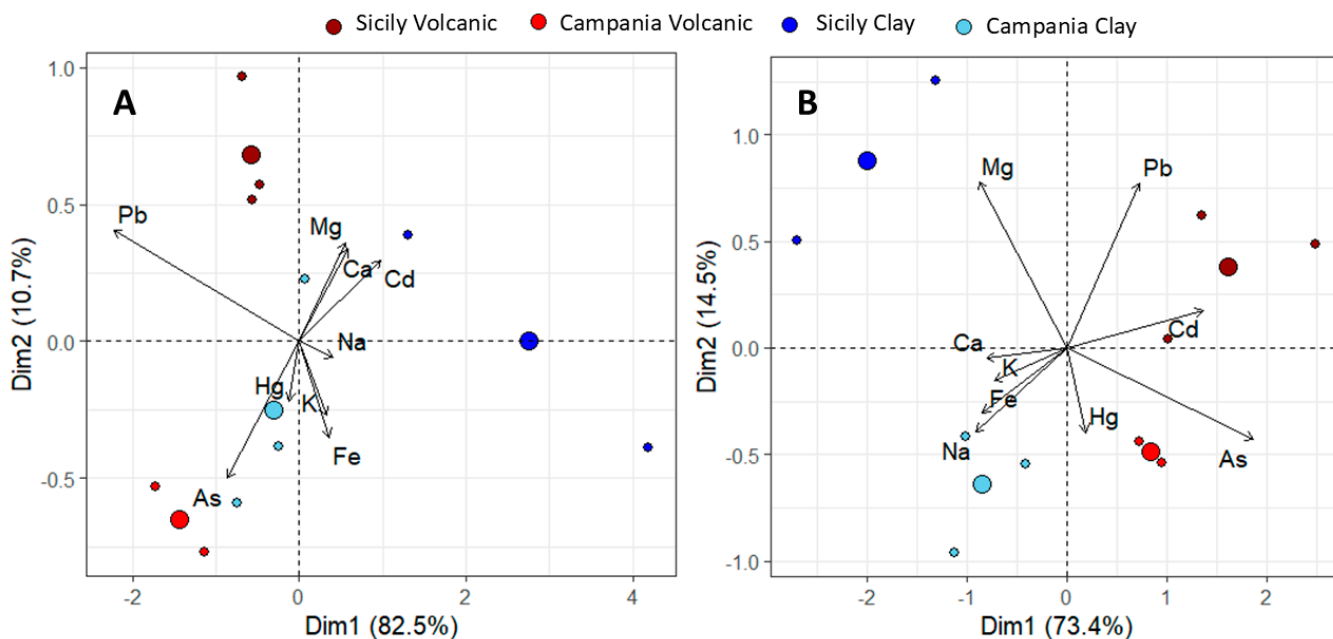


Figure 2. Principal component analysis biplot for soil (A) and plant samples (B). The colours indicate the different sites and soil categories investigated, and the larger circles represent the centroid of each group.

Figure 3 illustrates that while Cd and Hg generally exhibit higher BAF values compared to As and Pb, significant variability in BAF values can occur among samples due to fluctuations in various environmental factors. For example, Sicilian soils exhibit higher pH values than Campanian soils, which likely explains the lower BAF of Cd (more mobile under acidic pH) and higher BAF of As (more mobile under basic pH). Such conditions may not have a relation to the geological aspects of the area but could be attributed to the region’s low rainfall, which contributes to more alkaline soil conditions [61]. The similar BAF values between volcanic and clayey soils may arise because neither provides the optimal PTE uptake conditions, consisting of a low pH (except for As) and high CEC [62].

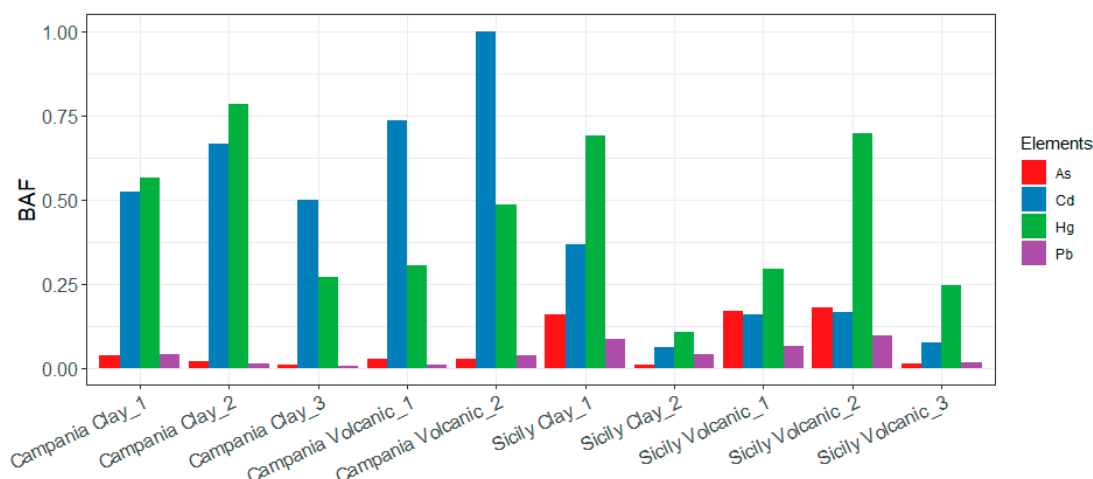


Figure 3. Bioaccumulation factor for the edible part of the investigated plants.

Another critical factor which could affect BAF values is the concentration of PTEs in soils, as they can exert toxic effects on plants at elevated concentrations, inducing physiological stress [63,64]. This stress may trigger protective mechanisms that limit metal uptake, resulting in reduced BAF values even when soil concentrations of PTEs are

high. Such phenomena may occur for As and Pb in Campanian samples, where soils are particularly enriched with these elements.

3.3. Health Risk Assessment

The estimated PTE daily intake (EDI) associated with the consumption of *B. rapa* L. cultivated in the four distinct soil types is presented in Table 5. This study used the mean concentration values of PTEs in plants from each soil group (Table 6), and applied relatively narrow intake ranges, representative of a varied diet that is not exclusively based on vegetable consumption. This approach was adopted in light of the limited dataset and the exploratory nature of the assessment. Consequently, the values reported in Table 5 should be interpreted as indicative risk ranges reflecting the typical exposure levels of broccoli consumers. For As and Pb, the mean EDI values for children and adults are ranked as follows: Sicily_volcanic > Campania_volcanic > Sicily_clay > Campania_clay. For Cd, the EDI values show the order: Sicily_clay > Sicily_volcanic > Campania_volcanic > Campania_clay. For Hg, the EDI values are ranked as: Campania_volcanic > Sicily_volcanic > Sicily_clay > Campania_clay.

The contribution of each PTE to non-carcinogenic risk is illustrated in Figure 4. The average target hazard quotient (THQ) values for the ingestion of *Brassica rapa* grown in the four investigated soil groups are as follows: Sicily_volcanic: 1.2 (As)-0.2 (Cd)-0.7 (Hg)-1 (Pb); Campania_volcanic: 0.6 (As)-0.08 (Cd)-1.1 (Hg)-0.2 (Pb); Sicily_clay: 0.7 (As)-0.2 (Cd)-0.3 (Hg)-0.4 (Pb); Campania_clay: 0.3 (As)-0.03 (Cd)-0.2 (Hg)-0.09 (Pb). These findings indicate that *Brassica rapa* grown on volcanic soils poses an intolerable non-carcinogenic risk (THQ > 1) due to elevated concentrations of As and Pb in Sicily, and Hg in Campania. Conversely, clay soils do not present intolerable non-carcinogenic risks associated with any single element. Notably, THQ values were consistently higher for children than adults across all investigated PTEs, suggesting increased susceptibility among children. Similar results were obtained in other studies [65–67]. Other comparative studies indicate that THQ values for As in plants collected in volcanic and clay soils from Sicily exceed those reported for other leafy brassicas studied in the Yangtze River Plain [68] and from greenhouse production in Xi’an [17], both of which are sites in China impacted by anthropogenic input of PTEs.

Table 5. The estimated daily intake $\text{mg kg}^{-1}\cdot\text{d}^{-1}$ of PTEs for the *Brassica rapa* ingestion in the four investigated soil groups.

		Ingestion Rates (g/day)	EDI_As	EDI_Cd	EDI_Hg	EDI_Pb
Sicily_clay	Children	50	1.1×10^{-4}	1.5×10^{-4}	6.2×10^{-5}	1.2×10^{-3}
	Children	150	3.2×10^{-4}	4.6×10^{-4}	1.8×10^{-4}	3.6×10^{-3}
	Adults	200	9.9×10^{-5}	1.4×10^{-4}	5.7×10^{-5}	1.1×10^{-3}
	Adults	350	1.7×10^{-4}	2.5×10^{-4}	9.9×10^{-5}	1.9×10^{-3}
Sicily_volcanic	Children	50	2.8×10^{-4}	1.4×10^{-4}	1.5×10^{-4}	2.7×10^{-3}
	Children	150	8.3×10^{-4}	4.2×10^{-4}	4.6×10^{-4}	8.2×10^{-3}
	Adults	200	2.5×10^{-4}	1.3×10^{-4}	1.4×10^{-4}	2.5×10^{-3}
	Adults	350	4.4×10^{-4}	2.2×10^{-4}	2.5×10^{-4}	4.4×10^{-3}
Campania_clay	Children	50	6.2×10^{-5}	2.3×10^{-5}	4.2×10^{-5}	2.3×10^{-4}
	Children	150	1.8×10^{-4}	6.9×10^{-5}	1.4×10^{-4}	6.9×10^{-4}
	Adults	200	5.7×10^{-5}	2.1×10^{-5}	4.2×10^{-5}	2.1×10^{-4}
	Adults	350	9.9×10^{-5}	3.7×10^{-5}	7.4×10^{-5}	3.7×10^{-4}
Campania_volcanic	Children	50	1.4×10^{-4}	6.2×10^{-5}	2.5×10^{-4}	5.7×10^{-4}
	Children	150	4.2×10^{-4}	1.8×10^{-4}	7.4×10^{-4}	1.7×10^{-3}
	Adults	200	1.3×10^{-4}	5.7×10^{-5}	2.3×10^{-4}	5.2×10^{-4}
	Adults	350	2.2×10^{-4}	9.9×10^{-5}	3.9×10^{-4}	9.1×10^{-4}

Table 6. Mean concentration of PTEs in mg kg⁻¹ fresh weight in the edible parts of *Brassica rapa*.

	As	Cd (mg kg ⁻¹ Fresh Weight)	Hg	Pb
Sicily Clay	0.07	0.1	0.04	0.77
Sicily volcanic	0.2	0.1	0.1	1.8
Campania Clay	0.04	0.015	0.03	0.15
Campania Volcanic	0.09	0.04	0.16	0.37

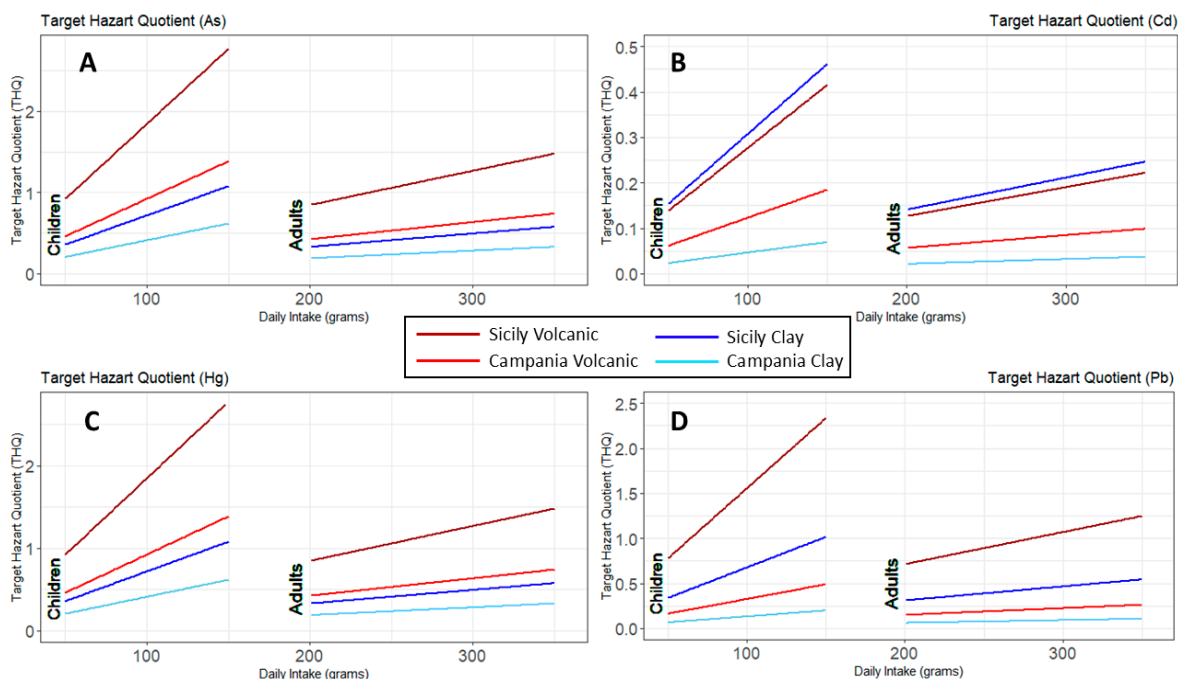


Figure 4. Contribution of the investigated PTEs to THQ. Arsenic (A), Cadmium (B), Mercury (C), Lead (D).

Higher THQ values for As were observed in *Brassica rapa* L. (turnip) cultivated using industrial wastewater in Pakistan [69], where THQ values reached up to 7.5. THQ values for Cd in *B. rapa* L. grown in Sicilian volcanic and clay soils align with those found in *Brassica oleracea* grown in polluted soils in Uganda [70] and a group of leafy brassicas from the Yangtze River Plain [68]. In contrast, higher THQ values for Cd were recorded in *B. rapa chinensis* from greenhouse production in Xi’an [17], reaching values up to 1.1. The Hg levels in *B. rapa* L. grown in volcanic soils were found to be higher than those reported from studies conducted in Uganda and the Yangtze River Plain; however, research on Hg accumulation in *Brassicaceae* tissues remains limited. The THQ values of Pb were elevated only in samples from Sicilian volcanic soils, showing values comparable to *B. chinensis* and *B. rapa* L. grown under strong anthropogenic pressure in the cities of Xi’an [17] and Lahore [59], respectively. Higher values were noted for a group of leafy brassicas from the Yangtze River Plain [68] and *B. rapa* L. from the Punjab city in Pakistan [69].

The contribution of As and Pb to carcinogenic risk (TCR) is depicted in Figure 5, with average values as follows: Sicily_volcanic: 0.0005 (As)-0.00003 (Pb); Campania_volcanic: 0.0003 (As)-0.00005 (Pb); Sicily_clay: 0.0002 (As)-0.00001 (Pb); Campania_clay: 0.0001 (As)-0.000003 (Pb). These results indicate that *B. rapa* L. sampled on volcanic soils presents an intolerable carcinogenic risk (TCR > 0.0001) due to high As levels across both studied regions, while tolerable risk was identified for plants grown in clay soils. As for THQ values, TCR values exhibited by the analysed PTEs are comparable to those estimated for *Brassica chinensis* grown in areas impacted by anthropogenic input of PTEs.

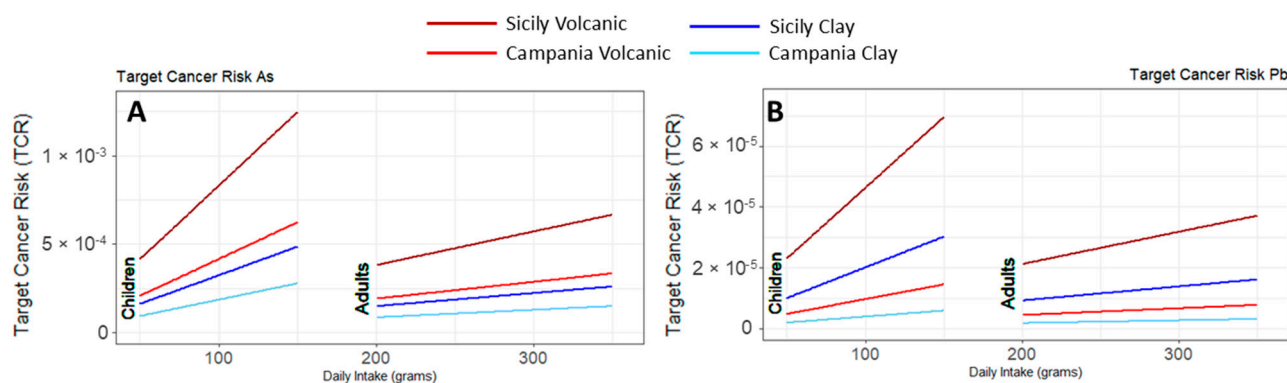


Figure 5. Contribution of Arsenic (A) and Lead (B) to Target Cancer Risk.

The cumulative carcinogenic and non-carcinogenic risks associated with the ingestion of the *B. rapa* L. analyzed in this first study are illustrated in Figure 6A, B, respectively. Our preliminary results indicate that the consumption of *B. rapa* L. grown in volcanic and clay soils of Sicily, as well as in volcanic soils of Campania, poses an intolerable cancer risk across all ingestion rates considered, for both children and adults. Conversely, the lowest metal concentrations detected in the three samples from clay soils in Campania correspond to a tolerable cancer risk up to approximately 60 g per day for children and 200 g per day for adults. Although the results are entirely exploratory, elevated risk levels appear to be primarily driven by high As, Hg and Pb concentrations that *B. rapa* L. accumulates from the soil, particularly in samples from volcanic areas where this element is naturally enriched. These findings suggest that the consumption of *B. rapa* L. from volcanic regions of southern Italy should be avoided or limited to only a few days per year to minimize health risks. The assessment of non-carcinogenic risks associated with the ingestion of *B. rapa* L. reveals a tolerable risk in Campania clay soils, while it is deemed intolerable in volcanic soils for children and adults. Specifically, *B. rapa* L. cultivated in Sicilian clay soils presents a tolerable risk only at low daily intake levels (below 210 g/day for adults and 70 g/day for children). This study indicates that even in soils devoid of anthropogenic contamination by PTEs, hyperaccumulator plants like *B. rapa* L. consumption can pose significant health risks due to natural soil enrichment with PTEs. Although a more comprehensive risk assessment will require evaluating the PTEs speciation in *B. rapa* L., our results indicate that the geochemical characteristics of the soil significantly influence the risk associated with the consumption of these vegetables. Consequently, meticulous planning based on the soil geochemistry of areas designated for cultivating *B. rapa* L. and potentially other edible hyperaccumulators is essential.

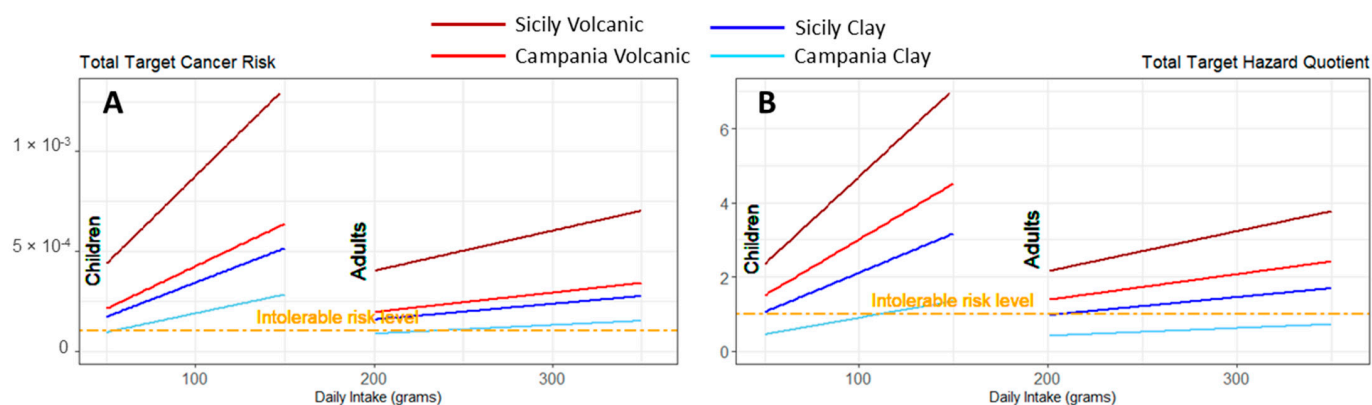


Figure 6. Contribution of the investigated PTEs to total target cancer risk (A) and total target hazard quotient (B).

4. Conclusions

This exploratory study demonstrates that natural soil geochemical backgrounds can strongly control the accumulation of PTEs in *Brassica rapa*, leading to concentrations in edible tissues that frequently exceed international food safety limits, particularly in volcanic soils. The elevated risks observed in volcanic soils are consistent with their geochemical properties, which favour PTE mobility and translocation to edible plant parts, particularly for Cd and Hg.

The primary novelty of this preliminary study lies in highlighting that the natural geochemical patterns of PTEs in soils are mirrored in the PTE concentrations within *B. rapa* L. The results provided by this study suggest that PTE levels in the edible parts of plants grown on volcanic soils can surpass the limits defined by the FAO and WHO by up to fourteen times. Volcanic soils were associated with intolerable carcinogenic and non-carcinogenic risks even at low consumption rates, whereas clay soils generally resulted in tolerable risk levels under similar intake scenarios. The risk assessment is preliminary and based on a limited sample size and average concentration values, without considering PTE speciation or full exposure variability. Therefore, the absolute risk levels should be interpreted cautiously. Despite these limitations, the results highlight that naturally enriched soils may represent a hidden source of dietary exposure to PTEs, comparable to contaminated environments. These findings underline the need for systematic soil geochemical characterization in agricultural planning and for further studies integrating PTE speciation and epidemiological data.

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Institutional Review Board Statement: All experimental research and field studies on plants, including the collection of plant material, comply with relevant institutional, national, and international guidelines and legislation.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

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Abbreviations

The following abbreviations are used in this manuscript:

BAF	Bioaccumulation Factor
<i>B. rapa</i>	<i>Brassica rapa</i>
CEC	Cation Exchange Capacity
CoDA	Compositional Data Analysis
EDI	Estimated Daily Intake
ICP-MS	Inductively Coupled Plasma–Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
NR	Not Regulated
PTEs	Potentially Toxic Elements
TCR	Target Cancer Risk
THQs	Target Hazard Quotients
TOC	Total Organic Carbon
TTCR	Total Target Cancer Risk
TTHQs	Total Target Hazard Quotients

References

- Roy, M.; McDonald, L.M. Metal Uptake in Plants and Health Risk Assessments in Metal-Contaminated Smelter Soils. *Land Degrad. Dev.* **2015**, *26*, 785–792. [[CrossRef](#)]
- Zhang, R.; Chen, T.; Zhang, Y.; Hou, Y.; Chang, Q. Health risk assessment of heavy metals in agricultural soils and identification of main influencing factors in a typical industrial park in northwest China. *Chemosphere* **2020**, *252*, 126591. [[CrossRef](#)]
- Zheng, S.; Wang, Q.; Yuan, Y.; Sun, W. Human health risk assessment of heavy metals in soil and food crops in the Pearl River Delta urban agglomeration of China. *Food Chem.* **2020**, *314*, 126213. [[CrossRef](#)]
- Gupta, N.; Yadav, K.K.; Kumar, V.; Kumar, S.; Chadd, R.P.; Kumar, A. Trace elements in soil-vegetables interface: Translocation, bioaccumulation, toxicity and amelioration—A review. *Sci. Total Environ.* **2019**, *651*, 2927–2942. [[CrossRef](#)]
- Emamverdian, A.; Ding, Y.; Mokhberdorran, F.; Xie, Y. Heavy metal stress and some mechanisms of plant defense response. *Sci. World J.* **2015**, *2015*, 756120. [[CrossRef](#)] [[PubMed](#)]
- Jan, A.T.; Ali, A.; Haq, Q.M.R. Glutathione as an antioxidant in inorganic mercury induced nephrotoxicity. *J. Postgrad. Med.* **2011**, *57*, 72–77. [[CrossRef](#)] [[PubMed](#)]
- Slavin, J.L.; Lloyd, B. Health benefits of fruits and vegetables. *Adv. Nutr.* **2012**, *3*, 506–516. [[CrossRef](#)]
- Antoniadis, V.; Shaheen, S.M.; Stärk, H.J.; Wennrich, R.; Levizou, E.; Merbach, I.; Rinklebe, J. Phytoremediation potential of twelve wild plant species for toxic elements in a contaminated soil. *Environ. Int.* **2021**, *146*, 106233. [[CrossRef](#)]
- Gómez-Campo, C.; Prakash, S. Origin and domestication. *Develop. Plant Gen. Breed.* **1999**, *4*, 33–58. [[CrossRef](#)]
- Rahman, M.; Haq, N.; Williams, I.D. Phytoaccumulation of Arsenic, Cadmium and Lead by *Brassica juncea* Parents and their F1 Hybrids. *J. Environ. Prot.* **2016**, *7*, 613–622. [[CrossRef](#)]
- Andersen, N.S.; Poulsen, G.; Andersen, B.A.; Kiær, L.P.; D’Hertefeldt, T.; Wilkinson, M.J.; Jørgensen, R.B. Processes affecting genetic structure and conservation: A case study of wild and cultivated *Brassica rapa*. *Genet. Resour. Crop Evol.* **2009**, *56*, 189–200. [[CrossRef](#)]
- Reeves, R.D.; Baker, A.J.M.; Jaffré, T.; Erskine, P.D.; Echevarria, G.; van der Ent, A. A global database for plants that hyperaccumulate metal and metalloid trace elements. *New Phytol.* **2017**, *218*, 407–411. [[CrossRef](#)]
- Mourato, M.P.; Moreira, I.N.; Leitão, I.; Pinto, F.R.; Sales, J.R.; Martins, L.L. Effect of Heavy Metals in Plants of the Genus *Brassica*. *Int. J. Mol. Sci.* **2015**, *16*, 17975–17998. [[CrossRef](#)] [[PubMed](#)]
- Zunaidi, A.A.; Lim, L.H.; Metali, F. Heavy metal tolerance and accumulation in the *Brassica* species (*Brassica chinensis* var. *parachinensis* and *Brassica rapa* L.): A pot experiment. *Heliyon* **2024**, *10*, e29528. [[CrossRef](#)]
- Gill, R.A.; Zang, L.; Ali, B.; Farooq, M.A.; Cui, P.; Yang, S.; Ali, S.; Zhou, W. Chromium-induced physio-chemical and ultrastructural changes in four cultivars of *Brassica napus* L. *Chemosphere* **2015**, *120*, 154–164. [[CrossRef](#)]
- Li, L.; Zhang, K.; Gill, R.A.; Islam, F.; Farooq, M.A.; Wang, J.; Zhou, W. Ecotoxicological and Interactive Effects of Copper and Chromium on Physiochemical, Ultrastructural, and Molecular Profiling in *Brassica napus* L. *BioMed Res. Int.* **2018**, *2018*, 9248123. [[CrossRef](#)]

17. Guo, J.; Zhang, D.; Wang, Y. Incorporating in vitro bioaccessibility into human health risk assessment of heavy metals and metalloid (As) in soil and pak choi (*Brassica chinensis* L.) from greenhouse vegetable production fields in a megacity in Northwest China. *Food Chem.* **2022**, *373*, 131488. [[CrossRef](#)] [[PubMed](#)]
18. Kottek, M.; Grieser, J.; Beck, C.; Rudolf, B.; Rubel, F. World map of the Köppen-Geiger climate classification updated. *Meteorol. Z.* **2006**, *15*, 259–263. [[CrossRef](#)]
19. Varrica, D.; Lo Medico, F.; Zuccolini, M.V.; Miola, M.; Alaimo, M.G. Geochemical baseline values determination and spatial distribution of trace elements in topsoils: An application in Sicily region (Italy). *Sci. Total Environ.* **2024**, *955*, 176951. [[CrossRef](#)] [[PubMed](#)]
20. Ambrosino, M.; Palarea-Albaladejo, J.; Albanese, S.; Cicchella, D. Mapping geochemical domains using stream sediment geochemistry: An approach based on compositional indicators in the Volturno River basin (South Italy). *J. Geochem. Explor.* **2024**, *265*, 107545. [[CrossRef](#)]
21. Guarino, V.; Solone, R.; Casalini, M.; Franciosi, L.; Dallai, L.; Morra, V.; Conticelli, S.; Melluso, L. The geochemistry of leucite-bearing lavas from early stages of the Somma-Vesuvius volcanic complex: Feeder systems and mantle enrichment processes in the Neapolitan district of the Roman Magmatic Province. *Geochemistry* **2024**, *84*, 126076. [[CrossRef](#)]
22. Martelli, M.; Nuccio, P.M.; Stuart, F.M.; Burgess, R.; Ellam, R.M.; Italiano, F. Helium-strontium isotope constraints on mantle evolution beneath the Roman Comagmatic Province, Italy. *Earth Planet. Sci. Lett.* **2004**, *224*, 295–308. [[CrossRef](#)]
23. Corsaro, R.A.; Pompilio, M. Dynamics of magmas at Mount Etna. *Geophys. Monogr. Ser.* **2004**, *143*, 91–110. [[CrossRef](#)]
24. Zuzolo, D.; Cicchella, D.; Lima, A.; Guagliardi, I.; Cerino, P.; Pizzolante, A.; Thiombane, M.; De Vivo, B.; Albanese, S. Potentially toxic elements in soils of Campania region (Southern Italy): Combining raw and compositional data. *J. Geochem. Explor.* **2020**, *213*, 106524. [[CrossRef](#)]
25. Ambrosino, M.; Albanese, S.; Capozzoli, A.; Lucadamo, A.; Cicchella, D. Identifying the geochemical fingerprint of volcanic material in soils of distal areas using a machine-learning approach. *Catena* **2025**, *258*, 109306. [[CrossRef](#)]
26. Ambrosino, M.; Palarea-Albaladejo, J.; Albanese, S.; Lin, X.; Ciarcia, S.; Cicchella, D. Assessing natural background concentrations of chemical elements in urban soils: A case study in Benevento (Italy). *Sci. Total Environ.* **2025**, *975*, 179298. [[CrossRef](#)]
27. Lo Medico, F.; Varrica, D.; Zuccolini, M.V.; Miola, M.; Scopelliti, G.; Alaimo, M.G. Geochemical baseline values and spatial distribution of major, trace, and rare earth elements in unpolluted soils of the Sicily region (Italy). *Environ. Geochem. Health* **2025**, *47*, 167. [[CrossRef](#)] [[PubMed](#)]
28. Reimann, C.; Birke, M.; Demetriades, A.; Filzmoser, P. *Chemistry of Europe's Agricultural Soils. Part A: Methodology and Interpretation of the GEMAS Data Set*; Schweizerbart Science Publishers: Bern, Switzerland, 2014.
29. Salminen, R.; Tarvainen, T.; Demetriades, A.; Duris, M.; Fordyce, F.M.; Gregorauskiene, V.; Kahelin, H.; Kivisilla, J.; Klaver, G.; Klein, H. *FOREGS. Geochemical Mapping. Field Manual Guide 47*; Geological Survey of Finland: Espoo, Finland, 1998; Available online: <https://nora.nerc.ac.uk/id/eprint/19017/1/FOREGSmanual.pdf> (accessed on 11 February 2026).
30. Lo Turco, V.; Di Bella, G.; Furci, P.; Cicero, N.; Pollicino, G.; Dugo, G. Heavy metals content by ICP-OES in *Sarda sarda*, *Sardinella aurita* and *Lepidopus caudatus* from the Strait of Messina (Sicily, Italy). *Nat. Prod. Res.* **2013**, *27*, 518–523. [[CrossRef](#)]
31. Di Salvo, E.; Tardugno, R.; Nava, V.; Naccari, C.; Virga, A.; Salvo, A.; Corbo, F.; Clodoveo, M.L.; Cicero, N. Gourmet Table Salts: The Mineral Composition Showdown. *Toxics* **2023**, *11*, 705. [[CrossRef](#)] [[PubMed](#)]
32. Magnusson, B.; Örnemark, U. (Eds.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods—A Laboratory Guide to Method Validation and Related Topics*, 2nd ed.; Eurachem: Teddington, UK, 2014; Available online: www.eurachem.org (accessed on 11 February 2026).
33. Aitchison, J. The Statistical Analysis of Compositional Data. *J. R. Stat. Soc. Ser. B* **1982**, *44*, 139–160. [[CrossRef](#)]
34. Egozcue, J.J.; Pawłowsky-Glahn, V. Simplicial geometry for compositional data. *Geol. Soc. Spec. Publ.* **2006**, *264*, 145–159. [[CrossRef](#)]
35. Cicchella, D.; Ambrosino, M.; Gramazio, A.; Coraggio, F.; Assunta, M.; Caputi, A.; Avagliano, D.; Albanese, S. Using multivariate compositional data analysis (CoDA) and clustering to establish geochemical backgrounds in stream sediments of an onshore oil deposits area. The Agri River basin (Italy) case study. *J. Geochem. Explor.* **2022**, *238*, 107012. [[CrossRef](#)]
36. Ambrosino, M.; Albanese, S.; De Vivo, B.; Guagliardi, I.; Guarino, A.; Lima, A.; Cicchella, D. Identification of Rare Earth Elements (REEs) distribution patterns in the soils of Campania region (Italy) using compositional and multivariate data analysis. *J. Geochem. Explor.* **2022**, *243*, 107112. [[CrossRef](#)]
37. Modabberi, S.; Tashakor, M.; Rajabian, N.; Khorasanipour, M.; Esmailzadeh, E.; Ambrosino, M.; Cicchella, D. Characterization and chemical fractionation of potentially toxic elements in soils of a pre-mining mineralized area; an evaluation of mobility and environmental risk. *Environ. Geochem. Health* **2023**, *45*, 4795–4815. [[CrossRef](#)]
38. Ambrosino, M.; El-Saadani, Z.; Khatita, A.A.; Mingqi, W.; Palarea-Albaladejo, J.; Cicchella, D. Geochemical Speciation, Ecological Risk and Assessment of Main Sources of Potentially Toxic Elements (PTEs) in Stream Sediments from Nile River in Egypt. *Water* **2023**, *15*, 2308. [[CrossRef](#)]

39. Filzmoser, P.; Hron, K.; Reimann, C. Univariate statistical analysis of environmental (compositional) data: Problems and possibilities. *Sci. Total Environ.* **2009**, *407*, 6100–6108. [CrossRef]
40. Templ, M.; Hron, K.; Filzmoser, P. robCompositions: An R-package for Robust Statistical Analysis of Compositional Data. In *Compositional Data Analysis: Theory and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2011. [CrossRef]
41. Kassambara, A.; Mundt, F. Package ‘factoextra’. CRAN-R Package. 2020. Available online: <https://cran.r-project.org/web/packages/factoextra/index.html> (accessed on 11 February 2026).
42. Agency for Toxic Substances and Disease Registry; U.S. Department of Health and Human Services; P.H.S. *Exposure Dose Guidance for Body Weight*; ATSDR: Atlanta, GA, USA, 2023; pp. 1–5. Available online: <https://www.atsdr.cdc.gov/pha-guidance/resources/ATSDR-EDG-Body-Weight-508.pdf> (accessed on 11 February 2026).
43. Abdelgawad, Z.A.; Abd El-Wahed, M.N.; Ahmed, A.A.; Madbouly, S.M.; El-Sayyad, G.S.; Khalafallah, A.A. Assessment of heavy metal accumulation and health risk in three essential edible weeds grown on wastewater irrigated soil. *Sci. Rep.* **2023**, *13*, 21768. [CrossRef]
44. Centro di Ricerca Alimenti e Nutrizione del Consiglio per La Ricerca in Agricoltura e L’analisi dell’economia Agraria (CREA). Linee Guida per una Sana Alimentazione Italiana. Available online: <https://www.crea.gov.it/web/alimenti-e-nutrizione/-/linee-guida-per-una-sana-alimentazione-2018> (accessed on 11 February 2026).
45. Smith, R.L. *EPA Region III Risk-Based Concentration Table Background Information*; Environmental Protection Agency: Washington, DC, USA, 1995; pp. 1–21. Available online: https://extapps.dec.ny.gov/data/DecDocs/828028A/Report.HW.828028A.1995-10-20.EPA_REGION111_RBC_TABLES.pdf (accessed on 11 February 2026).
46. Cadmium in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality. Available online: <https://iris.who.int/items/74ebe93f-d343-4605-9512-bf1856b9fbaa> (accessed on 11 February 2026).
47. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Mercury*; Agency for Toxic Substances and Disease Registry: Atlanta, GA, USA, 2024.
48. Safety Evaluation of Certain Contaminants in Food: Prepared by the Seventy-Second Meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA). Available online: <https://www.who.int/publications/i/item/9789241660631> (accessed on 11 February 2026).
49. OEHHA. *Appendix A: Hot Spots Unit Risk and Cancer Potency Values*; California Office of Environmental Health Hazard Assessment: Sacramento, CA, USA, 2019. Available online: <https://oehha.ca.gov/sites/default/files/media/downloads/crn/appendixa.pdf> (accessed on 11 February 2026).
50. USEPA. *Risk Assessment Guidance for Superfund. Human Health Evaluation Manual Part A, Interim Final, 1 Part A*; United States Environmental Protection Agency: Washington, DC, USA, 1989. Available online: https://www.epa.gov/sites/default/files/2015-09/documents/rags_a.pdf (accessed on 11 February 2026).
51. Cicchella, D.; De Vivo, B.; Lima, A. Background and baseline concentration values of elements harmful to human health in the volcanic soils of the metropolitan and provincial areas of Napoli (Italy). *Geochem. Explor. Environ. Anal.* **2005**, *5*, 29–40. [CrossRef]
52. De Vivo, B.; Lima, A.; Bove, M.A.; Albanese, S.; Cicchella, D.; Sabatini, G.; Di Lella, L.A.; Protano, G.; Riccobono, F.; Frizzo, P.; et al. Environmental geochemical maps of Italy from the FOREGS database. *Geochem. Explor. Environ. Anal.* **2008**, *8*, 267–277. [CrossRef]
53. Cicchella, D.; Ambrosino, M.; Albanese, S.; Guarino, A.; Lima, A.; De Vivo, B.; Guagliardi, I. Major elements concentration in soils: A case study from Campania Region (Italy). *J. Geochem. Explor.* **2023**, *247*, 107179. [CrossRef]
54. Tóth, G.; Hermann, T.; Da Silva, M.R.; Montanarella, L. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ. Int.* **2016**, *88*, 299–309. [CrossRef]
55. JECFA. *Evaluation of Certain Contaminants in Food: Seventy-Second [72nd] Report of the Joint FAO/WHO Expert Committee on Food Additives*; World Health Organization: Geneva, Switzerland, 2011; Available online: <https://iris.who.int/handle/10665/44514> (accessed on 11 February 2026).
56. FAO/WHO. General Standard for Contaminants and Toxins in Food and Feed (Codex Stan 193-1995). *Jurnal Ekonomi Malaysia*, 2015. Available online: https://www.fao.org/fileadmin/user_upload/livestockgov/documents/1_CXS_193e.pdf (accessed on 11 February 2026).
57. Hidayati, N.; Rini, D.S. Assessment of plants as lead and cadmium accumulators for phytoremediation of contaminated rice field. *Biodiversitas* **2020**, *21*, 1928–1934. [CrossRef]
58. Yaashikaa, P.R.; Kumar, P.S.; Jeevanantham, S.; Saravanan, R. A review on bioremediation approach for heavy metal detoxification and accumulation in plants. *Environ. Pollut.* **2022**, *301*, 119035. [CrossRef]
59. Mahmood, A.; Malik, R.N. Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from different irrigation sources in Lahore, Pakistan. *Arab. J. Chem.* **2014**, *7*, 91–99. [CrossRef]
60. Sun, W.; Zhao, Y.; Zhang, Z.; Li, B.; Li, Z.; Tang, X. Greenhouse Characterization of Inorganic Mercury, Methyl Mercury and Ethyl Mercury Migration and Transformation in Indian Mustard and Chinese Pakchoi. *Anal. Lett.* **2022**, *55*, 1425–1439. [CrossRef]

61. Palumbo, B.; Angelone, M.; Bellanca, A.; Dazzi, C.; Hauser, S.; Neri, R.; Wilson, J. Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. *Geoderma* **2000**, *95*, 247–266. [[CrossRef](#)]
62. Máthé-Gáspár, G.; Anton, A. Phytoremediation study: Factors influencing heavy metal uptake of plants. *Acta Biol. Szeged.* **2005**, *49*, 69–70.
63. Kovács-Bokor, É.; Domokos, E.; Biró, B. Toxic metal phytoextraction potential and health-risk parameters of some cultivated plants when grown in metal-contaminated river sediment of Danube, near an industrial town. *Environ. Geochem. Health* **2021**, *43*, 2317–2330. [[CrossRef](#)] [[PubMed](#)]
64. Pasricha, S.; Mathur, V.; Garg, A.; Lenka, S.; Verma, K.; Agarwal, S. Molecular mechanisms underlying heavy metal uptake, translocation and tolerance in hyperaccumulators-an analysis: Heavy metal tolerance in hyperaccumulators. *Environ. Chall.* **2021**, *4*, 100197. [[CrossRef](#)]
65. Ramazanov, E.; Lee, S.H.; Lee, W. Stochastic risk assessment of urban soils contaminated by heavy metals in Kazakhstan. *Sci. Total Environ.* **2021**, *750*, 141535. [[CrossRef](#)]
66. Wang, L.; Yin, X.; Gao, S.; Jiang, T.; Ma, C. In vitro oral bioaccessibility investigation and human health risk assessment of heavy metals in wheat grains grown near the mines in North China. *Chemosphere* **2020**, *252*, 126522. [[CrossRef](#)] [[PubMed](#)]
67. Cao, L.; Lin, C.; Gao, Y.; Sun, C.; Xu, L.; Zheng, L.; Zhang, Z. Health risk assessment of trace elements exposure through the soil-plant (maize)-human contamination pathway near a petrochemical industry complex, Northeast China. *Environ. Pollut.* **2020**, *263*, 114414. [[CrossRef](#)] [[PubMed](#)]
68. Liu, X.; Song, Q.; Tang, Y.; Li, W.; Xu, J.; Wu, J.; Wang, F.; Brookes, P.C. Human health risk assessment of heavy metals in soil-vegetable system: A multi-medium analysis. *Sci. Total Environ.* **2013**, *463–464*, 530–540. [[CrossRef](#)]
69. Ahmad, K.; Ashfaq, A.; Khan, Z.I.; Bashir, H.; Sohail, M.; Mehmood, N.; Dogan, Y. Metal accumulation in *Raphanus sativus* and *Brassica rapa*: An assessment of potential health risk for inhabitants in Punjab, Pakistan. *Environ. Sci. Pollut. Res.* **2018**, *25*, 16676–16685. [[CrossRef](#)]
70. Awino, F.B.; Maher, W.A.; Fai, P.B.A. Do crops grown at urban dumpsites contain metals at levels that pose unacceptable health risks to consumers? *Environ. Toxicol. Chem.* **2024**, *43*, 2628–2644. [[CrossRef](#)] [[PubMed](#)]

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