

Article

Environmental Assessment of Potentially Toxic Elements in Periurban Vineyard Area (North-Eastern Romania) Within the Context of Residential Area Expansion

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Abstract

This study evaluated potentially toxic element (PTEs) contamination (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) in soil and grapevine leaves across 36 sites in a historical vineyard near Iași, Romania, transitioning toward residential development. Soil samples were analyzed using energy-dispersive X-ray fluorescence (ED-XRF), while leaf tissues collected during the véraison stage (mid-August) underwent microwave-assisted acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS). Soil analyses revealed that average concentrations of Cr, Ni, and Pb exceeded national normal legal thresholds, while Cu and As surpassed alert permissible limits. Contamination factor (*CF*) and Geoaccumulation Index (*I_{geo}*) metrics confirmed significant anthropogenic Cu enrichment from historical viticultural treatments. Soil-to-leaf transfer factors (*TF*) approached or exceeded 1 for Cu and Zn, though grapevine was not identified as a hyperaccumulator. Spearman correlation modeling demonstrated a statistical decoupling between soil concentrations and foliar tissue levels for Cu ($r_s = -0.21$) and Zn ($r_s = 0.075$), confirming that canopy accumulation is governed by historical agrochemical spraying and atmospheric deposition rather than root-driven uptake. Conversely, Pb ($r_s = 0.43$) exhibited a moderate direct soil-to-leaf pathway. The potential ecological risk (*PER*) index indicated moderate-to-considerable cumulative risk, primarily driven by Cu ($E_{Cu} = 68.64$) and Cd ($E_{Cd} = 59.17$). Human health risk assessments established direct ingestion as the primary exposure pathway, with current non-carcinogenic hazards remaining within tolerable limits ($HI < 1$). However, the proposed residential conversion increases exposure risks for vulnerable cohorts, underscoring the necessity of systematic soil screening and remediation prior to land redevelopment.

Keywords: potentially toxic elements; soil-to-plant transfer; grapevine leaves; contamination indices; human health risk; land-use change; residential development

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1. Introduction

The accelerated expansion of urban environments into historical agricultural lands has created a complex geochemical legacy. In Romania, a country with a profound viticultural tradition [1], periurban vineyard areas are increasingly being converted into residential zones. This land-use transition raises critical environmental concerns, as long-term intensive viticulture—characterized by the recurrent application of copper-based fungicides and phosphate fertilizers—leads to the persistent accumulation of potentially toxic elements (PTEs) in the soil matrix [2–4].

Soil serves as the primary geochemical reservoir for pollutants, facilitating their transfer to the atmosphere, hydrosphere, and biomass [5–7]. While the presence of PTEs is well-documented in active vineyards, their behavior in “legacy soils” repurposed for residential use remains a significant knowledge gap. In these transitioning zones, the risk shifts from agricultural productivity to human health hazards, particularly for the most vulnerable groups: children and adults living in close proximity to contaminated areas [8–13].

A specific point of uncertainty in the study area concerns the role of *Vitis vinifera* foliage in the PTEs cycle. Traditionally, local knowledge suggests that vine leaves from treated vineyards are avoided for culinary purposes, whether fresh or preserved, due to the awareness of foliar chemical treatments. However, the environmental relevance of these leaves remains high due to their return to the soil as organic matter (organic debris). The decomposition of fallen leaves acts as a secondary pathway for PTEs cycling, potentially re-concentrating elements in the topsoil. In a residential context, this foliar debris no longer returns to an exclusively agricultural system but accumulates in gardens, playgrounds, and yard soils. Thus, understanding whether vine foliage acts as a secondary source of PTEs in topsoil is essential for evaluating long-term exposure for residents, particularly children.

Furthermore, the transition to residential use necessitates a targeted toxicological approach. Rather than focusing on average field concentrations, human health risk assessment must prioritize “hot-spots”—localized areas of high contamination often found in old vineyards due to uneven agrochemical application or historical mixing points. Consequently, this study evaluates the non-carcinogenic and carcinogenic risks for adults and children based on soil concentrations in these identified hot-spots, simulating a worst-case residential exposure scenario.

The primary objectives of this study are threefold: first, to quantify the concentration of eight PTEs (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) in the soil, utilizing national legislative thresholds and standardized geochemical indices to establish the exact degree of geochemical enrichment and contamination grades; second, to investigate soil-to-foliar dynamics, evaluating how these PTEs are partitioned within the plant and the implications of returning foliar biomass to the soil; and third, to characterize the human health risks (both carcinogenic and non-carcinogenic) for children and adults, focusing specifically on identified soil hotspots within transitioning residential zones.

By employing these geochemical indices and deterministic risk models, this research seeks to resolve uncertainties regarding the safety of historical vineyard soils, ultimately providing a diagnostic framework in alignment with the EU Soil Strategy for 2030 [14,15].

2. Materials and Methods

2.1. Site Description

The county seat, Iași, is a prominent city in Romania, recognized as a significant academic center with a vibrant scientific, cultural, artistic, and commercial community. Known as the “City of Seven Hills,” Iași is situated in the north-eastern region of Romania, 47.1° N and 27.3° E (Figure 1). The Copou vineyard sector considered in this study is

located along an active residential expansion front, where former vine parcels are progressively subdivided for housing. This makes it an ideal natural laboratory for assessing legacy PTEs in soils prior to land-use conversion.

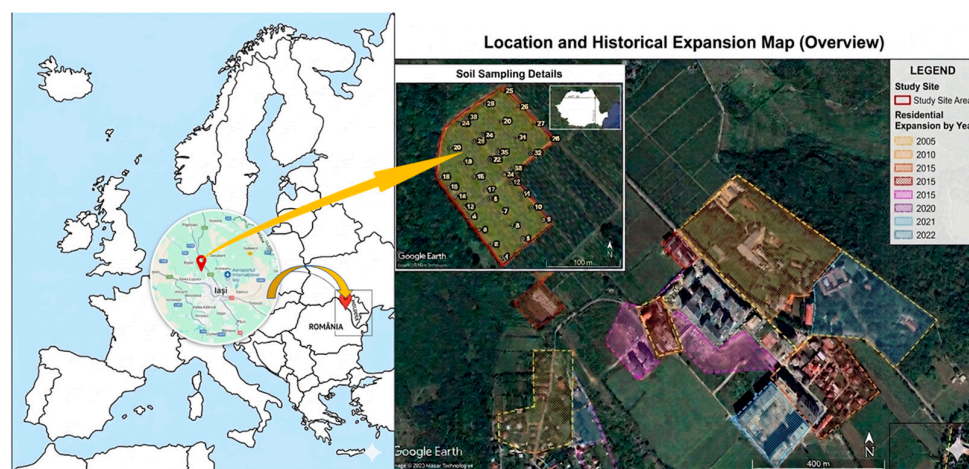


Figure 1. Study area location and historical expansion of residential area; sampling network.

The city is characterized by its dedication to orchards and vineyards, with an elevation that increases by up to 340 m from the northwest to the southeast. The region experiences a temperate climate, with temperatures ranging from -36°C to $+40^{\circ}\text{C}$, a multiannual mean of $+9.5^{\circ}\text{C}$, and a distinct continental influence [16]. The cultivation of grapevines typically occurs on agricultural land deemed unsuitable for other crops due to its mountainous (steep) terrain and sandy soils. Historical accounts of the Copou Vineyard date back to 1496 and 1608, describing the old town surrounded by vineyards. From 1938 onwards, the vineyards around Iași City were organized into four centers: Bucium, Miroslava, Copou, and Șorogari [17,18]. Geologically, the region corresponds to the Moldavian Platform, primarily composed of Sarmatian silty-clay deposits covered by newly loessoid deposits [19]. Three rivers, the Bahlui, Nicolina, and Șorogari, traverse Iași. The soil develops on Sarmatian deposits, consisting mainly of sand and silty sand layers interspersed with shale-clays. The parent material, identified as Sarmatian deposits, was found at a depth of 120–200 cm from the topsoil layers [20]. Previous studies of the region [21–23] indicate that Cambic Chernozem is representative of the soil type in the Copou vineyard center. Many studies have been carried out on the soil geochemistry of the Iași area and its surroundings [20–33].

However, the relationship between soil and plants, whether in cultivated or natural areas, has not been addressed in these studies. This aims to exhibit the impact of agricultural practices on the natural geochemical background and assess the health risks associated with converting land from vineyard to residential use.

2.2. Sample Collection and Conservation

A total of 36 samples of vine leaves and 36 samples of vineyard topsoil were collected from a regular network grid sampling site measuring 25×25 m (Figure 1). Each sampling location within the grid network yielded between 1.5 and 2 kg per soil sample. In accordance with geochemical sample characteristic guidelines, a complete soil sample comprises five subsamples arranged in a square with a 1 m side, centered on the grid's midpoint. At each site, composite samples (~ 2.5 kg) were obtained using the five-point method, homogenized, and reduced to a representative portion through coning and quartering. In the laboratory, all soil samples were air-dried at room temperature, homogenized, placed in

zip-lock bags, and sieved through a 1 mm stainless steel mesh after being crushed using a handled porcelain mortar.

Although grapevine leaves are not commonly consumed in the study area due to awareness of foliar treatments, we sampled them as key contributors of organic debris to the topsoil, which may influence long-term PTEs cycling under residential land use.

A plant sample consists of 60 to 80 green vine leaves, blades, and petioles collected between the bloom and véraison (ripening) stages of the vine (mid-August). The leaf samples were manually collected from the same grid network site as the soil samples. Only leaves from the basal position opposite a bunch were collected [34], typically corresponding to the fifth or seventh leaf from the top to the base of a stalk. To eliminate any residues from foliar treatments, dust, or other contaminants, the collected green vine leaves were promptly washed three times with deionized water and stored in paper bags [35]. The leaf samples were initially dried at room temperature for several days, followed by a three-hour drying period at a constant temperature of 105 °C, prior to being ground. Excess water was removed using filter sheets. The fine powder produced prior to acid digestion was achieved using an agate ball mill (Fritsch Planetary Mill Pulverisette 5, Fritsch GmbH, Idar-Oberstein, Germany) for 15 min at a speed of 180 rpm, ensuring sample homogeneity. All sampling equipment was washed with fresh water before each sample collection and rinsed with distilled water thereafter to prevent contamination during the sampling process. During laboratory procedures for sample preparation, an agate mortar was also rinsed after each sample with fresh water, followed by distilled water, and air-dried.

2.3. Physiochemical Analysis

The geochemical soil analyses were conducted using a size fraction of less than 1 mm in order to obtain the content of eight PTEs as follows: As, Cd, Co, Cr, Cu, Ni, Pb, and Zn. The preparation of pellets for ED-XRF investigation (ED-XRF PANalytical Epsilon 5 Spectrometer, Almelo, the Netherlands) adhered to the methodologies described in [31,36]. The standardization was performed by using 23 standards: 14 standards provided by the Geological Survey of Japan (JA-1-3: andesite powder; JB-1-3: basalt powder; JLk-1: lake sediment powder; JSd-1-3: stream sediment powder; JR-1-2: rhyolite powder; JMs-1-2: marine sediment powder), 8 standards provided by CCRMP-CANMET-MMSL Natural Resources Canada (SO-1-4: regosolic clay soil, podzolic B horizon soil, calcareous C horizon soil and chernozemic A horizon soil; STSD-1-4: stream sediment powder) and 1 standard provided by USGS, United States Geological Survey (RGM-1: rhyolite powder). The exposure time was set at 50 s for most elements, except for As and Cd, which required an exposure duration of 100 s. The detection limits for the measured elements were approximately 2 mg kg⁻¹ for Cr, Co, Cu, and Pb, 1 mg kg⁻¹ for As, and 0.1 mg kg⁻¹ for Cd. Quality control and assurance were evaluated using the SO-4 certified reference material (CRM). The standard was measured after every 10 sample measurements, and each sample was analyzed in triplicate. The results demonstrated analytical precision (relative standard deviation RSD < 5%) and accuracy within 4% for Cr, Co, Ni, Cu, Zn, Pb, and As. However, due to the low concentration of Cd in the CRM (0.34 mg kg⁻¹), which is near the instrument's detection limit (0.1 mg kg⁻¹), the RDS rises to 20% and the accuracy reaches up to 12%.

The soil reaction was measured using the potentiometric method with a 1:5 ratio of soil to distilled water using a pH-Meter Crison BASIC 20+, Barcelona, Spain. The total soil organic matter was determined using the conventional loss on ignition (LOI) method, which involved maintaining the crucible containing the samples at a constant temperature of 550 °C for 6 h, as described by [37].

At each location where soil samples were collected, a plant sample comprising 60–80 vine leaves was also obtained to monitor the distribution of eight PTEs (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) within the soil–vine leaf agro-system. The leaf samples underwent

microwave acid digestion, involving 0.2–0.3 g of fine powder treated with 8 mL of HNO₃, and were subsequently diluted with pure water to a total volume of 50 mL in polyethylene flasks (Microwave Sample Preparation System Mars 6, Matthews, NC, USA). The elemental composition of the leaf samples was then analyzed. From the digested solution, a 1 mL aliquot was extracted, combined with an internal standard (50 µg·mL⁻¹ Rh), and further diluted with pure water to a final volume of 15 mL in a polyethylene flask. The PTEs contents of the final solution were quantified using inductively coupled plasma mass spectrometry (ICP-MS). This analysis was conducted with an Agilent 7770X model (Hachioji, Tokyo, Japan) at the CERNESIM Center ICI-UAIC.

The quality control of ICP-MS data was assessed through the analysis of calibration standards and blank reagents prepared using commercially available solutions (Merck solution standards). To identify any potential loss of efficiency, appropriate calibration standards were periodically analyzed between samples, and certified reference materials were employed to evaluate the accuracy of the ICP-MS measurements. The supplier specified the following optimal parameters: an integration time of 0.3 s, radiofrequency power of 1550 W, carrier gas flow rate of 1.01 L min⁻¹, plasma gas flow rate of 15 L min⁻¹, and auxiliary gas flow rate of 0.70 L min⁻¹. The samples were subjected to three iterations of analysis.

2.4. Assessment of PTEs Contamination

Further evaluation of contamination levels in the soil and foliage from the collected samples in the inspected area is necessary if there is a potential environmental hazard. This investigation employed three soil pollution assessment indices: the Single Pollution Index (Pi), Geoaccumulation Index (Igeo) and the Pollution Load Index (PLI).

2.4.1. Contamination Factor (CF) or Single Pollution Index (Pi)

The contamination factor, also known in the literature as the Single Pollution Index (Pi), was initially proposed by [38] and subsequently employed by [39] to evaluate the concentration of PTEs in soil. The formula is expressed as follows:

$$CF = C_i/B_n, \quad (1)$$

where C_i represents the concentration of PTEs in the soil, and B_n denotes its ambient background value. The B_n values represent the local geochemical background, estimated using the median values from the C-horizon of three soil profiles located near the studied vineyard plots [31].

The CF is categorized into four classifications based on the results:

- Low contamination when $CF < 1$;
- Moderate contamination when $1 < CF < 3$;
- Considerable contamination when $3 < CF < 6$;
- Very high contamination when $CF \geq 6$.

2.4.2. The Geoaccumulation Index (Igeo)

Igeo, developed by [40], is a widely used tool for assessing PTEs contamination in soils and sediments by comparing measured concentrations to pre-industrial background or reference values. Researchers employ this index to determine the extent of pollution. The Igeo is calculated using the formula:

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

In this context, C_i represents the measured concentration of element i in the sample, B_n denotes the background or reference concentration of element n , and the factor 1.5 is incorporated to account for natural variations in background values and minimal anthropogenic influence.

The results of Igeo can classify the soil quality as follows:

- I—unpolluted ($I_{geo} \leq 0$);
- II—unpolluted to moderately polluted ($0 < I_{geo} < 1$);
- III—moderately polluted ($1 < I_{geo} < 2$);
- IV—moderately to highly polluted ($2 < I_{geo} < 3$);
- V—highly polluted ($3 < I_{geo} < 4$);
- VI—highly to extremely highly polluted ($4 < I_{geo} < 5$);
- VII—extremely highly polluted ($I_{geo} > 5$).

2.4.3. Pollution Load Index (PLI)

The Pollution Load Index is calculated using the formula established by the following [41]:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n} \quad (3)$$

Here CF represents the contamination factor for the respective PTEs, and n is the number of elements ($n = 8$).

Based on the PLI results, contamination can be classified into 3 categories:

- PLI < 1 indicates perfection;
- PLI = 1 reflects only baseline levels of pollution;
- PLI > 1 signifies deterioration of soil quality.

2.4.4. The Translocation Factor (TF)

Plants take or accumulate elements from the soil based on their concentration, availability, and the specific needs of the plant. The translocation factor (TF), also referred to as the bioaccumulator factor (BAC), is employed to examine the accumulation of elements from the soil near the roots to the plants. The TF evaluates the rate at which pollutants chemically accumulate in leaves derived from the soil. An increase in the TF score corresponds to a higher quantity of PTEs absorbed by plants. According to [42], the TF is calculated using the following formula:

$$TF = C_{\text{plant}}/C_{\text{soil}} \quad (4)$$

where C_{plant} represents the total concentration of the target element in the grapevine leaves, expressed in mg/kg dry weight (d.w.), and C_{soil} represents the total concentration of the element in the corresponding topsoil sample, also expressed in mg/kg dry weight (d.w.). Normalizing both analytical matrices to a standardized dry-mass substrate eliminates variations caused by vegetable moisture content, providing a mathematically sound, dimensionless partition coefficient [43]. While this concentration ratio functions as an operational index of element partitioning at the soil–foliar interface rather than an absolute volumetric biomass accumulation metric, its variability is explicitly evaluated alongside localized rhizosphere properties to reflect shifting bioavailability dynamics. As per [44], plants can be categorized into three groups based on their capacity to accumulate elements: (1) excluders ($TF < 1$), which maintain a normal level of elements in the plant regardless of soil content; (2) accumulators ($TF > 1$), which concentrate elements at the plant level; and (3) indicators, which absorb and transport elements within the plant, reflecting the soil content until toxicity effects become apparent.

2.5. Ecological Risk Assessment

The assessment of the risk of various types of PTEs pollution across ecosystem portfolios can be conducted using the potential risk technique. To estimate the potential ecological risk (PER) associated with PTEs contamination in soil, the potential ecological risk index method was employed to connect the ecological environment with the toxicological

effects of PTEs. The current study on PTEs contamination in the soils of Copou vineyards utilized the potential ecological hazard index technique.

$$Eir = Tir \times CFi \quad (5)$$

$$PER = \sum ni = Eir \quad (6)$$

The pollution factor of element *i* (CFi) was determined using Equation (1). The toxic response coefficient *Tir* of each PTEs indicates the toxic strength of the PTEs and the sensitivity of a specific water body to this PTEs. In this study, the *Tir* values were 10, 30, 2, 5, 5, 5, and 1 for As, Cd, Cr, Cu, Ni, Pb, and Zn, respectively [38,45].

Equation (5), which specifies the contamination level of an individual pollutant element, was used to determine the potential ecological risk index of a single PTEs (*Eir*).

Equation (6) was employed to generate the total potential ecological risk index (PER), which is divided into four categories and describes the overall sum of the potential ecological risk index for each element at each sampling location. The recommended thresholds are as follows: low risk $Eir < 40$; moderate risk $40 < Eir < 80$; considerable risk $80 < Eir < 160$; high risk $160 < Eir < 320$; very high risk $Eir > 320$.

While this formula is utilized globally for comparative ecotoxicological screening, it possesses an inherent mathematical constraint: elements with concentrations below natural background levels $CFi < 1$ still contribute positively to the aggregate PERI score due to their toxic response factors *Tir*. To prevent this mechanical aggregation from conflating natural background geochemical presence with actual anthropogenic contamination, individual element risk factors *Eri* were evaluated independently. Elements exhibiting $CFi < 1$ were classified as environmentally baseline and were not permitted to guide the interpretation of toxicological risks for the prospective residential development, ensuring that our final hazard conclusions are dictated solely by verified, site-specific threshold exceedances $CFi > 1$.

2.6. Assessment of Human Health Risks

To safeguard public health, various preventive methodologies have been developed to evaluate the health risks posed by pollutants. The human health risk assessment system can calculate the average daily dose (ADD) of an element entering the human body through a specific exposure pathway, based on known concentrations of PTEs. This calculation provides insights into both the non-carcinogenic risk associated with pollutant exposure and the carcinogenic risk linked to exposure to specific carcinogenic elements. The primary exposure pathways for assessing health concerns related to PTEs contamination in soil are ingestion, inhalation, and dermal contact [46,47]. Equations (7)–(9) were employed to determine the ADD of the PTEs for each pathway.

$$ADD_{ing} = Cs \times IngR \times EF \times EDBW \times AT \times 10^{-6} \quad (7)$$

$$ADD_{inh} = Cs \times InhR \times EF \times EDPEF \times BW \times AT \quad (8)$$

$$ADD_{der} = Cs \times SA \times AF \times ABS \times EF \times EDBW \times AT \times 10^{-6} \quad (9)$$

where ADD_{ing} , ADD_{inh} and ADD_{der} represent the mean average doses of PTEs by ingestion, inhalation and dermal contact, respectively ($mg \cdot kg^{-1} \cdot day^{-1}$); *Cs* denotes the concentration of PTEs in the soil ($mg \cdot kg^{-1}$) [46,47]. Table 1 provides a list of additional parameters related to human activity.

Table 1. List of additional parameters related to human activity for ADD estimation.

Formula	Definition	Unit	Children	Adult
ABS	dermal absorption factor	unitless	0.001	0.001
AT	average time	days	365	365
AF	skin adherence factor	mg/cm ² day	0.2	0.7
BW	body weight	kg	15	70
EF	exposure frequency	days/year	350	350
ED	exposure duration	years	6	24
IngR	ingestion rate of soil	mg/day	7.63	12.8
PEF	particle emission factor	m ³ /kg	1.36 × 10 ⁹	1.36 × 10 ⁹
SA	surface area of the skin	cm ²	1600	4350

To estimate the ADD of PTEs in soil, we use standard guidelines from the USEPA. These guidelines consider two groups—children and adults—because they react differently to toxins. Body weight is important here. Children are assumed to weigh 15 kg, while adults weigh 70 kg. This means children can absorb more toxins because they weigh less (Table 1).

Ingestion is a key way people, especially children, get exposed to soil toxins, often through hand-to-mouth actions. For skin contact, the amount of skin exposed and how much soil sticks to it matter. Adults usually have more soil sticking to their skin (0.7 mg/cm²) than children (0.2 mg/cm²) due to activities like gardening. However, the skin does not absorb much of these PTEs (0.001). Inhalation is measured by the Particle Emission Factor (PEF), which is 1.36 × 10⁹ m³/kg. This shows how soil particles become airborne and breathable (Table 1). The model assumes long-term exposure, with people exposed 350 days a year, taking into account 2 weeks of vacation away from home. Children are considered exposed for 6 years, and adults for 24 years. For non-cancer risks, the dose is averaged over 365 days to show daily intake. This approach explains the reasoning behind the USEPA's 2011/2025 guidelines (Table 1) [46,47].

The hazard index (HI) is employed to assess the non-carcinogenic risk to humans arising from PTEs contamination in the study area. It is calculated by summing the hazard quotients (HQs) determined for each PTEs. This calculation is performed using the following formula [46]:

$$HQ = ADD/RfD \quad (10)$$

$$HI = \sum HQ \quad (11)$$

where RfD represents the reference doses of PTEs (mg kg⁻¹ d⁻¹) (Table 2).

Table 2. The reference doses (RfD) for the PTEs.

Symbol	Cr	Ni	Cu	Zn	Cd	Pb	As
RfD _{ing}	3.00 × 10 ⁻³	2.00 × 10 ⁻²	4.00 × 10 ⁻²	3.00 × 10 ⁻¹	1.00 × 10 ⁻³	3.50 × 10 ⁻³	3.00 × 10 ⁻⁴
RfD _{inh}	2.86 × 10 ⁻⁵	2.06 × 10 ⁻²	4.02 × 10 ⁻²	3.00 × 10 ⁻¹	2.86 × 10 ⁻⁵	3.52 × 10 ⁻³	1.23 × 10 ⁻⁴
RfD _{derm}	6.00 × 10 ⁻⁵	5.40 × 10 ⁻³	1.20 × 10 ⁻²	6.00 × 10 ⁻²	6.00 × 10 ⁻⁵	5.25 × 10 ⁻⁴	8.60 × 10 ⁻⁶

PTEs pollution can have a negative impact on human health if either the HQ or HI value exceeds 1. Conversely, if both the HQ and HI values are less than 1, it indicates a negligible or non-significant risk from PTEs.

The cancer risk (CR) value quantifies the potential carcinogenic risk associated with specific PTEs that possess carcinogenic properties. Equations (12) and (13) are employed to calculate the cumulative carcinogenic risk (CCR) to human health in the area by summing the CR values of various elements:

$$CR = ADD \times CSF \quad (12)$$

$$CCR = \sum CR \quad (13)$$

where CSF represents the cancer slope factors of PTEs ($(\text{mg kg}^{-1} \text{ d}^{-1})^{-1}$). The specific cancer slope factors (CSFs) are 1.5, 0.5 and 0.0085 for As, Cr and respectively Pb [48]. If the CR or CCR value is less than 10^{-6} , the contamination by PTEs poses minimal to no impact on human health. A carcinogenic risk is present if the CR or CCR value ranges between 10^{-6} and 10^{-4} ; however, this level is deemed acceptable. A carcinogenic risk to human health is considered intolerable if the CR or CCR value reaches 10^{-4} [46,49,50].

3. Results

3.1. Potential Toxic Element Concentrations

3.1.1. PTEs in Vineyard Soil

In the vineyard soils of the Copou area, eight PTEs were analyzed: As, Cd, Co, Cr, Cu, Ni, Pb, and Zn. Descriptive statistics and comparative data against geochemical background levels and legislative standards are presented in Table 3.

Table 3. Descriptive statistics and comparative data for soil samples [mg/kg].

Parameter	Cr _{soil}	Co _{soil}	Ni _{soil}	Cu _{soil}	Zn _{soil}	Cd _{soil}	Pb _{soil}	As _{soil}
Mean	59	13.12	52	113	75	0.372	30.14	12.83
Kurtosis	0.046	0.633	−0.276	30.46	5.29	0.047	0.521	−0.416
Standard Deviation	10.04	0.470	2.360	67	5.89	0.148	2.870	0.485
Skewness	0.624	−0.239	−0.369	5.353	1.77	0.228	0.897	−0.082
Minimum	44	11.8	46	80	67	0.010	26.0	11.90
Maximum	84	14	56	486	98	0.710	38.0	13.90
No of Samples	36	36	36	36	36	36	36	36
¹ C-Horizon, Median	68.8	10.88	42.4	20.4	50.6	0.188	23	10.98
² Iancu&Buzgar, 2008 [23]	34.83	8.73	34.86	30.31	72.09	0.360	20.04	nd
³ Botanical Garden	55.5	12.6	54.8	73.5	113	0.360	33.81	12.36
Copou Park	94.5	18.6	41.1	47.8	212	nd	66.7	13.7
Expozitiei Park	77.2	20.5	45.4	37.3	113	nd	34.6	12.4
⁴ NVS	30	15	20	20	100	1	20	5
PAS	100	30	75	100	300	3	50	10
PIS	300	50	150	200	600	5	100	20

¹ PTEs Median, C-Horizon from [31] as geochemical background; ² median value threshold for Iași city and its surroundings [23]; ³ [29,30]; ⁴ [51] NVS= normal soil values; PAS= the alert thresholds.

3.1.2. PTEs in Vine Leaves

The analysis of the elemental composition in grapevine leaf samples is essential for comprehending plant nutrition, environmental influences, and potential stress factors that may impact vine health and productivity. Table 4 presents the statistical evaluation of data obtained from ICP-MS analysis of grapevine leaves collected from the Copou area in Iași, with the objective of identifying elemental concentrations and assessing their variability.

Table 4. Descriptive statistics for vine leaf samples [mg/kg].

Parameter	Cr _{leaves}	Co _{leaves}	Ni _{leaves}	Cu _{leaves}	Zn _{leaves}	Cd _{leaves}	Pb _{leaves}	As _{leaves}
Mean	1.20	0.425	7.48	107	21.3	0.032	0.936	0.089
Standard Deviation	0.673	0.116	1.97	39.3	7.85	0.037	0.588	0.015

Kurtosis	22.4	7.23	0.200	0.188	0.602	2.264	3.90	−0.411
Skewness	4.32	1.74	0.569	0.313	0.995	1.684	1.67	0.559
Minimum	0.517	0.187	3.69	36.6	10.3	0.001	0.007	0.065
Maximum	4.72	0.901	12.2	216	40.4	0.151	3.06	0.123
No of Samples	36	36	36	36	36	36	36	36

3.2. Pollution and Health Risk Indices

The contamination factor values varying degrees of pollution across the sampled sites. To better understand the specific contributions of each PTEs, Figure 2 illustrates their relative distribution within the overall contamination range of the study area.

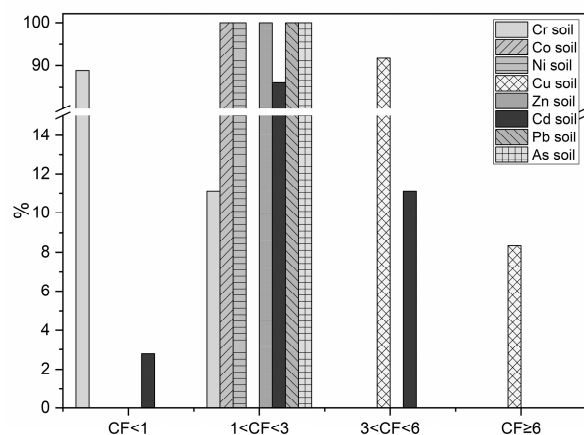


Figure 2. Contamination factor (CF).

To expand on this point, the Igeo index has been widely employed to assess the cumulative concentrations of PTEs in soils. The results of the Igeo analysis, presented in Figure 3, further emphasize the relative distribution of PTEs in relation to the overall contamination profile of the Copou–Iași vineyard area, thereby providing an additional perspective to the contamination factor evaluation.

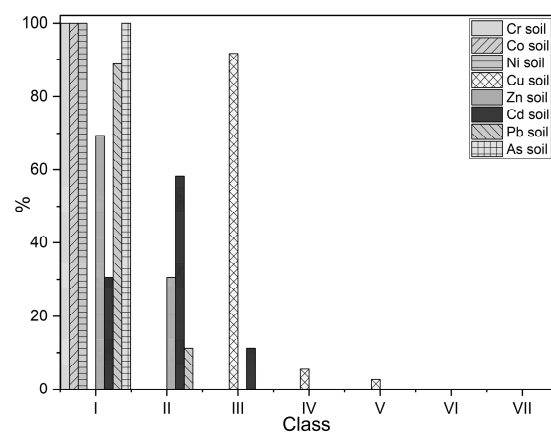


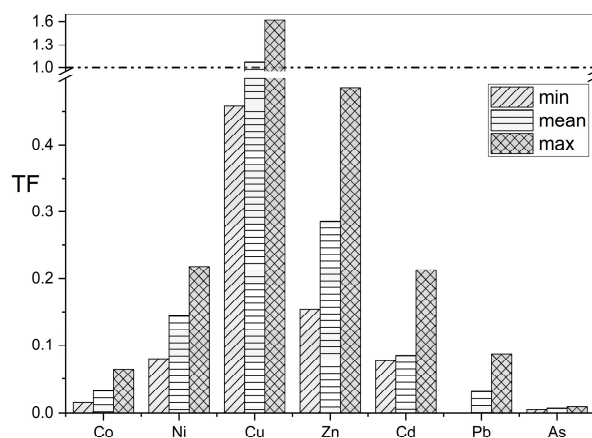
Figure 3. Geoaccumulation index as percent to PTEs.

The evaluation of PTEs contamination levels through the Pollution Load Index (PLI) in vineyard soils from the periurban area of Copou–Iași, as presented in Table 5, offers a thorough assessment of the extent of these elements within the studied region. This analysis highlighted the concentration levels of various PTEs by comparing them with established environmental standards or background values to determine the degree of contamination.

Table 5. Summary data regarding the PLI.

PLI Threshold	Interpretation	Number of Samples	Percentage (%)
PLI < 1	Indicates perfection (no pollution)	0	0%
PLI = 1	Reflects baseline levels of pollution	1	3%
PLI > 1	Signifies deterioration of soil quality	35	97%

The transfer factor (TF) values for both plants and soil are depicted in Figure 4, illustrating their minimum, mean and maximum values. This representation facilitates a clear comparison with the benchmark value of 1, which indicates the degree of element accumulation by vine plants.

**Figure 4.** The variation ranges and central tendencies (minimum, mean, maximum) of soil-to-plant TF for PTEs.

To further understand the mobility, source apportionment, and uptake mechanisms of PTEs, a Spearman's rank correlation analysis was performed between soil and leaf concentrations, as illustrated in the heatmap (Figure 5).

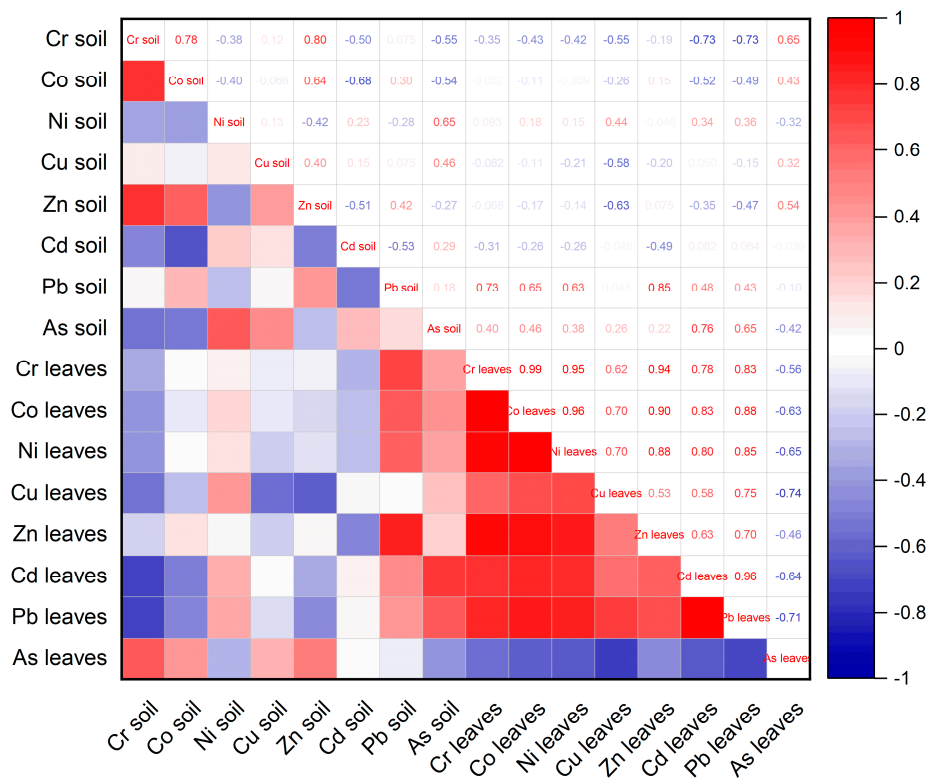


Figure 5. Soil–plant Spearman correlation heatmap.

The current study on PTEs contamination in the soils of Copou vineyards utilized the potential ecological hazard index technique, and the results are summarized in Figure 6.

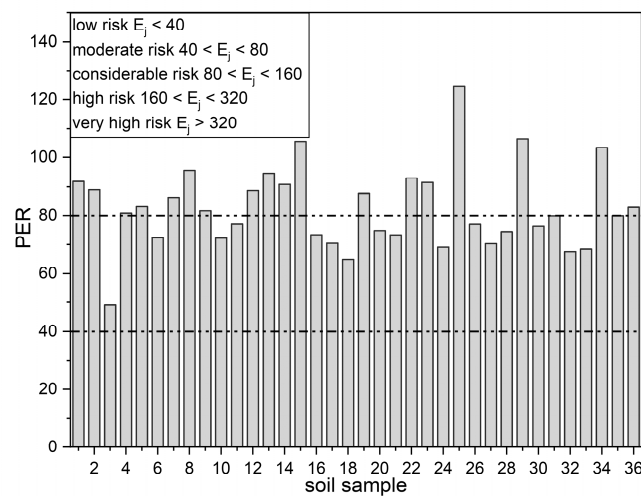


Figure 6. The PER variability on soil samples.

The prospective human health risk models formulated by the US EPA [46,47], which encompass both carcinogenic and non-carcinogenic risks, have been widely adopted and proven effective globally. Health risk assessment is an evaluative technique that examines the potential threat to human health by considering the pollutant in question as both a source and a receptor of risk. The results are presented as averages in Table 6.

Table 6. Mean values of HI and CR.

Parameter	Hazard Index (HI)		Carcinogenic Risk (CR)	
	Adults	Children	Adults	Children
Cr soil	5.77×10^{-2}	8.30×10^{-2}	0	0
Co soil	1.27×10^{-2}	1.84×10^{-2}	0	0
Ni soil	8.22×10^{-3}	1.60×10^{-2}	1.82×10^{-7}	3.57×10^{-7}
Cu soil	8.24×10^{-3}	1.18×10^{-2}	0	0
Zn soil	7.32×10^{-3}	1.05×10^{-1}	0	0
Cd soil	3.63×10^{-3}	4.24×10^{-5}	5.66×10^{-8}	6.61×10^{-10}
Pb soil	2.52×10^{-2}	3.62×10^{-2}	0	0
As soil	1.25×10^{-1}	1.80×10^{-1}	2.93×10^{-5}	4.21×10^{-5}

4. Discussion

The exceptional terroir of Romania has supported viticulture since antiquity, evolving into a modern agricultural sector of significant global and regional economic importance. As evidenced by recent International Organization of Vine and Wine (OIV) data, Romania's expansive 190,710 hectares of vineyards position it eighth globally in surface area and sixth within the European Union for wine production. This vast production capacity is underscored by the 2025 yield projections, where favorable late-season rainfall drove a 29% year-on-year increase to reach 4.1 million hectoliters, slightly surpassing the five-year national average [1]. However, sustaining these high yields requires a delicate balance of specific environmental variables, including temperate climatic conditions, optimal soil drainage, a precise pH range of 5.5 to 7.0, and a steady supply of nutrient-rich organic matter. Because viticultural landscapes are frequently established on fragile, highly sloping terrains stabilized by terraces or plateaus, they are inherently vulnerable to anthropogenic stress. The intensive agricultural practices required to manage these long-term monocultures—spanning from rigorous initial terrain preparation and continuous mechanical or manual labor to the routine application of agrochemicals—introduce significant disruptions to the local soil, water, and vegetation dynamics. Given that grapevines typically occupy the same plots for decades, and sometimes up to a century, this continuous cultivation aggressively depletes the natural nutritional reserves of the soil [2].

4.1. Content of PTEs

The soil exhibits a slightly acidic to slightly alkaline pH, ranging from 6.1 to 8.6, and contains a moderate average organic matter content of 6.1% [20,23,32,33]. The mean concentrations of PTEs in the soil samples are ordered as follows: Cu > Zn > Cr > Ni > Pb > Co > As > Cd (Table 3). Copper exhibits a notably high mean concentration of 113 mg/kg, with a substantial standard deviation of 67, indicating significant variability and the presence of potential hotspots. The standard deviation quantifies the dispersion of data around the mean, reflecting spatial heterogeneity; PTEs such as Cu (St Dev = 67) and Cr (10.04) demonstrate pronounced variability, indicative of uneven contamination distribution. Kurtosis assesses the “tailedness” of the distribution, with Cu (30.46) and Zn (5.29) displaying elevated values, signifying heavy tails and a higher probability of extreme values or outliers, which may correspond to localized contamination sources. Skewness measures the asymmetry of data distribution; positive skewness for Cr (0.624), Cu (5.353), Zn (1.77), and Pb (0.897) suggests a right-skewed distribution characterized by frequent high-concentration outliers, further corroborating the existence of hotspots. Conversely, negative skewness for Co (−0.239) and Ni (−0.369) indicates a slight left skew, reflecting a predominance of lower concentration values. The minimum and maximum values delineate the concentration range, with Cu reaching a maximum of 486 mg/kg, substantially

exceeding both the mean and regulatory thresholds, thereby highlighting critical contamination points.

Compared with the geochemical background values presented by [23] and [31] for Iași city and its surroundings (Table 3), the average contents of Cr, Co, Cu, and Pb in the Copou vineyard soils exceed the reported median or upper values. Meanwhile, Ni and As fall within the expected range of variation. For instance, the mean Cu concentration of 113 mg/kg in vineyard soil markedly exceeds the 30.31 mg/kg reported by [23] and the 17.8–35.4 mg/kg range from [20], determined for the soil in general. Thus, elevated contamination levels in vineyard soil can be observed by simple comparison.

Considering the increasing construction of residential properties, particularly for young families with children, on former vineyard sites, this study utilizes existing literature data on PTEs from major recreational areas in the vicinity for comparative analysis. The selected areas include Copou Park, the Expoziției Park, and the Botanical Garden (Table 3). In comparison to the values reported from the Botanical Garden, the average concentrations of Zn and Pb are lower, whereas both the maximum concentrations of Pb and all concentrations of Cu surpass the reference values provided by [30]. When compared to the two parks, the situation differs, as the site is in closer proximity to the main traffic artery. The Pb concentration values exceed those recorded for vineyard soils, which are subject to constant change due to land use modifications, and notably, this value even surpasses the alert thresholds (PAS) (Table 3). The concentrations of Cr and As are within the same range as those found in park soils, Co is below these minimum values, and as anticipated, Cu exhibits a significantly higher concentration in vineyard soils than in parks [29]. The Zn concentration in parks is higher than that observed in the studied soils.

The mean concentrations of Cr, Ni, and Pb exceed the NVS (normal values of soil) established by national regulations, while the mean concentrations of Cu and As surpass the alert thresholds (PAS) [51]. It is imperative to consider the maximum concentrations in these instances, as they may signal potential contamination hot spots. Although the mean concentrations of Zn and Cd in vineyard soils are below the NVS, their maximum concentrations are nearing this limit. Overall, these patterns demonstrate that anthropogenic activities have led to the accumulation of certain PTEs in the soil beyond natural background levels, and contamination remains a concern in specific locations.

In comparison with the existing literature, the mean values reported for the Huși vineyard soil are lower than those obtained for the Copou–Iași area, which shares similar geological characteristics. According to [36], the reported concentrations in Huși vineyard soils were 12 mg/kg for Co, 38.9 mg/kg for Ni, 84.9 mg/kg for Cu, 73.9 mg/kg for Zn, 0.13 mg/kg for Cd, 19.9 mg/kg for Pb, and 10.5 mg/kg for As. Notably, only the concentration of Cr was higher in the Huși area, at 146 mg/kg.

In the northwestern region of the country, the authors of ref. [52] report similar or lower values for Co (9.93 mg/kg), Ni (19.23 mg/kg), Zn (78.25 mg/kg), and Pb (16.27 mg/kg), whereas the values for Cd (0.56 mg/kg) and Cu (433.69 mg/kg) are higher than those found in the current study.

Secu and Lesenciuc (2024) [33] reported that in the same vineyard studied area, higher Cu pollution in the abandoned vineyard compared to the cultivated one resulted from the quantity of treatments applied, despite the abandoned vineyard being used for a shorter time. The paper highlighted that Cu concentration in soil decreases in the following order: stripped soil in abandoned vineyard, soil in abandoned vineyard, soil in cultivated vineyard, and soil in forest [33].

The accumulation of Cu in European vineyards is notably high, with an estimated 24.8 kg Cu/ha accumulating over time, significantly exceeding the net export rate of 0.29 kg Cu/ha. This suggests a continuous buildup of Cu in the soil, primarily due to the application of fungicides [53]. The European Union's regulatory cap of 4 kg Cu/ha annually

indicates that some vineyard regions may surpass no-effect concentration thresholds in the future, necessitating potential remediation efforts. Additionally, other PTEs such as Pb and Zn have been found at elevated levels in soils associated with vineyards, particularly in areas like coastal Tuscany, Italy, where urban agricultural soils, including those previously used for vineyards, have recorded Cu concentrations as high as 300 mg/kg [54]. In general, PTEs concentrations in European vineyard soils display significant variability, with Cu levels consistently surpassing natural background concentrations. Concerns also extend to Cd, Pb, Cr, and Zn, contingent on the historical agricultural practices and pollution sources in the area. Cu concentrations can vary widely, reaching over 1000 mg/kg in some European vineyard soils, while other PTEs are typically found in the tens of mg/kg range, with certain areas exceeding regulatory limits [53,55–57].

The data summarizing key statistical parameters for leaf element concentrations are presented in Table 4. These metrics reveal central tendencies, variability, and distribution shapes, with Ni_{leaves} showing high dispersion and maximum values, while Cd_{leaves} exhibits more stable concentrations. Positive skewness in several elements indicates the presence of higher-concentration outliers. The consistent sample size of 36 per element ensures reliable comparison across the dataset. This overview provides a solid basis for further ecological, environmental, or physiological analysis. The mean concentrations of PTEs in the leaves are ordered as follows: $Cu > Zn > Ni > Cr > Pb > Co > As > Cd$ (Table 4).

Previous studies examining Romanian vine leaves have reported the following values: in the Huși area, refs. [58,59] documented concentrations of 0.57 mg/kg for Cr, 0.128 mg/kg for Co, 2.17 mg/kg for Ni, 200 mg/kg for Cu, 26.92 mg/kg for Zn, 0.017 mg/kg for Cd, 0.671 mg/kg for Pb, and 0.099 mg/kg for As. In comparison, the average values obtained for the Copou-Iași vineyard area are higher for Cr (1.20 mg/kg), Co (0.425 mg/kg), and Ni (7.48 mg/kg) (Table 4); however, only the maximum value for Cu exceeds that of the Huși region. Bora et al., 2015 [52] reported the following average concentrations for the northwest area: 1.79 mg/kg for Co, 9.87 mg/kg for Ni, 55.02 mg/kg for Cu, 13.97 mg/kg for Zn, 0.13 mg/kg for Cd, and 2.02 mg/kg for Pb. These values surpass those obtained in the present study, except for Cu. A study conducted by Albulescu et al. [60] compared an industrialized area with a vineyard surrounding the garden. The findings indicated that the industrial area exhibited a range of Pb concentrations varying from 2.36 to 6.56 mg/kg.

4.2. Environmental Assessment of PTEs and Soil–Plant Transfer Dynamics

To evaluate the anthropogenic enrichment of potentially toxic elements (PTEs) relative to the natural geochemical baseline, the CF and Igeo were calculated. Because PTEs distributions in periurban soils subjected to long-term anthropogenic pressure are typically highly asymmetric, logarithmic transformations or statistical smoothing of these indices were deliberately avoided. This approach preserves extreme values associated with localized contamination hotspots, providing uncompressed information that is particularly relevant for environmental assessment and residential risk planning.

To ensure that the Igeo calculations were based on a representative local geochemical baseline, the background parameter (B_n) was derived from empirical data obtained from the pristine C-horizon of three local soil profiles [31], reflecting the mineralogical and granulometric characteristics of the study area. These background values are consistent with those previously reported in [28], supporting the reliability of the adopted baseline. Regional geochemical variability was further evaluated by comparison with the Geochemical Atlas of Iași City and its Surroundings [23].

Although both indices assess anthropogenic enrichment, they differ in their sensitivity. The CF is based on a simple linear ratio and therefore responds more readily to concentration changes, whereas the Igeo incorporates a correction factor (1.5) to account for natural lithological variability [40], providing a more conservative assessment.

Consequently, the two indices were interpreted jointly to obtain a more robust evaluation of soil contamination. In addition, when considering the combined effect of multiple PTEs, the PLI was used to provide an integrated assessment of overall soil quality.

The CF values were directly proportional to the degree of contamination, with elevated CF values indicating higher levels of pollution. The CF results for the Copou-Iași vineyard revealed moderate to low contamination levels for Co, Ni, Zn, Cd, Pb, and As (Figure 2). In contrast, Cu revealed considerably higher contamination levels, ranging from considerable to very high (Figure 2). This consistency between the Igeo and CF values reinforces the conclusion that Cu contamination is a critical issue in this region. The mean CF results followed a descending order: $\text{Cu} > \text{Cd} > \text{Zn} > \text{Pb} > \text{Ni} > \text{Co} > \text{As} > \text{Cr}$. Elevated Cu contamination levels indicate localized pollutant sources, which may be linked to agricultural practices, industrial activities, or natural geochemical anomalies in the area. These findings are consistent with those reported by [31], who documented similar contamination patterns in this region. This alignment with previous studies not only strengthens the credibility of the current data but also underscores the persistent nature of Cu pollution in the Copou-Iași vineyard. Given the severity and consistency of these contamination indicators, there is an urgent need for targeted remediation efforts, particularly those focused on mitigating Cu pollution. Such interventions are essential to prevent further environmental degradation and safeguard soil health and agricultural productivity in the most severely affected areas.

The Igeo values for the PTEs under study predominantly fell within class I, indicating an uncontaminated to moderately contaminated status ($0 < \text{Igeo} \leq 1$) (Figure 3). This suggests that for most elements, the soil quality remains relatively unaffected or only slightly impacted by pollution. However, Cu was an exception, exhibiting the highest percentage of samples corresponding to class III, which denotes moderate pollution ($1 < \text{Igeo} < 2$). This elevated Cu contamination level highlights its significant presence and influence in the studied area.

Furthermore, the mean Igeo values followed the same descending order as the Igeo of $\text{Cu} > \text{Cd} > \text{Zn} > \text{Pb} > \text{Ni} > \text{Co} > \text{As} > \text{Cr}$, emphasizing the dominant cumulative pollution potential of copper compared with the other elements. This pattern indicates that copper is the primary contributor to soil contamination in the Copou-Iași vineyard, necessitating focused attention on this issue.

A distinction must be made between the Igeo and CF results and the comparison with national legislative limits. While Igeo and CF highlight Cu as the primary element of anthropogenic concern due to its high enrichment relative to the background, other elements such as Cr, Ni, and Pb exceed legislative “normal values” (NVS). This indicates that while these elements may not be heavily enriched by recent human activity, their absolute concentrations still warrant monitoring according to environmental safety standards.

The PLI based on this dataset of 36 samples showed significant contamination in the tested area (Table 5). The high frequency of samples (97%) falling into the maximum contamination category provides compelling evidence that the observed pollution is predominantly anthropogenic in origin. It is critical to note that the PLI represents a conventional algebraic construct rather than an empirically proven ecological or toxicological axiom. Because the geometric mean can mathematically mask the high contamination intensity of an individual element if companion elements yield low baseline ratios, the PLI thresholds (<1 , 1 , >1) were not utilized as definitive indicators of environmental safety or human health risk. To prevent the concealment of highly localized single-element hotspots (e.g., legacy viticultural Cu), all subsequent human health risk modeling (Hazard Quotients and Carcinogenic Risk) was executed using element-specific, non-aggregated exposure parameters.

The accumulation of PTEs and hydrocarbons on impermeable surfaces is closely linked to the expansion of urban infrastructure, driven by emissions from high-traffic

corridors and their deposition through atmospheric and runoff processes. In residential areas, direct contact of children with contaminated soil in play areas represents a critical risk for ingestion or inhalation.

The variability in PTEs transfer within grapevines can be attributed to the plant's distinct characteristics, particularly its capacity to absorb essential nutrients such as Cu and Zn, alongside PTEs with toxic potential, including Pb, Cr, and Cd. The uptake and translocation of PTEs within grapevines are facilitated by root absorption efficiency, transport proteins, and compartmentalization mechanisms within plant tissues. Furthermore, environmental factors such as soil pH, organic matter content, and microbial activity further influence PTEs bioavailability and mobility. These TF values do not furnish quantitative evidence to unequivocally differentiate the anthropogenic source. Notably, Cu exhibits significant enrichment in the leaves, which is attributed to foliar applications of micronutrients and copper-based fungicides [3,61].

The study conducted by Lai et al. [61] describes how PTEs accumulate and are distributed within the plant, indicating a preference for storage in certain organs: grapes < annual roots < perennial woody parts < leaves. $TF < 1$ suggests that the grapevine is not a hyperaccumulator, but rather that the leaves are the main site of PTEs accumulation, due to absorption from foliar fungicides (Cu and Zn are often added during spraying) and atmospheric pollution.

In the present study, the TF values for Cu exceed 1, while those for Zn are close to 1 (Figure 4). This observation is supported by the explanation provided above, rather than by the hyperaccumulator characteristic.

To validate this mechanism, a Spearman correlation analysis was performed to cross-reference the concentrations between the matrices (Figure 5). This statistical modeling revealed that direct bioaccumulation—measured as the correlation between an element's absolute concentration in the soil and its corresponding concentration in the leaves—was surprisingly weak or even negative for nearly all elements. Crucially, despite Cu and Zn being the most abundant elements in both the soil and foliar tissue profiles (sharing the top hierarchy: Cu > Zn, as shown in Tables 3 and 4), their direct soil-to-leaf correlation coefficients were remarkably low ($r_s = -0.21$ for Cu and $r_s = 0.075$ for Zn). This complete statistical decoupling firmly confirms that the critical foliar accumulation of Cu and the elevated $TF > 1$ are governed by historical agrochemical spraying and atmospheric deposition on the leaves rather than root-driven translocation from the heavily enriched soil hotspots (Cu max = 486 mg/kg). The only exception was for Pb, which displayed a moderate direct uptake signature ($r_s = 0.43$ for Pb soil vs. Pb leaves), aligning with its steady accumulation beyond NVS limits in both matrices. Instead of direct transfer pathways, complex cross-element interactions and synergistic foliar accumulation patterns dominate the system. Within the leaf tissues, a highly coordinated co-accumulation block was observed among most PTEs, characterized by near-perfect positive correlations among Cr, Co, Ni, Pb, and Zn (with r_s values ranging tightly from 0.70 to 0.99). This uniform behavior suggests either a shared multi-element source in atmospheric drift or a highly synchronized physiological storage mechanism within the vine canopy. Conversely, foliar As (As leaves) acted as a major statistical anomaly, displaying a strong antagonistic relationship with all other foliar PTEs, marked by moderate-to-strong negative correlations (e.g., $r_s = -0.74$ with leaf Cu, and -0.71 with leaf Pb). Furthermore, the soil chemistry exerted cross-element control over leaf uptake. Elevated soil Pb and As concentrations—which Section 4.1 identified as exceeding regulatory safety thresholds (NVS and PAS, respectively)—were strongly and positively correlated with the foliar accumulation of other companion elements, including Cr, Co, Ni, and Cd. This indicates that soil contamination by Pb and As may physiologically facilitate or prime the plant for broader PTEs retention. Conversely, higher soil Cr and Co levels appeared to suppress overall foliar PTEs uptake,

exhibiting strong negative correlations with leaf Cd, Pb, and Zn (e.g., Cr soil vs. Pb leaves = -0.73). This matches the geochemical profile in which soil Co and Ni showed negative skewness, representing a stable, lower-concentration natural baseline that acts antagonistically toward the anthropogenically driven PTEs burden in the vineyard ecosystem. These multi-variable interactions demonstrate that PTEs kinetics in these long-term monocultures are governed by complex interactive transport dynamics rather than simple, independent soil-to-plant pathways.

Particular attention should be paid to the quantity returned to the soil during autumn. A study by Angelova et al. (1999) [62] examined the uptake of PTEs during various stages of vegetation. For PTEs such as Pb, Cu, Zn, and Cd, their concentrations tend to increase progressively during the vegetation stages, reaching a peak at the technological maturity of the grapes, after which a decline is observed [62]. This pattern suggests a dynamic uptake and redistribution of these PTEs within the plant over time, influenced by both physiological processes and external inputs. The observed trends emphasize the importance of considering both the growth stage and the nature of PTEs sources when assessing PTEs accumulation in vine plants.

The potential ecological risk index of a single PTEs is ranked as follows: $E_{Zn} < E_{Cr} < E_{Ni} < E_{Pb} < E_{Co} < E_{As} < E_{Cu} < E_{Cd}$. Most samples exhibited total potential ecological risk index (PER) values ranging from moderate to considerable risk (Figure 6). The highest recorded values were 68.64 for Cu and 59.17 for Cd, both classified as moderate ecological risk (Figure 6).

4.3. Health Risk Assessment

Assessing human health risks becomes a critical request during land reuse; contamination thresholds considered acceptable for agricultural use may present significant hazards when land is rezoned for residential development, where vulnerable populations, especially children, may come into direct contact with the variety.

The calculated hazard quotients (HQs) for the three exposure pathways in both children and adults revealed that ingestion is the most significant risk factor (ingestion > dermal > inhalation). The hazard index (HI) values for all PTEs in both adults and children were below 1, indicating no significant risk within the study area. In terms of carcinogenic risk, the carcinogenic risk (CR) values for Cd and Pb showed no substantial risk, whereas As presented an acceptable level of risk for both adults and children (Table 6). When evaluating the non-carcinogenic and carcinogenic findings for the vineyard, which is being converted for residential use, it becomes apparent that ingestion is the predominant exposure pathway.

The transformation of agricultural land into residential areas without prior decontamination can expose the population to historical pesticide and synthetic fertilizer residue. Point-source contamination from nearby production units or chemical processing facilities can cause PTEs to infiltrate the substrate.

5. Conclusions

Soil in periurban areas serves as a primary repository for potentially toxic elements (PTEs), where dynamic interactions between historical agriculture and expanding urbanization govern element mobility and bioavailability. Environmental and geochemical indices (CF, Igeo, and PLI) confirm that Cu is the sole element with significant anthropogenic enrichment, driven by historical viticultural treatments (e.g., Bordeaux mixture). In contrast, elevated levels of Cr, Ni, Pb, and As primarily reflect regional geogenic and lithogenic background characteristics of North-Eastern Romanian soils rather than contemporary industrial or traffic inputs.

Soil-to-plant transfer dynamics show limited root translocation across grapevine organs. Foliar accumulation of Cu and Zn decoupled from soil concentrations ($r_s = -0.21$ and

0.075, respectively), proving that canopy contamination is driven by past exogenous agrochemical spraying and atmospheric deposition rather than root uptake. Conversely, Pb displayed a moderate direct soil-to-leaf pathway ($r_s = 0.43$). A highly synchronized co-accumulation block was identified in the canopy, with foliar Cr, Co, Ni, Pb, and Zn exhibiting strong positive correlations ($r_s = 0.70$ to 0.99), while foliar As acted as an antagonist. The potential ecological risk index (RI) revealed a considerable cumulative risk, primarily driven by Cu ($EC_u = 68.64$) and Cd ($EC_d = 59.17$). Non-carcinogenic health hazards ($HI < 1$) and incremental lifetime cancer risks for As (10^{-6} to 10^{-4}) currently remain within acceptable safety thresholds, with ingestion identified as the primary exposure route. However, converting these historical agricultural plateaus to residential land uses increases exposure frequency and duration for vulnerable cohorts, particularly children. Additionally, the cyclical return of Cu to the topsoil via leaf-fall decomposition creates a continuous secondary enrichment loop. Therefore, systematic soil screening, localized risk assessments, and targeted remediation strategies are essential prior to urban land conversion.

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