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TRANSFER OF HEAVY METALS IN SOIL IN-PLUM CULTIVATION: A FIELD STUDY IN ADAMACHI IASI, ROMANIA

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ABSTRACT. Currently, global environmental concerns about heavy metal pollution are driven by rapid urbanization and industrial development. Therefore, a field study was conducted to assess the concentration of heavy metals (Pb, Co, Zn, Ni and Cu) in orchard soils and its transfer to two plum varieties (Stanley and Anna Späth) at Adamachi Farm – Iasi University of Life Sciences (IULS). In addition, heavy metal transfer (MTF), daily metals intake (DIM) and the index of health risk (HRI) were evaluated. The concentration of Pb, Co, Zn, Ni and Cu in soil and plum leaves samples were analyzed using atomic absorption spectrometry after acid digestion with a mixture of HNO_3 (65%), HCl (37%) and $HClO_4$ (60%). Metal concentration patterns occurred as follows 130.65>76.6>30.36>21.69>13.26 mg/kg for Cu, Zn, Ni, Pb and Co in soil samples and 20.16>10.00>2.10>1.68 mg/kg for Zn, Cu, Ni and Pb in plum leaves, while Co residue was not detected. The maximum heavy metal concentrations were found at the soil surface (0 – 30 cm depth) due to soil organo-mineral content and antifungal treatments. The health risk index predicted (HRI) for adults as well as children was in the sequence Pb > Cu > Ni > Zn, suggesting no health risk with values that did not exceed the safe limit (1). Therefore, it is essential to manage the causes and sources of heavy metal transfer prudently and effectively in order to prevent environmental contamination.

Keywords: concentrations; heavy metals; leaves; plum orchard; soil.

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INTRODUCTION

Heavy metals are among the most harmful pollutants threatening food security and public health due to their environmental persistence (ur Rehman *et al.*, 2023). Heavy metals influence soil fertility decrease which impairs the optimal plant nutrition conditions (Jităreanu *et al.*, 2020). Therefore, soil can be regarded as a reservoir where pollutants are accumulated, a gateway between various natural systems (hydrosphere, biosphere, geosphere, lithosphere) and an autonomous environment in itself (Burducea *et al.*, 2022).

These damaging elements originate from human induced actions and natural sources, parent geologic materials, forest fires, volcanic eruptions, etc. The main causes of soil pollution arise from human activity including but not restricted to the intensive use of insecticides and pesticides, the chemical waste disposal industry, as well as mining and military activities (ur Rehman *et al.*, 2023, Cara *et al.*, 2021).

Some elements such as Mn (Manganese), Cu (Copper), Co (Cobalt), Zn (Zinc), Fe (Iron) and Mo (Molybdenum) perform important functions in the metabolic processes of plants, therefore different amounts are necessary while causing no damage to the plants (Jităreanu *et al.*, 2021). Heavy metals that consist of both essential (Cu, Zn, Mn) and non-essential elements like Pb (Lead), As (Arsenic) and Hg (Mercury) are recognized as standard environmental contaminants which remain unaltered over long periods of time and convert soil into a sink for these metals.

Currently, the risk of heavy metal consumption from vegetables or fruits has increased in recent years. Usually, both environmental and physiological factors control the rate at which heavy metals accumulate in soil-plant ecosystems. Meanwhile, the process of metal transfer (from soil to plants) varies according to a complex combination of soil characteristics (influencing absorption and desorption processes)/ factors, such as organic matter, pH values, cation exchange capacity, presence of microorganisms corroborating with plant species, and environmental factors. Additionally, other elements include fine granulometric fraction (<0.02 mm), the presence of oxygen and organic matter transfer. Organic carbon (Țopa *et al.*, 2021) oxides and hydroxides, and ion concentration also have an impact on the transfer and accumulation of heavy metals in soil and plant systems.

Plants have the capacity to absorb a variety of heavy metals through the roots or the aerial parts, especially the leaves; the bioaccumulation of trace elements in soil frequently limits plant development and ecosystem normal functioning (Lungoci *et al.*, 2021, 2022).

Additionally, the soil-plant-human transfer or soil-plant-animal-human transfer of metals occurs due to plants' absorption during multiple phenological stages and ultimately reach the human body, probably presenting a threat to health (Carabulea *et al.*, 2022, Oprea *et al.*, 2022).

Prunus domestica L. is the most common horticultural variety of plum in Romania by both cultivated area and production. To date, there have been no investigations on heavy metal concentration and its transfer from soil to the fruit orchard in Romania. Therefore, it is essential to acquire knowledge about heavy metal accumulation in fruits and soil, as well as the potential human health risk.

Hence, the primary goals of the research were to assess the potential health risk associated with heavy metal absorption, translocation and accumulation from orchard soils to plum leaf, which are absorbed by the fruit during the phenological stages of development.

The specific objectives were to: (1) estimate the concentration of different heavy metals in the soil and in two plum varieties (Stanley and Anna Späth); (2) assess heavy metal transfer from soil to leaf; and (3) to evaluate the daily intake and potential health risk related to plum fruits consumption.

MATERIALS AND METHODS

Research area

The research was conducted at Adamachi Farm - Iasi University of Life Sciences (*47°15`N-27°30`E*), located on the Moldavian Plateau, northwest Romania, with an average altitude of 80-95 m, characterized by a strongly anthropic landscape. The climate is classified as temperate continental; the annual average temperature is approximately 10 °C and the annual rainfall is about 518 mm. The environmental conditions in 2022 (Apr. - Sep.) are presented in *Figure 1* and *Figure 2*.

The study was conducted in a plum orchard (*Prunus domestica* L.), which was planted in autumn 2014.

The plots of the plum variety have an area of 5500 m^2 and are separated by buffer strips with a width of 5 m.

The research was done in a variant with three replications. The soil type was classified as aric-cambic chernozem (Țopa *et al.*, 2021) with a loamy-clay texture, 6.65 pH, 4.05% humus content and 19.03 me/100 g soil cationic exchange capacity.

Sample collection and measurements

Samples from each plum variety plot were collected at two stages of cultivation, between July and early August (pre-harvest). The plum orchard plots were subdivided into three (3) sampling areas with five (5) sampling points in each area. To generate a homogenous sample that is typical of the stated area, plum leaves and soil samples were randomly collected into plastic bags.

A total of 90 leaf samples (31 trees) from the associated plot area were collected and mixed to provide a composite representation of each particular sample. From each plum variant a quantity of 450g (3x150g) healthy and mature plum leaves were carefully stored and brought to the lab for analysis.

With the aim to eradicate the chemicals utilized to combat diseases or pests and to eliminate the fine sand particles and unintended plant components, leaf samples were manually cleaned with ultrapure water.

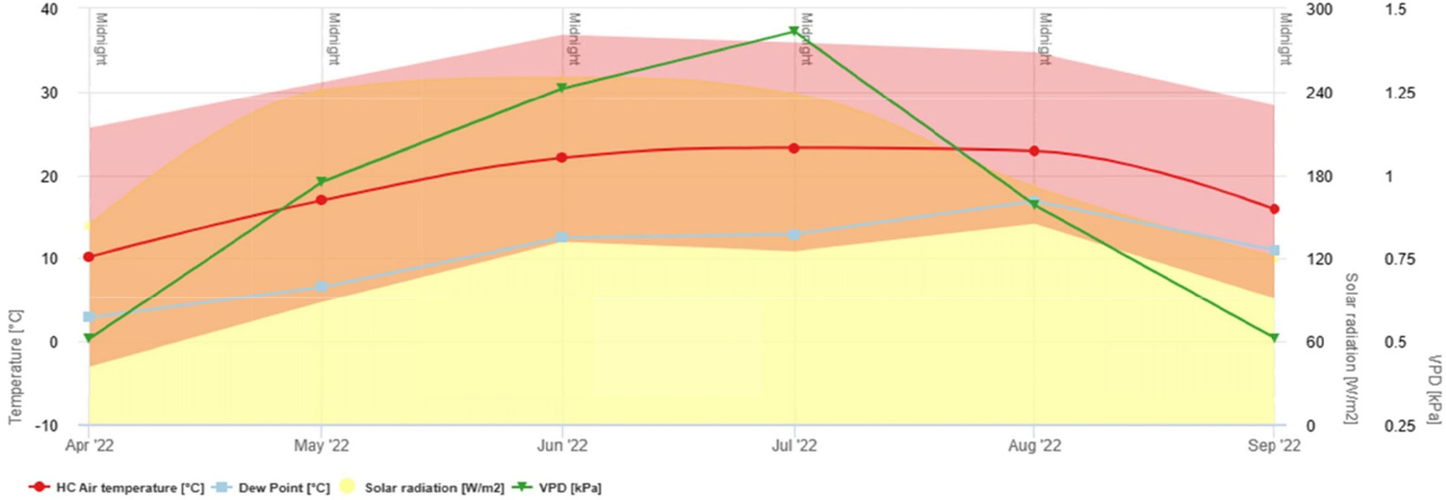

Figure 1 – The monthly temperature (°C) and solar irradiance (W/m²) of the growth period

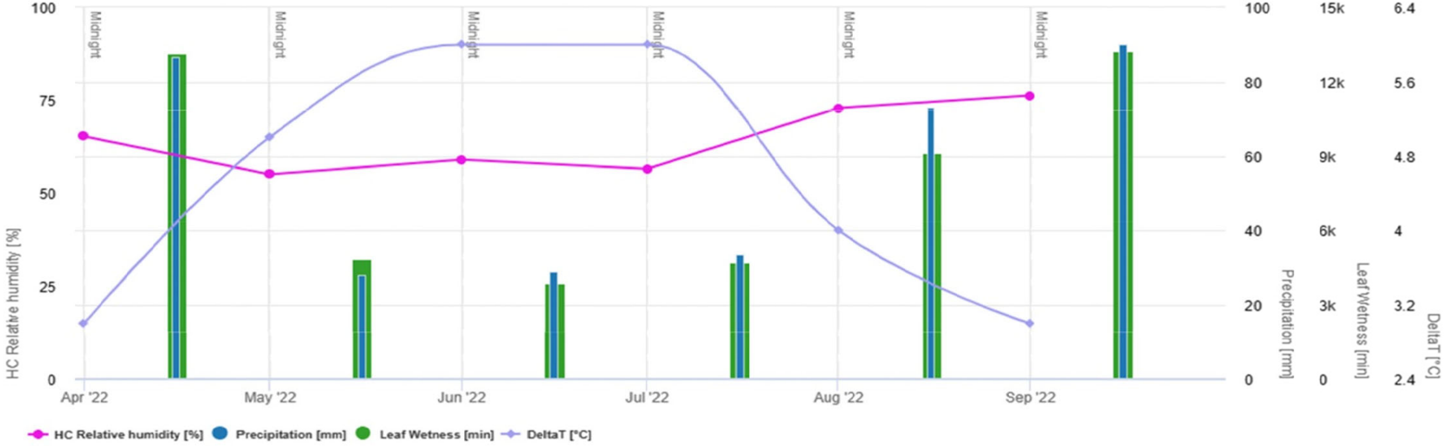

Figure 2 – The precipitation (mm) and relative humidity (%) of the growth period

Subsequently, as reported by Tariq *et al.* (2016) and Samsuri *et al.* (2019), the plum samples were allowed to air dry for 48 hours and then they were oven dried at 70°C for 72 h to achieve constant weight. To evaluate the quantity of heavy metals in samples, dry leaf samples were reduced to a finer consistency using a plant mill, followed by wet digestion method. Therefore, one (1) ± 0.0001 g from every plum variety sample was mineralized using 2 mL of HNO_3 65% at 95° C for 30 minutes using a heating plate. Next, each sample was treated with 0.5 mL of $HClO_4$ 60% and heated for 2 hours to 95° C ± 5°C temperature (Tariq F.S., 2021). After allowing the mixture to cool, it was filtered and transferred into 50 mL volumetric flasks with ultrapure water.

At the same time, 45 soil profile samples within the depths of 0-10 and 10-20 to 90-100 cm were collected using a manual auger and polyethylene spade. To remove stones and plant residues, the surface soil layers were carefully cleaned. From all depths, 250 g of soil was collected and then the average sample was constituted. Soil samples were dried naturally, ground and homogenized, sieved through a 2 mm sieve.

For the heavy metal analysis, 1 ± 0.0001 g of soil was weighed in Teflon digestion tubes of a microwave (Speedwave) and then 6 mL HNO_3 65% and 3 mL HCl 37% were added. The digestion tubes were sealed and the mineralization programme was performed (Stoleru *et al.*, 2022). The disaggregation programme included a ventilation stage in order to cool the samples for 30 minutes at the end of the process, and then the suction of the resulting gas. After that, the samples were filtered in 50 cm^3 volumetric flasks. Conventional procedures were used to assess several physical and chemical properties (soil pH, total organic carbon and organic matter content). Available K and P (extracted with neutral 1 N NH4OAc) and DTPA extractable Zn and Cu, were performed in accordance with the methodology provided by the National Institute of Research and Development in Soil Science, Agrochemistry and Environment, Bucharest (Topa *et al.*, 2021).

Measuring heavy metals in samples

Reagents and standards. In this study, only analytical grade reagents and chemicals were used. The working standard solution for the calibration curve was generated using nitric acid (HNO_3 Suprapur 65%) and mono-element containing stock standard solutions of Ni, Cu, Pb, Zn and Co (1000 mg L^{-1}).

In order to create the calibration curves the primary standards were diluted with 5% HNO_3 at five concentrations 0.05, 0.1, 0.2, 0.25, and 0.5 mg L^{-1}). For all dilutions high-purity deionized water was used.

Before beginning the soil and leaf plum samples mineralization, all glass flasks were thoroughly washed and stored in a suitable environment to prevent contamination. The cleaning of the laboratory equipment was performed through immersion in warm aqueous solution (10% HNO_3) for at least 6 hours, followed by ultrapure water rinse before the heavy metal analysis.

Atomic absorption spectrometry (AAS ContrAA 700) was used to determine the quantities of Pb, Co, Cu, Zn and Ni in soil and plum leaf samples. A high-resolution continuous source with a high-resolution echelle grating monochromator and a high-resolution xenon short lamp with UV arc in hot spot mode were the parameters used to calculate the concentration of heavy metal by AAS (*Table 1*) (Ungureanu *et al.*, 2022).

Data analysis

Bivariate correlation analysis

Bivariate correlation coefficients show the extent to which there is a dependence between two variables. In the case of the multiple linear regression model, the influence of the other independent variables is not taken into account.

At the population level it is noted by ρyxj and at the sample level by $r$yxj, with values in the range [-1,1]. If $\rho\in\{-1,1\}$ there is a perfect link between variables, $\rho\in(0,1)$ there is a direct link, , $\rho\in[-1,0)$ there is a reverse link, $\rho\in\{0\}$ there is no link between variables. The link is strong when $|\rho|\geq 0.7$, for a smaller value $|\rho|\in$ [0.4; 0.7) there is a moderate link, and for $|\rho|\in$ (0;0.4) the link between variables is low (Prematunga, 2012).

Factors of heavy metal transfer

The mobility of metals from contaminated soil to vegetables/fruits is expressed through this parameter (Samsuri *et al.*, 2019) and calculated applying the *Equation 1*.

$$MTF = \frac{C_V}{C_S} \quad (1)$$

where, C_v is the concentration of metals in plum leaves (mg/kg) and C_s the average concentration in the soil (mg/kg).

Metal Daily Intake (DIM)

The estimated daily oral intake of metals (mg kg^{-1} d^{-1}) from soil through leaves was estimated using *Equation 2* described by Zunaidi *et al.* (2023).

$$DIM = DCV + MCV + Cf \quad (2)$$

where, DCV is the average daily intake of vegetables/fruits (0.243 kg/person/day for children and 0.345 kg/person/day for adults), MCV is the value of metals in plum leaves (mg/kg) and Cf is the version factor (0.085).

Metals Estimated
Daily Exposure (EDEM)

The EDEM assesses an individual's intake of metals through fruit consumption (mg/kg/day) based on body weight (adults – 73 kg; children – 32.7 kg) and was calculated using *Equation 3* (Zunaidi *et al.*, 2021).

Table 1 – Operating parameters for AAS analysis

Parameters	Setting
Elements	Zn, Cu, Pb, Co, Ni
Measurement	Absorbance
Flame	C_2H_2 - Air
Replicates	3
Burner height (nm)	5-9
Slit width (nm)	0.2-1
Fuel Flow (L/h)	25-40

$$\text{EDEM} = \frac{DIM}{Average\ body\ weight} \quad (3)$$

Health risk index (HRI)

The HRI was implemented to investigate the risk in adults and children by the proportion of plum leaves contaminated with heavy metals to the reference standard oral dose or oral intake (RfDo) (USEPA, 2010; 2015). *Equation 4* was used to calculate the HRI (Tariq, 2021).

$$HRI = \frac{EDEM}{RfDo} \quad (4)$$

where, RfDo (mg/kg/day) is the reference dose values: 0.03, 0.037, 0.0035 and 0.02 mg/kg/day for Zn, Cu, Pb and Ni, respectively (Tariq, 2021).

Fruit consumption was used to determine the potential health risk (Zunaidi *et al.*, 2023).

Statistical analysis

Statistical data was processed using the IBM SPSS v20 software.

RESULTS AND DISCUSSION

An overview of heavy metal concentrations (Zn, Cu, Pb, Co and Ni) in the soil-plum orchard system are provided in *Tables 2*, *3* and *4* respectively. According to the results, Cu and Zn appeared to be the most common in the samples which were examined, with Zn showing increased values in the majority of samples.

In soil, heavy metal concentrations are impacted by moisture, soil reaction (pH), organic carbon and texture (Han *et al.*, 2022). *Table 2* presents the detailed characteristics of soil collected from the plum orchard area. In the orchard soil profile, pH and organic matter were 6.2-7.2 and 0.19-3.17%. Likewise, the concentrations of Zn, Cu, Pb, Co and Ni, collected in July, were highest at the surface (0-10 cm depth) with appropriate values at sub-surface 10-20 and 20-30 cm depth due to soil organo-mineral content and antifungal treatments leaching (*Table 2*). Soil physico-chemical properties present a stronger influence on heavy metal bioavailability. The higher content of organic matter (4.57%) at a 0-30 cm depth can significantly influence metal behaviour, by binding with toxic metals, increasing metal toxicity.

Similarly, pH presents a significant influence on the availability and mobility of heavy metals. In low pH soil, heavy metals tend to be more mobile compared to soil with higher pH (Sintorini *et al.*, 2021).

The results generally suggest that the levels of heavy metals are reduced and they depend on the soil depth, cultivation stages, soil and climatic conditions.

Industrial waste disposal could be partially responsible for the presence of metal in soil. In addition, Pb concentration might be released during the recycling of Pb-acid batteries, while higher Zn concentration could have resulted from various pharmaceutical waste.

An explanation of higher Ni concentration might be the use of agricultural fertilizers, vehicular exhaust and other industrial waste disposals (Alam *et al.*, 2021).

For all of the experimental versions, statistically significant results were recorded in August samples (pre-harvest) (*Table 3*).

Table 2 – Selective chemical soil properties in July

Depth (cm)	**0-10**	**10-20**	**20-30**	**30-40**	**40-50**	**50-60**	**60-70**	**70-80**	**80-90**	**90-100**
Texture	**Loamy-clay**									
pH	7.2 ± 0.60 ns	6.8 ± 0.60 ns	6.2 ± 0.48 ns	6.4 ± 0.87 ns	6.4 ± 0.36 ns	6.4 ± 0.54 ns	6.3 ± 0.43 ns	6.4 ± 0.31 ns	6.4 ± 0.74 ns	6.5 ± 0.79 ns
Organic C (%)	3.17 ± 0.27 a	2.87 ± 0.20 a	1.93 ± 0.10 b	1.4 ± 0.16 bc	0.96 ± 0.12 cd	0.56 ± 0.03 de	0.68 ± 0.04 de	0.62 ± 0.03 de	0.37 ± 0.02 de	0.19 ± 0.01 e
Humus content (%)	5.47 ± 0.74 a	4.94 ± 0.28 a	3.32 ± 0.28 b	2.47 ± 0.17 bcd	2.51 ± 0.12 bc	1.08 ± 0.13 de	1.18 ± 0.14 cde	0.96 ± 0.05 e	0.64 ± 0.04 e	0.32 ± 0.01 e
N_t (%)	0.26 ± 0.01 a	0.25 ± 0.01 a	0.17 ± 0.01 b	0.12 ± 0.01 c	0.13 ± 0.01 c	0.06 ± 0 d	0.07 ± 0 d	0.05 ± 0 de	0.03 ± 0 ef	0.02 ± 0 f
P (mg/kg)	94 ± 5.33 b	114.4 ± 6.74 a	82.8 ± 1.58 b	21.4 ± 0.13 c	16.2 ± 0.12 cd	4.04 ± 0.01 de	4.37 ± 0.02 de	1.94 ± 0.02 e	0.79 ± 0.02 e	3.04 ± 0.03 de
K (mg/kg)	445.2 ± 34.84 a	413 ± 55.93 a	396.6 ± 22.16 a	254.6 ± 21.46 b	174.8 ± 11.96 bc	116.8 ± 5.76 c	111.0 ± 12.90 c	106.6 ± 12.94 c	91.6 ± 5.20 c	87.2 ± 5.13 c
Zn (mg/kg)	73.34 ± 4.10 a	75.45 ± 6.36 a	74.78 ± 5.12 a	75.87 ± 3.73 a	60.23 ± 6.99 ab	50.45 ± 6.12 b	48.83 ± 2.77 b	43.03 ± 2.53 b	40.01 ± 0.76 b	39.05 ± 0.24 b
Cu (mg/kg)	97.17 ± 8.55 a	102.56 ± 8.03 a	104.79 ± 14.19 a	40.65 ± 2.27 b	33.82 ± 2.85 b	21.67 ± 1.48 b	22.42 ± 1.10 b	21.14 ± 2.45 b	19.20 ± 2.33 b	18.30 ± 1.04 b
Pb (mg/kg)	24 ± 1.18 a	22 ± 2.55 a	19 ± 2.30 ab	17.89 ± 1.01 ab	18.21 ± 1.07 ab	15.67 ± 0.30 bc	15.06 ± 0.09 bcd	13.11 ± 0.09 bcd	10.39 ± 0.02 cd	9.04 ± 0.04 d
Co (mg/kg)	11.86 ± 0.99 ab	12.04 ± 1.06 a	11.76 ± 0.92 ab	12.65 ± 1.72 a	12.78 ± 0.72 a	11.53 ± 0.97 abc	10.12 ± 0.69 abc	9.10 ± 0.45 abc	6.87 ± 0.80 c	7.03 ± 0.85 bc
Ni (mg/kg)	21.52 ± 1.20 abcd	23.41 ± 1.97 abc	26.71 ± 1.83 a	24.16 ± 1.19 ab	19.38 ± 2.25 bcde	16.87 ± 2.05 cdef	15.12 ± 0.86 defg	12.72 ± 0.75 efg	11.81 ± 0.23 fg	9.31 ± 0.06 g

Values associated with different letters are significantly different according to Tukey's test at $p < 0.05$; * - WHO/FAO, 2021

The trend of heavy metal concentrations according to the depth of the samples is as follows: Cu > Zn > Ni > Pb > Co.

The concentration of Zn (Zinc) in the soil varies in function of the depth of the samples. From 38.75 mg/kg in the sample from a 90-100 cm depth to 78.95 mg/kg in the sample analysed at a 10-20 cm depth. All values are under the maximum permissible limit (300 mg/kg) with regards to WHO/FAO, 2021.

Antifungal treatments (with Cu) were used in the recommended quantities in order to maintain the variety of fruit species to ensure their productivity and for the care of the plum orchard to lower the chance of ecosystem contamination with contaminants. Their use consequently caused a rise in Cu concentrations.

Concerning Cu concentration in the analysed samples, significant changes were observed from 18.94 mg/kg at a 90-100 cm depth to 130.65 mg/kg at a 20-30 cm depth. At the first 3 depth ranges (0-10 cm, 10-20 cm, 20-30 cm) the values of Cu concentrations exceeded the permissible maximum, but they didn't exceed the intervention thresholds (*Table 3*).

Cu adsorption in the soil increases with the increase in organic matter content (4.58 %) while the soil pH influences Cu behaviour, and its concentration decreases once pH grows. Lead content varied significantly too, from 9.45 mg/kg at a 90-100 cm depth to 21.69 mg/kg at a 10-20 cm depth, no values being found above the permissible limit (250 mg/kg). Furthermore, Co in soil samples ranged from 8.47 mg/kg to 13.26 mg/kg. The concentration was equally below the maximum allowed limit (40 mg/kg).

As regards Ni concentrations, detected values were again below the maximum allowed limit of WHO/FAO (50 mg/kg). It ranged from 12.57 mg/kg at a 90-100cm depth to 30.36 mg/kg at a 20-30 cm depth.

Table 4 reported the value of the investigated heavy metals in plum leaves samples. The trend of heavy metal concentrations in plum leaf was: Zn > Cu > Ni and Pb. It was observed that all heavy metal concentrations were higher in the Stanley variety compared to Anna Späth, due to its adsorption capabilities and metal accumulation. Zn and Cu were the most frequently detected metals in the plum leaf, similar to that of the soil samples.

Higher values of Cu with a concentration of 10 mg/kg in the Stanley variety were detected, while Co was not detected. Zn, Cu and Ni were present in both plum varieties, but with no significant differences between the concentrations.

The safe limits of the Food and Agriculture Organization (FAO) and World Health Organization (WHO) were compared with the results obtained and from a statistical standpoint, significant values were found just for nickel. The concentration of Zn, Cu and Ni in both varieties are below safe limits of 60 mg/kg for Zn, 40 mg/kg for Cu and 67 mg/kg for Ni.

Table 3 – The influence of depth sampling on soil heavy metals concentrations

Depth (cm)	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Co (mg/kg)	Ni (mg/kg)
0-10	76.60 ± 6.37 ab	111.55 ± 9.28 a	20.28 ± 1.71 d	11.02 ± 1.49 ab	26.27 ± 1.49 bc
10-20	78.95 ± 6.95 a	123.15 ± 10.84 a	21.69 ± 1.49 cd	12.14 ± 0.68 ab	28.83 ± 1.70 ab
20-30	75.25 ± 5.89 ab	130.65 ± 10.22 a	21.30 ± 1.05 bcd	12.66 ± 1.07 ab	30.36 ± 0.58 a
30-40	76.15 ± 10.31 ab	39.65 ± 5.37 b	19.27 ± 2.24 abc	13.26 ± 0.91 a	29.97 ± 0.18 ab
40-50	66.60 ± 3.72 abc	32.15 ± 1.80 b	19.78 ± 2.40 abc	13.11 ± 0.64 ab	23.12 ± 0.17 cd
50-60	52.10 ± 4.39 abc	25.25 ± 2.13 b	17.77 ± 1.01 ab	11.20 ± 1.30 ab	20.85 ± 0.04 de
60-70	50.40 ± 3.45 bc	25.36 ± 1.74 b	17.36 ± 1.02 a	10.93 ± 1.33 ab	17.72 ± 0.08 ef
70-80	43.90 ± 2.16 c	21.45 ± 1.06 b	12.37 ± 0.24 a	9.50 ± 0.54 ab	16.48 ± 0.15 f
80-90	40.20 ± 4.66 c	19.99 ± 2.32 b	11.64 ± 0.07 a	8.51 ± 0.50 ab	15.34 ± 0.26 fg
90-100	38.75 ± 4.70 c	18.94 ± 2.30 b	9.45 ± 0.07 a	8.47 ± 0.16 b	12.57 ± 0.14 g
Safe limit*	**300**	**100**	**250**	**40**	**50**

Values associated with different letters are significantly different according to Tukey's test at $p < 0.05$; * - WHO/FAO, 2021

Table 4 – The influence of plum variety on leaf heavy metals concentrations

Variety	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Co (mg/kg)
Stanley	19.03 ± 1.06	10.00 ± 0.78	1.68 ± 0.21	2.10 ± 0.14	nd
Anna Späth	20.16 ± 1.70	7.73 ± 1.05	1.15 ± 0.06	1.43 ± 0.07	nd
Signification	**ns**	**ns**	**ns**	*	-
Safe limit**	**60**	**40**	**0,3**	**67**	**20**

Values associated with different letters are significantly different according to Tukey's test at $p < 0.05$; ns - not significant; *- $p < 0.05$; nd - not detected; ** - WHO/FAO, 2021

It was found that Pb concentrations (1.68 mg/kg for Stanley and 1.15 mg/kg for Anna Späth), in both varieties had higher values than the values that the WHO/FAO organization had established (0.3 mg/kg). This may represent a significant threat to fruit quality and yield, due to the fact that one common effect of Pb is the loss of photosynthetic pigments corroborating with biomass production decrease (Yongsheng *et al.*, 2011).

The correlation of heavy metals content between soil and plum leaves was performed from 10 to 10 cm to 1 m soil depth for each variety studied (*Table 5*). Thus, a strong direct relationship is observed within the soil-plant system in Anna Späth at the following elements and depths, with corresponding correlation coefficients (CC): Cu-0–10 cm (CC = 0.871), Pb-70–80 cm (CC = 0.840); a moderate direct correlation for Cu-60–70 cm (CC =

0.529), a low direct correlation for Pb-30–40 cm (CC = 0.155) and a strong reverse correlation for Ni-80–90 cm (CC = -0.904). For the Stanley variety, a strong direct correlation was reported for Cu-0–10 cm (CC = 0.871), Ni-20–30 cm (CC = 0.803), Zn-40–50 cm (CC = 0.963), Zn-90–100 cm (CC = 0.786); a moderate direct correlation for Cu-60–70 cm (CC = 0.529), a strong reverse correlation for Zn-10–20 cm (CC = -0.876) and a moderate reverse correlation for Pb-30–40 cm (CC = -0.672). Other correlations in the soil–leaves systems are presented in *Table 5*.

To evaluate the orchard management practices on human health risk for heavy metal exposure through food ingestion and consumption, three international parameters were applied as follows: MTF, DIM and HRI.

A crucial measure that is usually used to estimate the rate of heavy metal transfer from soil to plants is the transfer factor of heavy metal (MTF).

Where an MTF value ≤ 1 indicates that plants only have the ability to absorb metals but have not accumulated, an MTF value >1 is considered a plant accumulator metal (Tariq *et al.*, 2016). *Table 6* shows the MTF values of heavy metals.

The calculated MTFs ranged between 0.06 and 0.33, with Zn having the highest value of MTF. The values of MTF for the Stanley variety were 0.31, 0.18, 0.098, 0.09 for Zn>Cu>Pb>Ni and for the Anna Späth variety was 0.33, 0.14, 0.067, 0.06 for Zn>Cu>Pb>Ni. According to the results of Zheng *et al.* (2020), the potential health risk due to Cd, Cr, Pb and As, varies among crop species, with health risk values higher in maize and rice than cucurbit or brassica samples.

Overall, the study findings revealed that none of the metals had MTF values more than 1. This demonstrated that the different plum varieties only absorbed but did not accumulate the heavy metals. Therefore, it cannot cause human exposure to metal and consequently a health risk effect (Tariq, 2021).

The physiology and metabolic activity of different varieties, as well as climatic conditions, may influence the transfer and mobility of heavy metals from agricultural soils to plants and could be the cause of the difference in MTF values (Garg *et al.*, 2014).

The food-chain transmission of these heavy metals to humans requires exposure through oral intake, skin contact and inhalation of dust (Garg *et al.*, 2014). Obtained values of DIM, EDEM, RfDo and HRI are presented in *Table 7*.

Both in adults and in children the EDEM values are lower than 1. The highest values were found for ZN in both varieties: 0.007 in Stanley and 0.008 mg/kg/day in Anna Späth and 0.012 mg/kg/day. Data published by by Zhang *et al.* (2020) revealed that the average human health risk in an industrial park in northwest China is above acceptable safe limits with dietary intake the most common route of exposure to heavy metals. Heavy metals transfer from soil to plant system is controlled by the distance from the industrial enterprises, pH and soil altitude etc.

Table 5 – The correlation on heavy metals in the soil-leaves systems

Variety	Depth (cm)	Heavy metals			
		Zn	Cu	Pb	Ni
Stanley	0-10	-0.736	0.871	-0.996	0.564
Anna Späth		-0.992	0.871	-0.981	0.997 (*)
Stanley	10-20	-0.876	-0.075	-0.824	-0.813
Anna Späth		-0.993	-0.075	-0.634	0.098
Stanley	20-30	-0.200	0.516	0.402	0.803
Anna Späth		-0.730	0.516	0.132	0.918
Stanley	30-40	0.769	0.991	0.386	0.727
Anna Späth		0.257	0.991	0.155	0.958
Stanley	40-50	0.963	0.760	0.998 (*)	0.596
Anna Späth		0.628	0.760	0.975	-0.397
Stanley	50-60	-0.219	-0.853	-0.672	0.268
Anna Späth		0.387	-0.853	-0.440	-0.700
Stanley	60-70	1.000 (**)	0.529	-0.901	0.485
Anna Späth		0.818	0.529	-0.986	-0.515
Stanley	70-80	-0.756	-0.206	0.657	0.976
Anna Späth		-0.995	-0.206	0.840	0.300
Stanley	80-90	-0.459	0.655	-0.999 (*)	-0.823
Anna Späth		-0.889	0.655	-0.974	-0.904
Stanley	90-100	0.786	-0.882	-0.961	-0.397
Anna Späth		0.282	-0.882	-1.000 (**)	-0.993

*The correlation is significant at the level of 0.05 (two-sided);
**The correlation is significant at the level of 0.01 (two-sided).

Table 6 – Values for heavy metal transfer factor (MTF)

Variety	Heavy metals			
	Zn	Cu	Pb	Ni
Stanley	0.31	0.18	0.098	0.09
Anna Späth	0.33	0.14	0.067	0.06

Table 7 – Metal reference dose, daily intake, daily exposure estimate and health risk index for both adults and children

Variety	Heavy metals	RfDo (mg/kg/day)	Adults			Children		
			DIM (mg/day)	EDEM (mg/kg/day)	HRI	DIM (mg/day)	EDEM (mg/kg/day)	HRI
Stanley	Zn	0.0035	0.558	0.007	0.025	0.393	0.012	0.040
	Cu	0.037	0.293	0.004	0.108	0.206	0.006	0.170
	Pb	0.02	0.049	0.001	0.192	0.034	0.001	0.303
	Ni	0.14	0.061	0.001	0.042	0.043	0.001	0.066
Anna Späth	Zn	0.0035	0.591	0.008	0.027	0.416	0.012	0.042
	Cu	0.037	0.226	0.003	0.083	0.159	0.004	0.132
	Pb	0.02	0.033	0.001	0.132	0.023	0.001	0.207
	Ni	0.14	0.041	0.001	0.028	0.029	0.001	0.045

The DIM values for children were higher than those for adults for all metals results. Due to their low body weight compared to adults, children have higher DIM values than adults. According to Tariq *et al.* (2021), the amount of heavy metals consumed per day and the suggested oral reference dosages have a significant impact on the value of the health risk index. Recent studies by Ugbede *et al.* (2021) on the transfer of heavy metals from soil to rice plants revealed higher values of daily limits intake (DI) and hazard index (HI) of the metals in the children's group in both soil and rice samples. The values were below the permissible safe level of 1.0.

The values obtained for the HRI are lower than the value 1 from which a potential health risk can be considered

The calculated values of the health risk index for adults in the variety Stanley were Pb (0.192), Cu (0.108), Ni (0.042), Zn (0.025) and in Anna Späth were Pb (0.132), Cu (0.083), Ni (0.028), Zn (0.027), while for children they were Pb (0.303), Cu (0.170), Ni (0.066), Zn (0.040) for Stanley and Anna Späth Pb (0.207), Cu (0.132), Ni (0.045, Zn (0.042).

The HRI value obtained did not exceed the safe limit (1) with an overall sequence in both adults and children in the order Pb > Cu > Ni > Zn. According to Wang *et al.* (2021) for all heavy metals analysed, the higher HRI value obtained in children than in adults suggested the possibility that children could be more exposed to these metals. This finding demonstrates the low translocation possibility into fruit, indicating that there is no possible human health risk due to the low HRI and MTF values. These results are in accordance with the results of Ugbede *et al.* (2021) who obtained an acceptable non-carcinogenic limit of less than 1 of the rice cultivated and therefore is safe for human consumption.

CONCLUSIONS

Taking into account the concern for food safety and human health, soil contamination with heavy metals and the transfer to food are both critical global issues. Throughout this study, the concentrations of Zn, Cu, Pb, Co and Ni in soil and plum leaf were evaluated in a field study conducted at Adamachi Farm, Romania. The concentrations of heavy metals in soil were reported to be moderate and below the international reference criteria at each agricultural stage and depth. The higher concentrations were found at 0-30 cm depth in the soil due to its organic carbon content but did not exceed the maximum allowed values in 4 out of 5 cases. However, when referring to Cu concentrations, they surpassed the upper limit (according to WHO/FAO regulations as of 2021). These deviations were recorded at the following depth ranges: between 0 - 10 cm, 10 - 20 cm and 20 - 30 cm, but they did not go beyond intervention thresholds. The results of HRI values indicate that contamination with Zn, Cu, Pb and Ni in leaves is low and the MTF index is also low respectively, indicating that a plum fruit translocation possibility decreased. These findings highlight the effective and cautious management of heavy metal pollution sources with recorded values that prove that heavy metal concentrations in the soils permit optimal fruit species nutrition.

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