

Bioaccumulation and Biomagnification from Soil to Nettle-Snail and Extension Heavy Metal Pollution of Mining Activity “Ferronikel” in Drenas

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ABSTRACT

In this research project, we measured the impact of the activity of “Ferronikel” factory on the concentrations of heavy metals (Pb, Zn, Ni) in soil, plant (*Urtica dioica* L.) and shell of snail (*Helix pomatia* L.) in the locality of Drenas. Large quantities of these metals come from natural and anthropogenic sources including mining activity, agriculture, pesticide use, industrialization, and inadequate disposal of mineral waste and artificial fertilizers. These inorganic pollutants are deposited in the soil, water, and atmosphere in various forms of complexes and are thus transmitted from plants, animals to humans. Climatic factors such as winds, rains, and temperatures are believed to be major contributors to the spread over time and space of heavy metals in the environment. Soil samples, nettle plant and snail, were collected from the selected pollution source of factory “Ferronikel” at distances of 1 km, 2 km, and 5 km in the radius circles divided into four geographical areas. The samples were digested in microwave at 200 °C for 45 min and have been read in two types of absorbers Thermo and Contra AAA. Higher concentrations of Pb, Zn, and Ni were recorded in the southern parts of the country compared to that control with significant differences ($p < 0.01$). Bioaccumulation and biomagnification levels of these heavy metals have also been recorded in the roots, stalks, and leaves of the stinging nettle plant as well as in snail shells. The results show that the stinging nettle plant has translocated larger amounts of these heavy metals especially Pb along with the vegetative organs wherefrom these they are carried in the snail shell, which is fed on the stinging nettle plant. Also, results shown that the nettle plant *Urtica dioica* can be used in phytoremediation process whereas snail *Helix pomatia* can be used like bioindicator of heavy metal pollution.

Keywords: soil, bioaccumulation, mine, metals, plants, stinging nettle.

INTRODUCTION

In terrestrial ecosystems, the common and rare heavy metal cations Cd, Cu, Zn, and Ni are found in food chains. A compartment-based strategy metal transfer across trophic pathways is viewed as a network of interconnected compartments. The regulation of the movement of metals from the soil to arthropods is greatly influenced by plants (Tibbett et al, 2021). As the

world community focuses increasingly on heavy metal pollution of soil, the enrichment and pollution of heavy metals in cultivated lands is of critical relevance to many sectors of society and scholars from various disciplines (Li et al., 2018). Therefore, heavy metals constitute a hazard to human survival and health in addition to harming the growth and development of plants and animals (Xu et al., 2017). Heavy metals are gaining a lot of attention as environmental contaminants

due to their capacity to infiltrate on the food chain through polluted soil, bioaccumulation in plants and animals, as well as their transfer to humans, which is currently being researched in ecotoxicological disciplines. Human activities such as mining, traffic, intensive agriculture, and others can cause heavy metal air pollution by releasing particles in the air and soil. Especially in cases when the weather is dry and windy (Briffa et al. 2020).

The main factors determining the concentration of heavy metals in the soil are the chemical properties of the soil and the distance from the source of contamination. The amount of heavy metals accumulated and absorbed by plants is dependent on the kind and concentration of heavy metals, as well as the plant and animal species characteristics that make the food chain (Jolly et al., 2013).

The exploitation of mineral resources has brought about enormous monetary wealth, but it has also brought about a number of ecological and environmental issues, such as air, groundwater, and soil contamination (Zhang et al., 2021). As the basis of agriculture, soil and water play an irreplaceable role, heavy metal contamination of soil and water has become a severe environmental problem in mining areas. Their environmental quality has a direct bearing on the quality of agricultural products, which in turn affects the health of those who consume them. Soil and water-related environmental issues are therefore essential (Sun et al., 2019). Heavy metals are one of the most damaging groups of pollutants discharged into the soil due to their capacity to remain. Heavy metals can naturally accumulated by organisms that live from feed on the soil, its components and products, such as land snails and plants including *Urtica dioica* and they pass those metals on to other organisms in the food chain (Baroudi, 2020).

In today's climate, heavy metal toxicity and persistence are important environmental problems. Due to both natural and anthropogenic activity, including illegal mining and extensive mineral exploiting in mining zones, heavy metals accumulate in our environment. As a result, a lot of waste is produced, which causes the discharge of dangerous elements into the environment, especially heavy metals (Abdu, 2013).

The prevalence and extent of potentially toxic elements (PTEs) pollution differ considerably by the geochemical and mineralogical aspects of both ore and host rocks (Nieder & Benbi, 2023). Additionally, research showed that Pb and Zn had the highest concentration with most values exceeding

the maximum allowable limits established by various countries, and they are responsible for nearly all of the total potential ecological harm in the analyzed locations (98.64%) (Sharhabil et al., 2021).

The environmental influence on the food chain, on the other hand, has received very little attention. The most prevalent plants, leaves, and herbs in the researched area include common nettles, which are widely utilized as a herb and food additive in the local population's diet and are ranked among the most popular foods worldwide due to high vitamin and mineral content (Filimon, et al. 2021). Heavy metals, particularly Pb, Zn, and Ni, bioaccumulate in the shell and tissues of snails, and this bioaccumulation is more common in industrial areas and along urban highways. These are sites that could be polluted as a result of human activities (Salih et al., 2021). The issue of soil heavy metal pollution and the risks it poses to human health has gained attention both domestically and internationally (Zhang et al., 2018). Our daily lives now contain more pollution, which has detrimental effects on our health. While it is best to avoid all forms of pollution, heavy metals have the most detrimental and permanent impacts.

Because of bio-magnification, which causes major health problems and a high mortality rate in both humans and animals, there is a higher metal concentration than maximum allowed dosage (Ali et al., 2019). So due to several factors, including industrialization and urbanization, the contamination of soil and water with heavy metals like Cd, Pb, Ni, Cu, and Fe is growing every day. Lead (Pb), Cadmium (Cd), and Nickel (Ni) are a few examples of potential heavy metals that can collect in various areas of a plant and living things are not essential elements, but usually accumulate in vegetative parts and biomagnificate from root to stalk and leaf with >1 factor translocation value (Bislimi et al., 2021). Additionally, because nutrient-dense plants are grown in these soils and their products are ingested, the potential bioavailability of metals near these sources has demonstrated extremely high levels (Zogaj, et al., 2014).

MATERIALS AND METHODS

The municipality of Drenas lies in the central part of Kosovo, in the valley of Drenica, 32 km from the capital Pristina. The NewCo "Ferronikeli" mine operates in this municipality, which according to environmental studies is considered

one of the main polluters in the country with heavy metals, mainly nickel (Ni).

Soil samples, nettle *Urtica doica* and snail *Helix pomatia* were used as material for researching the impact of heavy metal pollution in the locality of the Municipality of Drenas. One hundred and twenty (120) samples of soil, nettle and snails were collected according to radius circles 1 km, 2 km, 5 km from the point of contamination Drenas. Concentric circles are divided into 4 geographical areas northwest, northeast, southeast, southwest. While 30 soil samples, nettles and snails were collected in the unpolluted locality Brezne-Opoja. The results of this research were calculated with the programs Minitab and the statistics methods such as Tuckey Kramer and ANOVA.

Applied methods

Soil samples were collected by hand probe at a depth of 15 cm in the virgin lands around the Kosova A power plant at distances of 1 km, 2 km, 5 km. Samples were collected according to the purposive sampling method (Minkina, et. al. 2018). Samples were collected in these

coordinates: Longitude N:42.6821537, Latitude 21.0884580; S:42.673995, 21.094527 for 1km radius circle. Also, 42.6910814, 21.0972603 and 42.6590480, 21.0857567 for 2 km, whereas for 5 km 42.720892, 21.085643 in 4 areas.

According to this method from three selected points in a geographical area of radius circles are made by 10 drilling of the soil which is then mixed (DIN ISO11466, 1995). These soil samples were brought to the laboratory, ground in a soil mill and placed in glass cups and dried in a thermostat at 105°C for 48h in order to remove moisture. They were then weighed 0.3 g and treated with 69% HNO₃ and HCl (Merck Millipore) reagents concentrated in a 2: 6 ratio in teflon columns and digested in the analyticyena TOP wave microwave at 200°C for 45 min. The contents were filtered and placed in normal 50 ml glasses in distilled H₂O. Merck Millipore ICP multi-element standard solution 111355 for metals Pb, Zn, Ni are applied for read in flame types of absorber Analyticjena Contra AAA. In addition, nettle and snail samples were collected according to the selection where the older individuals were used. The nettle samples were separated from the vegetative organs

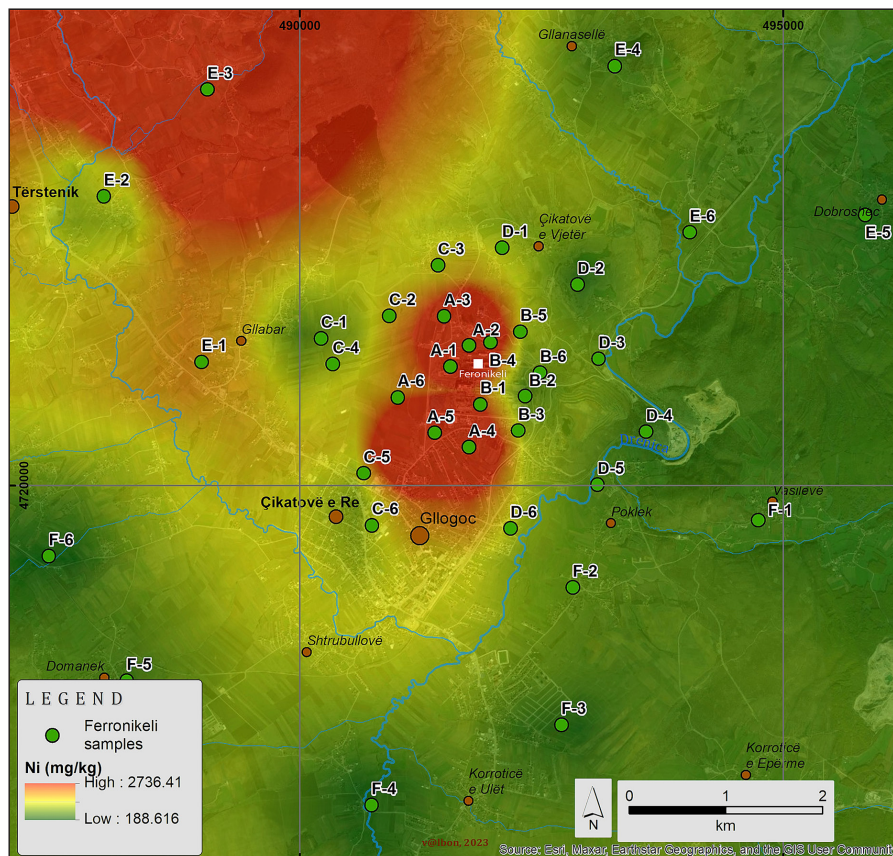


Fig. 1. Nickel distribution

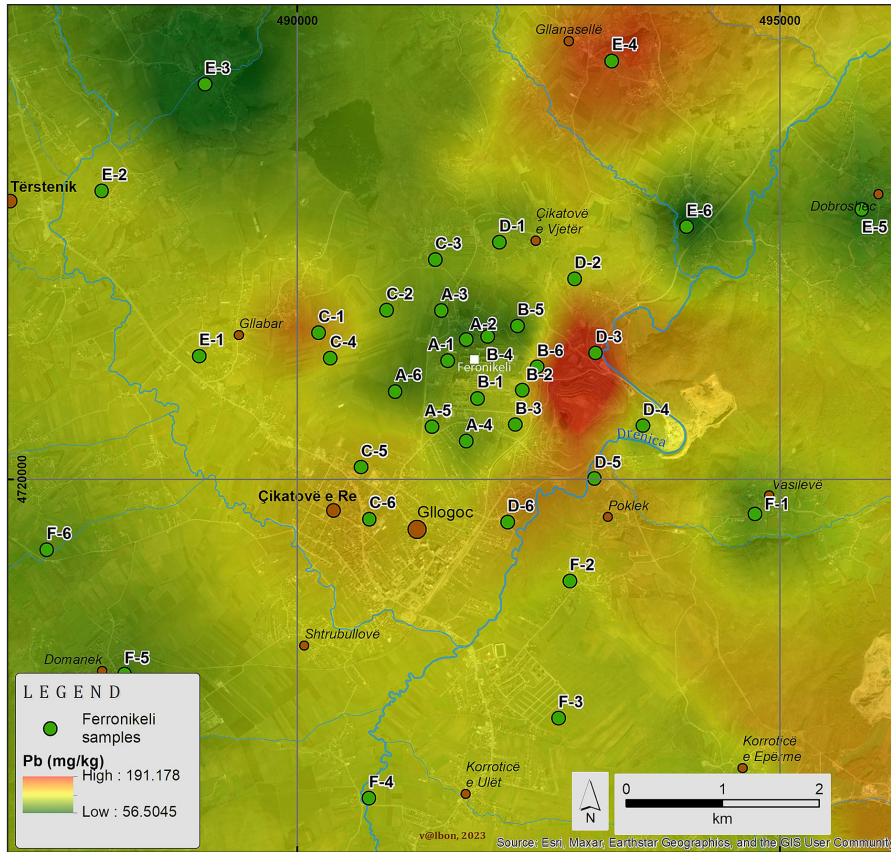


Fig. 2. Lead distribution

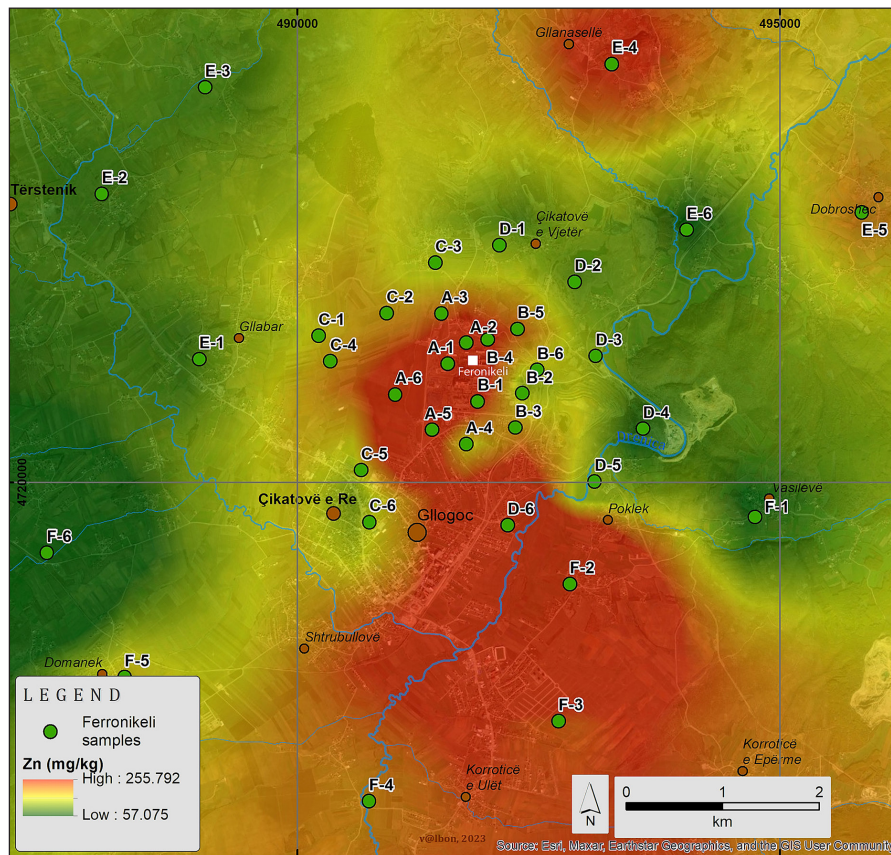


Fig. 3. Zinc distribution

(roots, stalk, leaves) and the snail shells were washed in distilled H₂O, dried in a thermostat at 105°C for 24–48h, then ground with a Philips kitchen mixer and 0.5 g of the sample was treated with Merck Millipore reagents; nitric acid 69% ultra pure (HNO₃) in report 1: 3 Lachner H₂O₂ 30% and digested in microwave at 200°C for 45 min.

The contents were filtered and placed in normal glasses of 50 ml, normalized with distilled H₂O and the metals Pb, Zn, Ni were read in 2 flame absorbers types of Thermo and Contra AAA. The bioaccumulation coefficient is calculated using the standard formula:

$$BCF = C_{plant\ parts} / C_{soil} \quad (1)$$

where $C_{plant\ parts}$ – metal concentration in plant or animal tissue, mg/kg dry weight; C_{soil} – concentration in soil mg/kg in dry weight.

While the enrichment factor (EF) is computed using the formula $EF = C_{samples} / C_{soil}$, the translocation factor (TF) is derived using the formula $TF = C_{plant\ shoot} / C_{plant\ root}$ (Galal & Shehata, 2015).

RESULTS

The results are shown in the summary Tables, bioaccumulation, and translocation Tables and dendogram. Average data of heavy metals (Pb, mg/kg, Ni, µg/kg, Zn, mg/kg), reported as dry weight values, in all sample types: soil, nettle parts (rhizomes, stems and leaves), overall nettle plant, and snail shells from Drenas and Opoja are reported in Table 2, High values of nickel were recorded in soil samples and vegetative organs;

therefore we reported it in mg/kg for nettle and shell samples in all cases. Concentration, bioaccumulation factor (BCF), transfer factor (TF) and enrichment factor (EF) of heavy metals from soil to rhizomes, from rhizomes to stems and leaves, and from leaves to shells in Drenas (1 km, 2 km and 5 km) are reported in Table 2. The results from Table 1 show that in the analyzed soil samples, the concentrations of the three metals Pb, Zn, Ni increase as they move away from the point of contamination. Also, the concentration of these metals has significant differences with the control samples.

According to Table 2 we registered that the value of Pb is below the standard limit, while the level of Ni in the soil exceeds 5 times the standard values. While Zn according to the UK standard is in the limit, while according to the standard values of Germany it exceeds the values at 290 (mg/kg). From (Table 3) of the locality control we see that the concentrations of metals have significant differences ($p < 0.001$) in all types of analyzed samples with contaminated site Obiliq in our cases. When the translocation coefficient was calculated, we registered that, for example, in the parts of the nettle plant, the root, stalk, leaf and shell, Pb and Zn in some cases reach the coefficient < 1 which means that it is biomagnified along the food chain. These results are the same as those of other authors (Salih et al., 2021), while in some other cases it is at the limit of the coefficient 1. We calculated the concentration for metal Ni by conversation from mg/kg to µg/kg were recorded low values in nettle and shell samples in our cases.

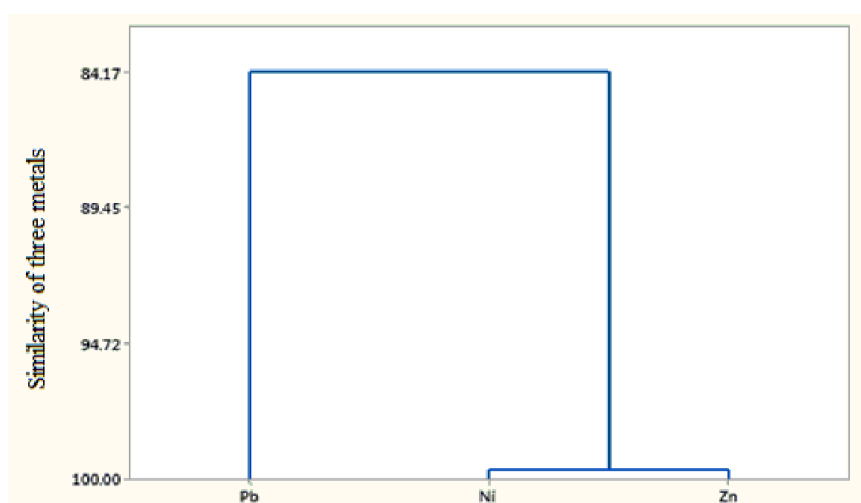


Fig. 4. Dendogram of similarity for three metals in three distances in contaminated site Drenas

Table 1. Tabular presentation of sampling coordinates in polluted area Drenas

Sample 1 km	Coordinates longitude/latitude	Sample 2 km	Coordinates longitude/latitude	Samples 5 km	Coordinates longitude/latitude
A-1	42.643478, 20.896993	C-1	42.646083, 20.880669	E-1	42.643873, 20.865590
A-2	42.645451, 20.899295	C-2	42.648198, 20.889230	E-2	42.659292, 20.853252
A-3	42.648158, 20.896167	C-3	42.652916, 20.895410	E-3	42.669232, 20.866255
A-4	42.635972, 20.899322	C-4	42.643715, 20.882123	E-4	42.671472, 20.917689
A-5	42.637302, 20.894995	C-5	42.633533, 20.886061	E-5	42.657635, 20.949297
A-6	42.640605, 20.890363	C-6	42.628695, 20.887139	E-6	42.655978, 20.927174
B-1	42.639974, 20.900749	D-1	42.654550, 20.903490	F-1	42.629208, 20.935843
B-2	42.640732, 20.906413	D-2	42.651141, 20.913017	F-2	42.622924, 20.912432
B-3	42.637512, 20.905512	D-3	42.644204, 20.915667	F-3	42.610134, 20.911059
B-4	42.645719, 20.902036	D-4	42.637417, 20.921675	F-4	42.602648, 20.887112
B-5	42.646730, 20.905813	D-5	42.632492, 20.915554	F-5	42.614192, 20.856213
B-6	42.642910, 20.908302	D-6	42.628418, 20.904600	F-6	42.625782, 20.846386

Table 2. Summary of average concentration of metals in all types of samples analyzed in polluted locality Drenas

Drenas 1 km										
Nettle/snail										
Sample/metal	Soil	RSD%	Root	RSD%	Stalk	RSD%	Leaf	RSD%	Shell	RSD%
Pb	126.45	1.5	6.38	1.2	6.9	1.1	8.34	1.3	9.87	1.6
Ni	1053.4	3.2	0.77	0.8	0.39	0.3	0.61	0.4	0.42	0.9
Zn	188.3	1.8	12.48	1.9	26.83	2.3	12.11	1.9	4.83	2.1
Drenas 2 km										
Nettle/snail										
Sample/metal	Soil	RSD%	Root	RSD%	Stalk	RSD%	Leaf	RSD%	Shell	RSD%
Pb	105.89	1.3	9.47	1.6	6.56	1.6	9.86	1.8	3.16	2.2
Ni	217.9	2.1	0.19	0.3	0.07	0.2	0.27	0.2	0.11	1.3
Zn	132.3	1.6	15.36	2.1	25.43	2.1	16.1	2.1	4.22	1.4
Drenas 5 km										
Nettle/snail										
Sample/metal	Soil	RSD%	Root	RSD%	Stalk	RSD%	Leaf	RSD%	Shell	RSD%
Pb	89.46	0.9	9.39	1.8	8.48	1.4	8.46	1.5	5.75	2.5
Ni	522	2.7	0.42	0.5	0.11	0.8	0.29	0.3	0.29	0.8
Zn	145.8	1.7	17.96	2.2	28.71	2.4	16.2	2.4	4.1	3.2
Significant of 1:2:5 km	P<0.05		P<0.05		P<0.05		P<0.05		P<0.05	

However, it is interesting that Ni has not shown translocation affinity in this food chain.

DISCUSSION

Measurements of metal concentration in soil samples in our research are as follows (in

mg/kg) Ni >1053.4, Zn >188.3, Pb>126.45 in 1km, while for 2km Ni>522, Zn>132.3, Pb>105.89, while in 5 km Ni>522, Zn>145.8, Pb>89.46, these results in this locality are same with other authors such as Pb > Fe > Ni > Cd > Mn > Al > Cu > Zn and > Cr, (Demaku et al., 2022). The high levels of nickel concentration in the three areas, especially at 5 km from

the southern area, are explained by the fact that the sources of nickel in polluted area, are from drilling soil, throwing dust from chimneys into the air and wastewater. In this case the factors such as spread, winds and anthropogenic activities, have an impact in distribution of these metals. This is in line with the findings that nickel is a transition element that is widely dispersed in the environment, including the air, water, and soil. It could come from both anthropogenic activity and natural sources (Genchi et al., 2020). The uptake and accumulation of

heavy metals by plant roots occurs through an interrelated network of physiological and molecular mechanisms, including the binding of metals to extracellular exudates and cell wall components (Angulo-Bejarano et al., 2021)

So that administering a complicated investigation involving heavy metal pollution analyses in soil water, air, plant and animal life in agricultural production areas and virgin soils would reveal their dynamic evolution over time, resulting in more accurate results in the future (Zejnnullahu et al., 2017).

Table 3. Summary of metals in uncontaminated site Opoja

Summary table of samples of control locality - Opoja										
Sample/Metal	Soil	RSD%	Root	RSD%	Stalk	RSD%	Leave	RSD%	Shell	RSD%
Pb	9.23	0.9	0.16	0.12	0.078	0.035	0.012	0.09	0.09	0.02
Ni	25.1	1.3	0.021	0.019	0.034	0.013	0.054	0.026	0.011	0.05
Zn	46.2	0.62	0.042	0.021	0.026	0.018	0.045	0.017	0.025	0.09
Significant with pollution site	p<0.001		p<0.001		p<0.001		p<0.001		p<0.001	

Table 4. Permissible total metals values (mg/kg) in the soil in the UK and Germany

Metals	UK (1989)			Germany (1992)	
	pH 6–7	pH 5.5–6	pH 5–5.5	pH > 6	pH 5–6
Pb	300	300	300	100	100
Ni	75	60	50	50	50
Zn	300	250	200	200	150

Table 5. Concentration of heavy metals from soil to root, root to stalk, stalk to leaf of *Urtica dioica* and leaf to shell of *Helix pomatia* in the contaminated site (Drenas) 1 km

Metal	Sample	Concentration, ppm	BCF	EF	TF
Pb, mg/kg	Soil	126.45		1.54	
	Root	6.38	0.050	425.33	
	Stalk	6.90	0.054	164.28	1.08
	Leaf	8.34	0.065	130.31	1.30
	Shell	9.87	0.078	822.5	1.18
Zn, mg/kg	Soil	188.3		4.07	
	Root	12.48	0.066	832	
	Stalk	26.83	0.142	638.80	2.1
	Leaf	12.11	0.064	0.084	0.97
	Shell	42.83	0.227	669.21	3.53
Ni, µg/kg	Soil	1053.4		7.34	
	Root	0.77	0.0731	70	
	Stalk	0.39	0.0372	43.33	0.50
	Leaf	0.61	0.0579	43.57	0.79
	Shell	0.42	0.0399	32.30	0.69

Table 6. Concentration of heavy metals from soil to root, root to stalk, stalk to leaf of *Urtica dioica* and leaf to shell of *Helix pomatia* in the contaminated site (Drenas) 2 km

Metal	Sample	Concentration, ppm	BCF	EF	TF
Pb, mg/kg	Soil	105.89		1.96	
	Root	9.47	0.089	631.33	
	Stalk	6.56	0.061	156.19	0.69
	Leaf	9.86	0.093	154.06	1.04
	Shell	31.16	0.294	2596.67	3.16
Zn, mg/kg	Soil	132.3		4.56	
	Root	15.36	0.192	264.82	
	Stalk	25.43	0.121	591.39	1.65
	Leaf	16.1	0.356	206.41	1.04
	Shell	47.22	1.647	143.09	2.93
Ni, µg/kg	Soil	217.9		1.54	
	Root	0.19	0.0872	17.27	
	Stalk	0.069	0.0317	7.66	0.36
	Leaf	0.27	0.01239	19.28	1.42
	Shell	0.107	0.0491	8.23	0.40

Table 7. Concentration of heavy metals from soil to root, root to stalk, stalk to leaf of *Urtica dioica* and leaf to shell of *Helix pomatia* in the contaminated site (Drenas) 5 km

Metal	Sample	Concentration, ppm	BCF	EF	TF
Pb, mg/kg	Soil	89.46		1.65	
	Root	9.39	0.10	626	
	Stalk	8.48	0.0947	201.90	0.90
	Leaf	8.46	0.0945	132.18	0.90
	Shell	50.75	0.56	4229.16	6.1
Zn, mg/kg	Soil	145.8		5.02	
	Root	17.96	0.123	309.65	
	Stalk	28.71	0.111	667.67	1.60
	Leaf	16.2	0.329	207.69	0.90
	Shell	48.1	3.580	145.75	2.97
Ni, µg/kg	Soil	522		3.70	
	Root	0.42	0.080	38.18	
	Stalk	0.107	0.020	11.88	0.25
	Leaf	0.29	0.056	20.71	0.69
	Shell	0.29	0.056	22.30	1

CONCLUSIONS

From our results of this research, we can conclude that, soil pollution with heavy metals comes as a result of their release from the chimneys of the mine “Ferronikel”, traffic and ash dump. We also conclude that climatic factors such as wind, wind rosettes and fly ash in a southerly direction contribute to the spread of these metals. From the values obtained from this research, a trend of

the bioaccumulating and translocating ability of the nettle plant is observed in our cases. We can also emphasize that the nettle plant *Urtica dioica* can serve as a base plant in the phytoremediation and soil amendment from heavy metal pollution process exclusively for Pb. *Helix pomatia* snails can used as bioindicators for measuring pollution with heavy metals and their impact on the transfer processes of these metals in the food chain and their effects on the biochemical and physiological

processes of living organisms. Since these two types of organisms are used for human consumption, there is a strong possibility that this sensitive link in the trophic chain will be contaminated and have major consequences for public health.

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