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BIOACCUMULATION OF COPPER, LEAD AND ZINC BY *TARAXACUM OFFICINALE AGG.* GROWING ON URBAN SOILS OF DIFFERENT LAND-USE TYPES

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Abstract

Common dandelion *Taraxacum officinale agg. (T. officinale* F.H. Wigg) is a plant species commonly found on urban areas. It is characterised by low habitat requirements and proven bioindication properties. The aim of this study was to assess the possibility of using *T. officinale agg.* for monitoring of the urban soils in the City of Kielce with regard to selected heavy metal concentrations, i.e. Pb, Cu and Zn. Twenty-one soil and dandelion samples (roots and leaves) were collected from the area of Kielce. The study areas were designated with regard to land-use types, i.e. industrial areas, urban parks and forests, urban green areas, and urban allotment gardens. The total heavy metal concentrations were determined in the soil and plant material by the ICP-AES (inductively coupled plasma atomic emission spectroscopy) method, after mineralisation of the samples in a mixture of $HCl\text{-}HNO_3$ (3:1). Moreover, the soil samples were analysed in terms of pH values. The concentrations of heavy metals in the analysed soils were oscillating at: 16.5-290 mg/kg d.m. for Pb; 7.11-41mg/kg d.m. for Cu; 55.7-338 mg/kg d.m. for Zn In the case of dandelion leaves, the concentration range was recorded at: 1.07-3.11 mg/kg d.m. for Pb; 3.11-14.1 mg/kg d.m. for Cu; 19.7-121 mg/kg d.m. for Zn. Regarding the dandelion roots, the concentration range was as follows: 0.54-2.09 mg/kg d.m. for Pb; 2.89-8.11 mg/kg d.m. for Cu; 15.8-67.1 mg/kg d.m. for Zn. The study indicated that the concentrations of analysed heavy metals adopted the sequence of soil>leaves>root. The above relationship may indicate a significant impact of heavy metals contained in the air on their concentrations in the upper parts of plants. The pH of analysed soils were oscillating at 3.99-7.92 and was not correlated with the concentrations of heavy metals in the soils. Heavy metal concentrations were not significantly affected by the land-use types, which may indicate that urban pollution emission zones are not limited only to industrial and transportation areas.

Key words: heavy metals, urban soils, Kielce, *Taraxacum officinale* agg.

INTRODUCTION

Urban environment is particularly susceptible to all kinds of contamination. Dust and gases enter the atmosphere due to production processes and transportation. As a result of deposition, harmful substances are introduced into the soils and thus change their physicochemical parameters. High concentrations of heavy metals are a serious threat to the urban soils. Heavy metals belong to a group of inorganic substances which are very resistant to all kinds of neutralisation. Heavy metals once introduced into the soils are accumulated in an unchanged form.

Cities are specific ecosystems with limited self-regulatory mechanisms, which perform important economic, social and cultural functions. That is why, the issues related to contamination of urban soils with heavy metals are widely analysed by many scientists (Imperato et al. 2003; Świercz, Smorzewska 2015; Ferreira et al. 2016; Radziemska et al. 2016; Jaffar et al. 2017). Bioindicators are commonly used in studies on the heavy metal concentrations in the urban soils. They have the ability to accumulate high concentrations of heavy metals in their tissues without significantly affecting their physiology or life processes (Petrova et al. 2013; Gjorgieva et al. 2011). Bioindicators, due to the ease of adapting to various environmental conditions and relatively low costs of biological tests, are recommended to assess the level of contamination in the soils or atmosphere.

Selecting plants for biomonitoring is a key element in determining the appropriateness of conducted studies. Accumulation of heavy metals in plant tissues depends on their morphological characteristics and soil properties (Preeti, Tripathi, 2011). It is recommended to use higher plants for biomonitoring, as they have the ability to determine the actual impact of anthropogenic factors on the state of environment, and especially on the concentrations of heavy metals. The studies on the soils and aboveground and underground parts of plants give the possibility of fair assessment of the natural environment quality. The Asteraceae family is a recognised group of plants used in biomonitoring (Gawroński et al. 2011). One of the well-known bioindicators is *T. officinale agg.* which has a multiplied ability to accumulate heavy metals (Czarnowska, Milewska 2000).

The aim of the study was to assess the concentrations of selected heavy metals in the urban soils of Kielce and in the leaves and roots of *T. officinale agg*. in relation to the land-use types. The idea of the study was based on the following study questions:

(1) Does the land-use type have any impact on the contamination of urban soils with heavy metals? (2) Is there a relationship, on the example of urban soils in Kielce, between heavy metal concentrations in the soils and heavy metal concentrations in the leaves and roots of *T. officinale agg.*? (3) Which part of *T. officinale agg.* (root, leaves) accumulates heavy metals most effectively?

METHODOLOGY

Study area

The study was conducted in Kielce – the provincial capital city with an area of nearly 110 km^2, which is inhabited by nearly 200 000 inhabitants. Kielce is the city of industrial origins, where metallurgical and machine-building industries were being dynamically developed especially in 18^{th} and 19^{th} centuries. Nowadays, the areas around Kielce are associated with the activity of cement and lime industry which is developing in a relatively small area known as the Kielce District for Exploitation of Carbonate Resources (Dulewicz 2016). Most part of the city lies in a local hollow whose axis is determined by the valley of Silnica River. The topography of Kielce indicates the characteristics of a depressed landform which results in poor air circulation in the city. This, in turn, conditions a frequent occurrence of smog in winters and poor quality of air (Jędras, Kaleta 2017).

Selection of plant bioindicator

The study was conducted using the common dandelion – a plant species which due to its small habitat requirements and adaptability to the most unfavourable urban conditions, is considered to be a very good bioindicator. Common dandelion is an invasive plant which is easy to identify and commonly found in the environment. It has versatile use in herbalism and medicine. Its young leaves are often an ingredient of salads, its flowers are a component of syrups, and the extract from its aboveground parts is an effective preparation in protecting plants against certain insects. The issues related to the ability of common dandelion to accumulate heavy metals in its tissues occupy a special place in the studies on *T. officinale agg.* properties. Studies in this field were carried out all over the world (Kuleff, Djingova, 1984; Kabata-Pendias, Dudka, 1991; Keane et al. 2001).

Fieldworks

Twenty-one soil and dandelion samples (roots and leaves) were collected from the area of Kielce in 2014 (first half of July). The study involved designating representative sites being appropriate for each type of land use. The sampling locations were determined by the distribution of individual land-use types, and the collection of samples was itself determined by the availability of common dandelion population in a given area. The samples were collected according to such area categories as: industrial areas, urban allotment gardens, urban green areas, and urban parks and forests.

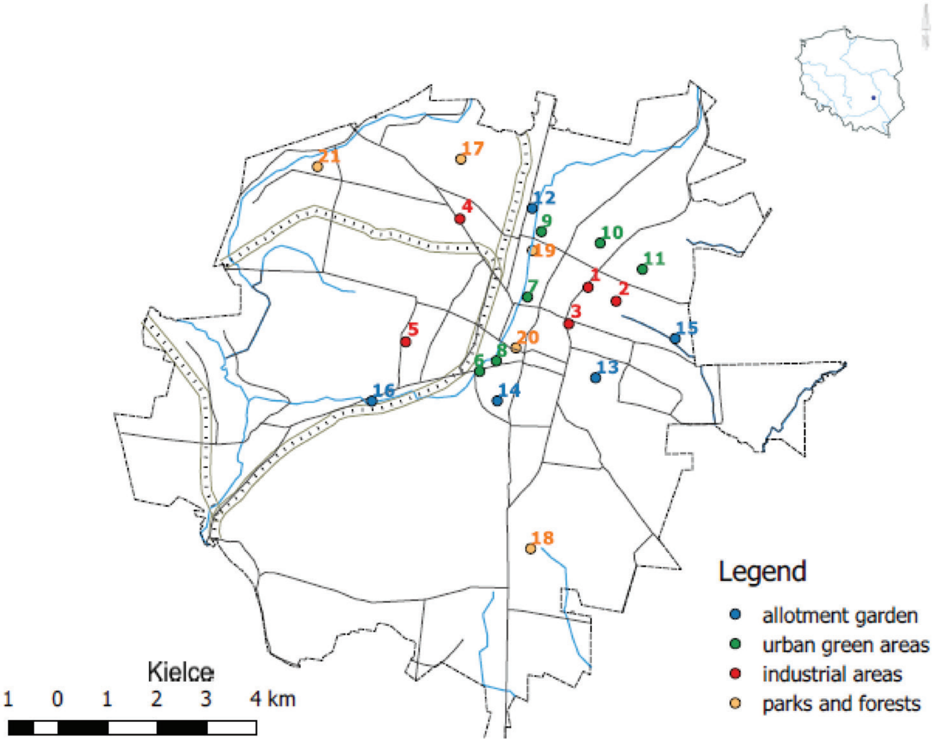

Figure 1. Sampling collections with regard to land-use types

Each analysed soil sample consisted of the plant biomass and soil material that was collected using the Egner's sampling stick from the surface layer up to 25 cm in a 100 x 100 cm plot.

The mixed sample was made up of the soil material coming from 10 points of puncture by the Egner's sampling stick within one plot and plant biomass (roots and aboveground parts) consisting of 20 specimens collected with a garden weeder. There were efforts made to collect the plants of similar size and growth stage (at full flowering and of similar leaf size and root length) to form a homogeneous study sample. In each 100 x 100 cm plot, a few plants were collected from randomly chosen points and then mixed into one representative sample.

Figure 2. Fieldworks – collection of common dandelion and soil samples

Laboratory studies

The collected soil samples were deprived of non-humificated organic matter and then dried at room temperature. The soil samples were ground in an agate mortar and sieved through a 2 mm mesh sieve. The concentrations of total forms of heavy metals, i.e. Pb, Cu and Zn in the soils were determined after mineralisation in *aqua regia* (HCl-HNO_3-3:1) in three repetitions by the ICP-AES method.

Also, pH_{KCL} was analysed by the potentiometric method using a pH meter and Elmetron electrode in a ratio of 1:2.5 1M KCL soil (Ostrowska 1991). Common dandelion was deprived of soil immediately after collection, washed with running water, and then with distilled water. Fresh plants were carefully divided into the aboveground (leaves) and underground (root) parts. Such obtained material was dried at room temperature. After being air-dried, the plant parts were homogenised in an analytical mill PULVERISETTE 14 Premium Line. The obtained samples were subjected to laboratory analysis for the total concentrations of heavy metals, i.e.: Pb, Cu and Zn. The concentrations of total forms of heavy metals in the plant biomass were determined after mineralisation in a mixture of (HCl-HNO_3-3:1) by the ICP-AES (inductively coupled plasma atomic emission spectroscopy) method. Each analysed plant sample was analysed in three repetitions.

Graphic elaboration and statistical analysis

The data was analysed and elaborated using the statistical package R.2.11.1. In order to analyse the data distribution, the Shapiro-Wilk's test (at a confidence level <0.05) was performed.

Graphic analysis of the sampling locations was performed using the program Quantum Gis v.2.6.3.

STUDY RESULTS

The results concerning the concentrations of analysed heavy metals and pH in the collected soil samples are presented in tab. 1 and fig. 2-4. A crucial role in the processes of heavy metal activation or immobilisation is performed by the soil pH (Cappuyns, Swennen 2008). It is one of the most important physicochemical parameters which determines the occurrence of different forms of heavy metals in the soils. In the soils with acidic pH, the amount of soluble forms of chemical elements increases. This is due to dissolution of iron, calcium and manganese oxides, as well as processes of decomposition of primary and secondary minerals, which are intensified by acidic pH. In the case of Zn, the value of pH at which this chemical element is largely mobilised amounts to 6.0; for Cu, it is about 5.5. The weakest solubility is characteristic for Pb. The pH values of analysed soils in Kielce were ranging from 3.99 to 7.92, with the median of 6.97. The measured pH values were similar to each other, as evidenced by the standard deviation (SD = 0.85 pH units). The lowest pH values were recorded for the urban parks and forests. For other land-use types, the pH values were similar. Golcz et al. 2014 as well as Dzierżanowski and Gawroński 2011 point out, based on literature data, that urban areas have either neutral or alkaline pH. This is confirmed by the results of the present studies.

The concentrations of analysed heavy metals adopted the sequence of soil>leaves>root.

Lead concentrations in the analysed soil samples were very diversified. The values were in the range of 16.5-290 mg/kg s.m., with the arithmetic mean of 64 mg/kg s.m. Lead in soils partly originates from natural sources, but its significant amounts reach the soils as a result of precipitation of contaminants from the air. The average concentrations of Pb in uncontaminated soils, reported by various scientists, are typically in the range of 20-40 mg/kg. Lead is considered to be a chemical element which is very poorly mobilised in the soil environment and poorly absorbed by plants from the soils. Increased Pb concentrations in a plant material is usually associated with direct deposition of dust on aboveground parts of plants rather than with intensive uptake of lead from contaminated soils. Lead is typically subjected to strong accumulation in surface soil layers, which results from its affinity with organic matter (Najeeb et al. 2014; Chibuike, Obiora 2014; Jaishankar et al. 2014).

Uptake of Pb by plant roots is proportional to the concentrations of its soluble forms in the soils. Lead is one of those chemical elements which are very toxic to plants, and natural concentrations of Pb in the plants are ranging from 0.1 to 10 mg/kg s.m. (Kabata-Pendias, Pendias 1999). The aboveground parts of common dandelion contained from 1.07 to 3.11 mg/kg s.m., while the roots had from 0.54 to 2.09 mg/kg s.m. of Pb.

Copper is another chemical element to be analysed in the study. It belongs to microelements which are necessary for plants. Average Cu concentrations in the Earth's crust are about 50 mg/kg; however, various types of rocks are characterised with considerably different Cu concentrations. The lowest Cu concentrations are typical of carbonate rocks (below 10 mg/kg) and acidic igneous rocks (about 13 mg/kg on average). Copper deficiency is often observed for carbonate soils and those made out of sands and sandstones. Also noteworthy is the limited Cu bioavailability for plants in organic soils, which is related to a strong affinity with organic matter, as in the case of Pb, which Cu joins and thus creates long-lasting chelate junctions. Contrary to Pb, Cu is considered as a chemical element which easily builds its soluble forms in the soil environment (Kabata-Pendias, Pendias 1999; Horváth et al. 2014). With regard to the analysed soils, the concentrations of Cu were ranging from 7.11-41.0 mg/kg s.m., with the arithmetic mean of 8.61 mg/kg s.m.

Copper, as mentioned before, is a chemical element which is essential for the proper development of plants, but it may be toxic when its values are above 25 mg/kg s.m. When it comes to the dandelion leaves, the Cu concentrations were in the range of 3.11-14.1 mg/kg d.m, while the dandelion roots contained significantly less Cu, i.e. 2.89-8.11 mg/kg d.m. As reported by Kabata Pendias, Pendias 1999, the mobility of Cu and thus its bioavailability depend on pH in the soil environment. The analysed urban soils of Kielce were characterised with either neutral or slightly alkaline pH which indicates the limited mobility of Cu and thus its limited bioavailability for common dandelion. However, no significant correlation was found in order to prove the argument mentioned above.

Table 1. Average concentrations of analysed heavy metals in the soils and *T. officinale agg.* collected from the area of Kielce ($p < 0.05$)

No.	Location	Soil pH	Pb content			Cu content			Zn content		
			soil	leaves	root	soil	leaves	root	soil	leaves	root
1	Industrial areas	6.54	27.9	2.12	0.54	12.4	10.1	7.12	120	48.2	29.8
2		6.62	120	3.11	2.09	41.0	12.7	8.11	210	99.4	32.1
3		6.97	39.1	2.20	1.11	8.60	7.05	6.22	57.5	19.7	15.8
4		7.05	26.4	3.03	1.01	13.6	9.14	7.99	78.3	49.9	26.7
5		7.11	290	3.11	1.42	8.40	4.05	3.12	88.9	57.1	44.1
6	Urban green areas	7.92	72.4	1.92	1.19	13.5	8.99	7.06	293	121	59.0
7		6.57	57.5	1.89	1.09	14.1	4.82	3.66	66.2	31.9	26.9
8		7.11	63.3	2.09	1.43	15.3	5.11	3.24	230	89.7	67.1
9		7.53	16.5	1.07	0.88	14.9	3.11	2.89	156	49.0	21.8
10		6.21	27.1	1.32	0.89	8.90	4.66	2.90	80.1	44.7	36.1
11		7.29	22.5	1.89	1.09	7.32	3.89	2.99	55.7	30.1	20.8
12	Urban allotment gardens	7.53	33.4	2.17	1.16	16.3	7.00	6.11	338	99.7	56.9
13		6.75	78.9	2.33	1.44	12.8	5.43	4.33	91.5	79.0	26.5
14		6.72	63.2	1.99	1.09	10.9	5.00	4.01	270	89.7	42.1
15		6.54	142	2.08	1.99	25.6	9.02	4.89	207	101	44.9
16		7.13	77.1	2.32	1.66	19.2	6.00	3.61	105	71.1	34.9
17	Parks and forests	6.99	30.3	1.68	1.12	7.64	4.09	3.77	55.9	30.2	22.1
18		3.99	29.9	1.99	1.78	7.11	4.77	3.00	61.5	38.9	33.8
19		7.44	50.9	1.33	0.99	21.8	10.9	4.99	174	90.0	33.9
20		5.38	51.6	1.89	1.11	31.3	14.1	7.07	161	100	52.1
21		5.95	24.4	1.34	1.08	8.41	4.11	3.60	78.6	40.7	28.4
	min	3.99	16.5	1.07	0.54	7.11	3.11	2.89	55.7	19.7	15.8
	max	7.92	290	3.11	2.09	41.0	14.1	8.11	338	121	67.1
	mean / median*	6.97	64.0	2.04	1.25	15.2	6.86	4.79	141	65.8	36.0
	standard deviation	0.85	61.1	0.55	0.38	8.64	3.13	1.81	86.4	30.2	13.8

*median value provided for pH

Zinc, like copper, belongs to those microelements which are necessary for plants. The level of geochemical background for Zn amounts to about 75 mg/

kg, while the average Zn concentrations in various rocks are differentiated and are usually in the range of 20-120 mg/kg (Kabata-Pendias, Pendias 1999). The lowest Zn concentrations are found in carbonate rocks and coarse-grained sedimentary rocks which have less Zn than 30 mg/kg. Zinc sources in soils may be either natural or come from atmospheric precipitation, as this chemical element is present in emissions produced by various industrial plants (e.g. metalworks, metallurgical plants, power plants, combined heat and power plants). Zinc, apart from cadmium, belongs to the most mobile chemical elements in the soil environment. Zinc is easily leached into the soil profile, but it may be often re-accumulated in the soil layers rich in iron oxides with which Zn has a strong affinity (Kabata-Pendias, Pendias 1999; Pytel 2014).

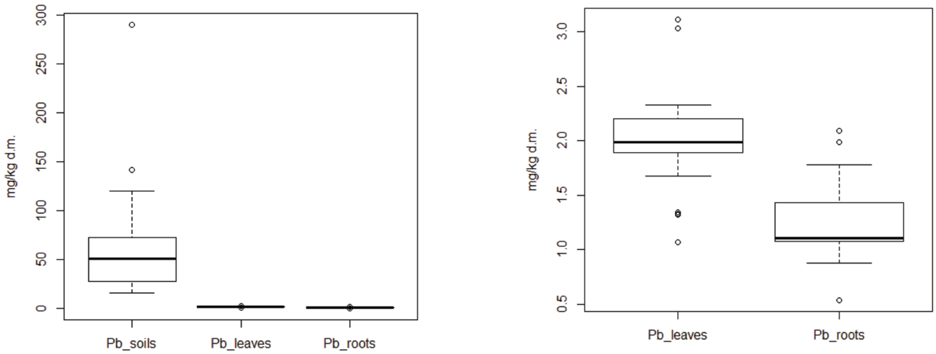

Figure 3. Distribution of Pb concentrations in the analysed soils and *T. officinale agg.* collected from the area of Kielce

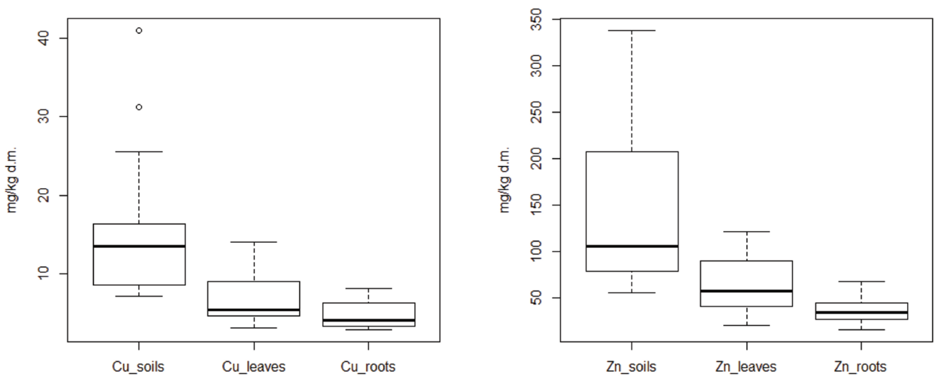

Figure 4, 5. Distribution of Cu and Zn concentrations in the soils and *T. officinale agg.* collected from the area of Kielce

The measured Zn concentrations in the analysed soils were ranging from 55.7-338 mg/kg d.m. In the case of dandelion leaves and roots, the concentrations of Zn were in the range of 19.7-121 and 15.8-67.1 mg/kg d.m., respectively. The critical level of Zn concentrations in plants is 100 mg/kg d.m. (Pytel 2014).

The critical values specified for Pb, Cu and Zn, which would cause toxicity for plants, were not exceeded in the analysed material. The concentrations of analysed heavy metals were higher in the dandelion leaves than in its roots (fig. 2-4). Land plants uptake heavy metal ions mainly from soils through the root system, and they also have the ability to absorb microelements directly from the atmospheric air through the stomata and leaf surfaces (Siwek 2008); hence the aboveground biomass is very often characterised with higher heavy metal concentrations than the underground one.

Table 2. Spearman's rank correlation coefficients in the relationship soil-leaves-roots *

	Cu_{soil}	Cu_{leaves}	Cu_{root}	Pb_{soil}	Pb_{leaves}	Pb_{root}	Zn_{soil}	Zn_{leaves}	Zn_{root}	pH
Cu_{soil}		0.681	0.477	0.410	0.142	0.195	0.674	0.742	0.414	0.140
Cu_{leaves}			0.887	0.349	0.362	0.150	0.469	0.596	0.319	-0.119
Cu_{root}				0.277	0.456	0.096	0.349	0.448	0.116	-0.040
Pb_{soil}					0.561	0.732	0.451	0.583	0.505	0.034
Pb_{leaves}						0.558	0.135	0.218	0.107	0.063
Pb_{root}							0.198	0.369	0.341	-0.043
Zn_{soil}								0.897	0.747	0.276
Zn_{leaves}									0.769	0.205
Zn_{root}										0.031

*Shapiro-Wilk's test performed at a confidence level <0.05 in most cases indicates a basis for rejecting the hypothesis of normal distribution of the analysed characteristic

The concentrations of analysed heavy metals in the soils and *T. officinale agg.* were conditioned by the land-use types. In each analysed land-use type, extreme high concentrations of heavy metals were identified. Significantly higher concentrations of analysed heavy metals in the leaves than in the roots may be caused by contaminants emitted into the atmosphere. Similar conclusions were drawn by Petrova et al. 2013 who conducted their studies in the area of Bulgaria. As noted by Bomze et al. 2007, traffic contamination in urban areas, emitted to the atmosphere, are being accumulated along the entire sections of a city. The amount of such contaminants depend on traffic volumes. Significantly higher heavy metal concentrations in the aboveground dandelion parts than in those underground ones may indicate diverse origins of heavy metals, which result especially from air pollution. No clear relationships between the land-use types and heavy metal concentrations may result from the fact that the contamination emitters in urban areas are not accumulated in one place, but are usually dispersed.

Statistical analysis showed a strong correlation between the concentrations of Cu and Zn in the soils as well as between the soils and dandelion roots and aboveground parts within each analysed heavy metal (tab. 2).

CONCLUSIONS

1. The conducted studies indicate that the heavy metal concentrations in the soils and *T. officinale agg.* had no homogeneous character. Significant relationships between the heavy metal concentrations in the soils and plant material as well as partial relationships between the various heavy metals in the soils (Cu-Zn) were noted.
2. The analysed soils of Kielce were characterised by the pH typical of urban soils, which was in the range of 3.99-7.92 and had the median amounting to 6.97. There were no relationships between the heavy metal concentrations and pH values.
3. The studies indicate that the concentrations of Cu, Zn and Pb in the soils and common dandelion from Kielce were not dependent on the land-use types. Extreme high concentrations of analysed heavy metals were reported for all types of land use.
4. The concentrations of analysed heavy metals adopted the sequence of soil>leaves>root which may indicate the presence of atmospheric heavy metal forms in the total concentrations of the analysed heavy metals in the dandelion leaves.

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