Polish J. of Environ. Stud. Vol. 20, No. 1 (2011), 115-124

Original Research

Influence of a Transboundary Emission on Bioavailability of Metals of Stinging Nettle from Soil

Jolanta Kowol*, Jerzy Kwapuliński, Barbara Brodziak-Dopierała, Andrzej Paukszto, Mariusz Bogunia, Robert Rochel, Bożena Ahnert

Department of Toxicology, Medical University of Silesia,
Jagiellonska 4, 41-200 Sosnowiec, Poland

Received: 22 February 2010
Accepted: 8 July 2010

Abstract

Bioavailability of individual chemical forms of metals occurring in soil is a basic source of its accumulation in plants. Soils from a root layer collected from the stands of stinging nettle *Urtica dioica* L., reflect different habitat conditions in the area of Wisła, a town in southern Poland. The Bukowa, Czarne, Głębce, Jawornik, Kubalonka, Malinka, Kobyla, and Salmopol also were research subjects. The content of the following metals in soils, as well as in fallout dust, was measured using the AAS method: Cd, Ni, Cr, Pb, Cu, Zn, Mn, and Fe. Accuracy was controlled by using CRM 277 and IAEA-SOIL-7 as reference materials. Speciation analysis in accordance with Rudd's method allowed for evaluation of bioavailability of those metals in plants. The most bioavailable elements in an exchangeable form on all examined stands were Zn, Pb, Cu, and Cr resulting from a complex influence of transboundary emission, traffic emission, and low emission from coal combustion.

Also organic bounds might be potentially bioavailable during acid rainfalls as well as carbonates of particular elements, and the biggest proportion was noticed for Zn, Pb, and Fe. It may result in a higher accumulation of those elements in medicinal plants that are collected in a natural state. The range of metal pseudo-total contents in soil in the area of Wisła was limited to the following values ($mg \cdot kg^{-1}$): Cd – 5.3-12.9, Cr – 4.7-14.2, Cu – 9.4-27.1, Ni – 8.2-18.5, Pb – 41.3-99.7, Zn – 106.7-480.6, Mn – 106.2-481.9, and Fe – 7,000.0-16,300.0.

Keywords: soil, metal speciation, bioavailable forms of metals, transboundary emission, dust fallout

Introduction

In anthropogenically unchanged environments, the crucial source of heavy metals for plants is a natural geochemical content of elements in soil determined by a parent rock type. However, in the border areas and in accordance with the wind rose, the inflow of transboundary contamination is possible together with long range emissions that might influence the level of plant contamination by accumulation from soil, as well as dust on the surface of leaves. The emission of pollution to air is a complex problem and usually has a global character. Polluted gas and fine dispersive dusts emitted in the area of one country or region to the areas of other countries cause adverse changes in the natural environment [1, 2]. Such a mechanism of transfer has a transboundary character.

---

*e-mail: jkowol@sum.edu.pl

The problem of transboundary transport of contaminations in Europe has become a subject of research conducted in accordance with an international co-operation programme called the European Monitoring and Evaluation Program (EMEP) regarding air pollution long-range transport under the Geneva Convention issued in 1979 [3].

The main direction of dust pollution inflow in Poland is southwest and west [4, 5]. Of course, the distance of migration of the pollution is also dependent of its physical state, dispersive content of dusts, aerosols, air mass turbulences, and frequency of chosen wind directions, as well as weather, anemological, and meteorological conditions. It should be emphasized that air quality is worse when temperature and insolation are higher; then, the content of fine dispersive dusts and ozone is higher. As a result of the long-term influence of imission of fine dispersive dusts (including heavy metals), the progressive secondary enrichment of surface soil layer in Cd, Pb, Zn, Cr can be noticed.

The bioavailability of chosen metal compounds in soil for plants determines the physicochemical properties of the fallout [6]. As a result of dynamic soil processes, both biological and biochemical (cation exchange, complex forming, leaching and mineral weathering, fungi incorporation), there is a possibility of conversion from dust contamination form into dissoluble one. This results in an increase of bioavailability of heavy metals from a soil solution for plants. In heavy metals the migration process from solid soil stage to the soil solution in which metals are easy available by plants, a significant role is played by changes of pH, redox potential, fluctuation of temperatures, and organic matter decomposition or mycorrhiza [7, 8].

One of the methods allowing for the evaluation of heavy metals content in soil is identification of a pseudo-total element content in soil. This might be the first information from a sequence that indicates the intensity of the degradation of a given ecosystem. It allows for initial classification of the soil regarding the level of its contamination [9, 10]. However, it does not define the level of bioavailability of those elements for plants so the attention should be paid to a proper evaluation of metal accumulation in soils.

Bioavailability of metals for plants depends on the chemical form of elements present in the soil. Speciation analysis is a method allowing for identification of metal chemical forms in soil, which reflects mobility of particular elements including intensity of leaching, level of absorption by plants, and a toxicity of metals [11]. Speciation analysis provides valuable information regarding the level of metal hazard for a given ecosystem, especially the poorly anthropogenically changed area (semi-recreational). Speciation allows for a real estimation of accumulation of metals in soil.

The results of speciation analysis of metals in soil in the surface layer of organic levels were supposed to give the authoritative evaluation of transboundary emission influence. The evaluation of metal migration in a soil-plant system was conducted on the basis of a sequential speciation analysis in accordance with Rudd's method [12]. The objective of the work was the determination of contents and bioavailability of chosen metals: Cd, Ni, Cr, Pb, Cu, Zn, Mn, and Fe – both in soil from stinging nettle stands (*Urtica dioica* L.) and in the total fallout dust in the examined area of Wisła (latitude 49º38'50"N, longitude 18º52'03"E).

Wisła is a mountain resort that shall be covered with a specific control and protection against contaminations.

Material and Methods

Research Location

The research covered the administrative area of Wisła, situated in the Silesian Beskids in southern Poland, in the western Polish Carpathian Mountains where (depending on geographical location) transboundary pollutions inflow in especially exposed ways. In the area of the Moravian Gate the main pollution centres on the Czech side are: Trinec, Karvina, Detmarovice, and Ostrava. Regarding physiography, Wisła is a specific area, including 13 valleys surrounded by mountain slopes, with the steepest ones in the north. From the west and south is surrounded by a range of the Czantoria Mountains, from the east by the Barania Góra Mountains, and from the north its branch – Równica Mountain. With such physiography, occurrences of air temperature inversion are connected with the unfavourable influence of dispersion of contaminations. The air in lower layers is colder than in upper ones, which hinders the proper vertical mixing that takes place when heated air masses rise and cold masses settle. This is a cause for stoppage of gases and aerosols next to the surface soil. Periodic deterioration of air quality in the area is connected with the long-range emission influence of the Upper Silesian Industrial Area on the Polish side and the area of Ostrava and Karvina on the Czech side with the wind circulation from a south-north direction. In the examined area, acid brown and typical brown soils are dominating, with mull-morder type of the humus and covers 57.4% and podzol soils 33.4%.

Sample Collection and Analytical Procedures

Soil

Soil in Wisła was collected in autumn 2004 from areas that represented the most physiographically typical areas: Jawornik – I, Bukowa – II, Malinka – III, Czarne – IV, Głębce – V, Kubalonka – VI. The locations of stands are presented in Fig. 1. The area of strongest impact of anthropopression, e.g. Wisła Center, was excluded from the research. Kobyla and Salmopol Pass, located beyond the area of Wisła, were chosen as a reference point for comparison.

Soil using an Egner sampler was collected from root layer (0-10 cm) from stands of stinging nettle *Urtica dioica* L. Each sampling point was selected at a sufficient distance from the nearest tree to avoid "throughfall" precipitation from the trees (distance of 5 m from the nearest tree and 3 m from the nearest bush) [13, 14].

On each stand (I-VI), six points of soil sample collection were chosen to receive the most representative results of determinations. From combined and well-mixed individual samples from each point, one homogenized sample was prepared in the amount of about 0.5 kg. The samples in laboratory conditions, after prior air desiccation, were dried at 40ºC, powdered in a porcelain mortar, and standardized on sieves with mesh diameter 1 mm. The samples of soil were stored in polyethylene containers.

In the soil samples the content of organic matter, pH, and pseudo-total content of metals were measured and speciation analysis was performed.

Pseudo-Total Contents of Metal in Soil

To determine pseudo-total contents of a metal in soil, we used the hot mineralization method 65% of HNO_3 (V) (Merck). The analytical sample of the soil (1.0000 g) placed in a crystallizer gave 5 cm^3 of 65% HNO_3 (V) and was mineralized under the cover at 90-95ºC in a water bath; it took 1 hour, until the evaporation of the analyte occurred. Successively, we added 10 cm^3 of 65% HNO_3 (V) and again heated for 1 hour. To wash iron ions, the analyte was filtered to the measuring flasks with capacity of 50 cm^3 using a filter paper rinsing the precipitate with 1% of hot HNO_3. Once the analyte cooled, the flask was made up to the mark with redistilled water.

Determination of Soil pH

Determination of hydrogen ion concentration in soil suspension (10 g) in 25 cm^3 1M KCl was indicated potentiometrically by using a microprocessor pH-meter: CP-551 Elmetron. Model buffer solutions produced by POCH were used.

Determination of Organic Matter Content

Organic matter content in soil was indicated by the gravimetric method from the sample mass loss during the soil sample roasting in a muffle furnace at 550ºC. To the evaporating dish (which was previously roasted and then cooled in a desiccator over $CaCl_2$) 2 g of air dry soil were weighed and roasted at 550ºC for about 7 hours, and after cooling it was again weighed. Activities were repeated until a solid mass of the soil sample was received.

Sequential Speciation Analysis of Metals in Soil

Metal speciation in soil was conducted using Rudd's method [12] and subsequent six fractions of metal were extracted from the 1.0000 g analytical sample, in accordance with the following extraction scheme:

1. Exchangeable form – 1 M KNO_3
2. Adsorbed form – 0.5 M KF, pH=6.5
3. Organically bound – 0.1 M $Na_4P_2O_7$
4. Carbonates – 0.1 M EDTA
5. Sulphides – 6 M HNO_3
6. Residues – 65% HNO_3

Soil samples were treated by particular extractants in 1:40 proportion for 24 hours at room temperature. After centrifuging, the extractant was directed to analysis for metal content, the deposit was flushed with distilled water,

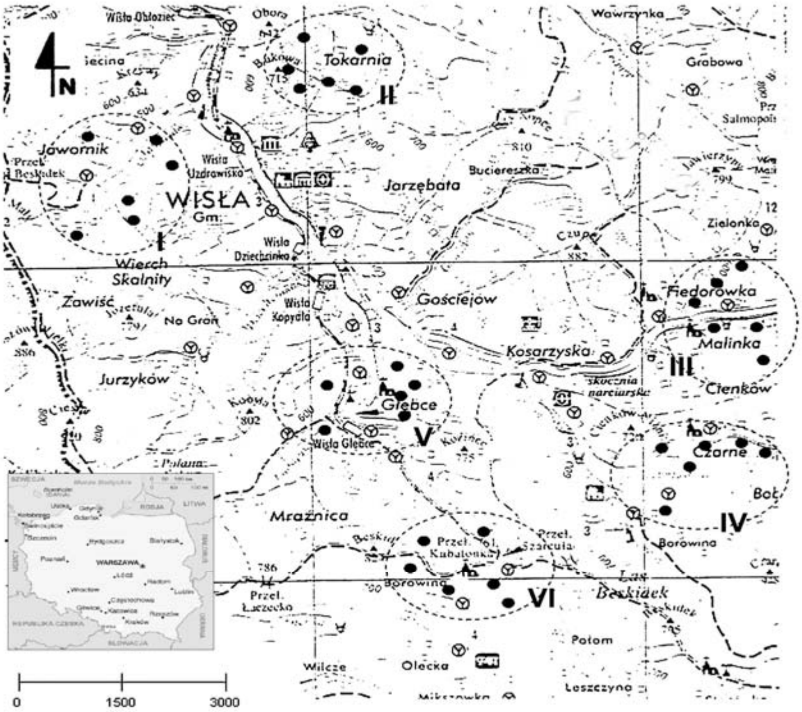

Fig. 1. Location of sampling sites in the Wisła area.

Table 1. Reference material IAEA-SOIL-7 and CRM 277 – analysis results ($mg\cdot kg^{-1}$).

Metal	Certified value	Measured value (N=6)	Recovery (%)
IAEA-SOIL-7			
Cr	60	64±0.06	106.7
Cu	11	10.1±0.23	91.8
CRM 277			
Pb	146	135±2.2	92.5
Cd	11.9	12.9±0.59	108.4
Ni	43.4	42.9±0.21	98.8
Zn	547	530±4.8	96.9

and was treated with other extractant. In order to receive a fraction of residues, the samples were treated in accordance with procedure-relating soil.

Dust Fallout

Total dust fallout samples were collected to a polyethylene cuvette with a surface of 0.12 m^2 filled with distilled water, placed in an open area, not afforested at the level of 2.5 m. Sample collection was conducted in a constant manner with one month intervals, during the whole period of plant vegetation from May to October 2004.

The content of elements in the total fallout in dissoluble and insoluble forms was indicated from mass difference after filtering through weighed quantitative filter paper to the crystallizer with known mass whose content was vaporized to dryness. The known amount of deposit was digested in 5 cm^3 of 65% HNO_3 (V) (Merck) and was transferred to measuring flasks with 25 cm^3 capacity. Quantitative filter papers were dried, weighed, and incinerated in a muffle furnace at 420ºC for 24 h. Received ash was treated by 5 cm^3 of 65% HNO_3 (V) (Merck) and transferred into measuring flasks with 25 cm^3 capacity.

Determination of Metal Content in the Samples

The content of Cd, Ni, Cr, Pb, Cu, Zn, Mn, and Fe was determined by the atomic absorption spectrometric method (AAS) using a Philips Pye Unicam SP-9 spectrometer. Measurement calibrations were made using a spectrally pure standard solution (mass concentration standard sample) with a content of 1.000 g $Me^{n+}\cdot L^{-1}$, produced by the Central Office of Measures (Poland). For each series of determined samples, the zero reactive samples were prepared and these amounts were included in calculations. Accuracy of the method was controlled by the analysis of the CRM 277 and the IAEA-SOIL-7 reference material – Table 1. Validation of the used method was made on the basis of the intercalibration research, simultaneously conducted in co-operation with the Department of Inorganic Chemistry of the Silesian University of Technology in Gliwice, Poland.

Statistical analysis was carried out using Statistica 7.1.

Results

The characteristic of the pseudo-total metal contents of metals in soils in the area of Wisła reflects the changes in six habitats specific for that area – Table 2. The average concentration of metals in soil in the area of research contained in the range of contents: n x 10^0 – n x 10^3 in $mg\cdot kg^{-1}$ d. m.

Including the content of elements corresponding to the geometric average ($mg\cdot kg^{-1}$) as a criterion, the following sequence of metal occurrence might be formulated:

Cd, Cr 9 x 10^0 < Ni, Cu, Pb 1-6 x 10^1 <
Zn, Mn, 2-3 x 10^2 < Fe 12 x 10^3.

Variations of element occurrence, excluding Zn, remained at the level of 39%. Frequency of Pb, Cu, Zn, and Ni occurrence has a normal character. The other elements have a distribution developed on the left, which indicates predominance of its content close to an environmental con-

Table 2. Statistical characteristic of metal occurrence in soil in the Wisła area ($mg\cdot kg^{-1}$).

Metal	Geometric mean	Percentile		Coefficient			Geochemical background
		10	95	Excess	Kurtosis	Variability %	Min Max
Cd	9.06	5.31	12.94	-0.28	-1.48	32	0.5-1.0
Ni	10.94	8.22	18.51	1.45	2.14	34	20-40
Cr	9.25	4.70	14.28	-0.27	-0.61	35	10-20
Pb	61.65	41.35	99.77	1.24	2.30	31	25-50
Cu	16.41	9.40	27.16	0.47	-0.03	36	10-20
Zn	187.48	106.78	480.64	2.18	5.10	64	50-100
Mn	300.80	106.23	481.94	-1.05	1.85	39	500-1,000
Fe	12,200.00	7,000.00	16,300.00	-1.10	2.01	25	20,000

Table 3. Average metal content in soil at chosen points in the Wisła area (geometric mean) (mg·kg^{-1}).

Site	Cd	Ni	Cr	Pb	Cu	Zn	Mn	Fe
Bukowa	9.41	12.29	10.97	99.77	27.16	480.64	294.76	12,000.00
Czarne	5.31	18.51	14.28	56.25	18.91	148.68	481.94	14,600.00
Głębce	6.74	8.31	7.72	53.44	13.23	190.01	349.09	12,300.00
Jawornik	12.54	9.26	8.84	65.22	14.79	179.02	338.18	13,400.00
Kubalonka	10.12	8.22	4.70	41.35	9.40	106.78	106.23	7,000.00
Malinka	12.94	11.89	12.49	67.92	20.66	167.31	415.77	16,300.00
Kobyla	1.71	11.46	8.54	42.94	15.68	133.07	349.50	12,900.00
Salmopol	1.45	10.95	10.30	52.49	18.00	151.96	405.35	14,500.00

centration. The range of content changes in particular metals in examined habitats was included in the following boundaries (mg·kg^{-1}): Cd 5.31-12.94, Ni 8.22-18.51, Cr 4.70-14.28, Pb 41.35-99.77, Cu 9.40-27.16, Zn 106.78-480.64, Mn 106.23-481.94, and Fe 7000.00-16300.00.

The biggest contents of Pb, Cu, and Zn in soil were observed in the stand in Bukowa (mg·kg^{-1}): Pb 99.77, Cu 27.16, Zn 480.64: as well as on the stand in Wisła-Czarne: Ni 18.51, Cr 14.28, and Mn 481.94, and in Malinka: Cd 12.94, and Fe 16300.00 (Table 3). The lowest metal content was found in the soil from the highest stands (around 760 m above sea level) on Kubalonka, excluding Cd (10.12 mg·kg^{-1}) with the average content of that element for Wisła being 9.06 mg·kg^{-1}.

The range changes of metal content in soil on the reference stands in Kobyla and Salmopol for chosen metals was likely as follows (mg·kg^{-1}): Cd 1.45-1.71, Ni 10.95-11.46, Cr 8.54-10.30, Pb 42.94-52.49, Cu 15.68-18.00, Zn 133.07-151.96, Mn 349.50-405.35, and Fe 12900.00-14500.00.

The content of bioavailable forms (exchangeable and adsorbed) of a given element in soil, in particular habitats, was different (mg·kg^{-1}):

Bukowa: 0.02 Cd < 0.99 Ni < 9.83 Cr < Fe 12.10 < 20.88 Mn < 26.46 Pb < 28.66 Cu < Zn 80.84
Czarne: 0.02 Cd < 1.02 Ni < 10.71 Cr < 17.10 Mn < 32.05 Cu < 65.3 Pb < 132.10 Zn < Fe 240.37
Głębce: 0.02 Cd < 0.33 Ni < 9.97 Cr < 10.73 Mn < 26.50 Cu < 36.3 Zn < 45.84 Pb < Fe 206.52
Jawornik: 0.02 Cd < 1.28 Ni < 11.1 Cr < 22.66 Mn < 26.74 Cu < 42.8 Pb < 46.97 Zn < 154.44 Fe
Kubalonka: 0.02 Cd < 0.31 Ni < 9.41 Cr < 28.87 < Mn 29.45 Pb < 30.41 Cu < 44.98 Zn < 161.52 Fe

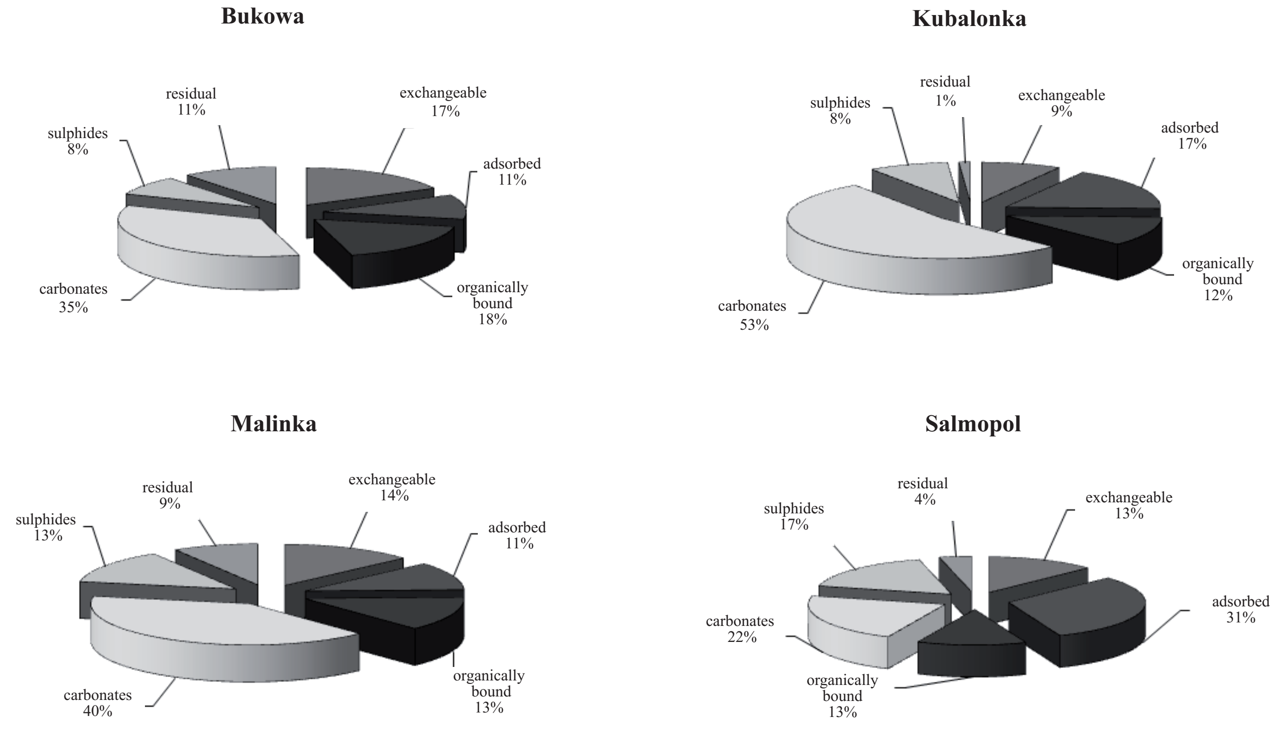

Fig. 2. Percentage share of Pb chemical form occurrences in soil from Bukowa, Kubalonka, Malinka, and Salmopol sites.

Table 4. Average metal content in soil in different occurrence forms – Wisła (geometric mean) (mg·kg^{-1}).

Metal	Forms					
	Exchangeable	Adsorbed	Organically bound	Carbonates	Sulphides	Residual
Cd	0.01	0.01	0.42	0.57	0.61	4.31
Ni	0.20	0.49	0.66	1.60	2.79	4.76
Cr	7.40	2.91	2.72	2.45	3.91	3.43
Pb	13.01	20.63	12.41	35.47	9.22	37.99
Cu	21.35	8.17	9.43	11.50	10.06	3.22
Zn	2.92	59.07	33.45	31.11	53.64	27.34
Mn	5.56	10.70	56.44	128.01	61.94	0.50
Fe	8.86	32.02	327.46	1,150.00	3,800.00	6,000.00

Malinka: 0.02 Cd < 1.3 Ni < 10.81 Cr < 19.98 Mn < 22.14 Pb < 30.16 Zn < 31.7 Cu < 37.18 Fe
Kobyla: 0.02 Cd < 0.96 Ni < 9.27 Mn < 10.56 Cr < 17.58 Fe < 25.84 Pb < 29.9 Cu < 93.82 Zn
Salmopol: 0.02 Cd < 0.66 Ni < 10.4 Cr < 22.41 Mn < 32.28 Cu < 41.8 Pb < 103.84 Zn < 155.4 Fe.

Acid rain in the Wisła area has pH 2.0-5.5, which might increase the resources of metals that are bioavailable from soil for plants from organically bound and carbonates (mg·kg^{-1}), namely:

Bukowa: 1.48 Cd < 3.94 Ni < 5.41 Cr < 24.16 Cu < 49.49 Pb < 147.02 Zn < 180.15 Mn < 1547.99 Fe
Czarne: 0.92 Cd < 2.04 Ni < 5.61 Cr < 21.56 Cu < 52.36 Pb < 53.04 Zn < 248.77 Mn < 1896.06 Fe
Głębce: 0.7 Cd < 3.33 Ni < 5.48 Cr < 19.66 Cu < 45.84 Pb < 49.99 Zn < 211.18 Mn < 1828.49 Fe
Jawornik: 0.77 Cd < 1.93 Ni < 4.34 Cr < 18.47 Cu < 41.61 Zn < 41.68 Pb < 177.93 Mn < 1407.36 Fe
Kubalonka: 1.89 Cd < 2.51 Ni < 5.65 Cr < 26.36 Cu < 74.92 Pb < 150.69 Zn < 209.05 Mn < 1400.52 Fe
Malinka: 0.88 Cd < 2.29 Ni < 4.92 Cr < 20.2 Cu < 48.28 Pb < 58.92 Zn < 218.62 Mn < 1541.74 Fe
Kobyla: 1.05 Cd < 1.6 Ni < 5.28 Cr < 19.47 Cu < 50.27 Pb < 72.79 Zn < 183.56 Mn < 1431.63 Fe
Salmopol: 0.89 Cd < 2.64 Ni < 4.96 Cr < 19.82 Cu < 33.19 Pb < 48.56 Zn < 187.69 Mn < 1,003.95 Fe

The high content of adsorption form Zn 59.07 mg·kg^{-1} is on average 20 times higher with reference to exchangeable form (2.92 mg·kg^{-1}). Potential bioavailability of Zn from organically bound and carbonates is comparable with part directly bioavailable and amounts to 32 mg·kg^{-1}. Content of Cu in bioavailable forms should also be considered high. The sum of bioavailable chemical forms amounts to 30 mg·kg^{-1}, whereas bioavailability from forms potentially available for plants is lower, at 21 mg·kg^{-1}. The increased bioavailability of Cr in exchangeable form from soil to the plants might be also disturbing, amounting to 7.40 mg·kg^{-1}. Moreover, organic connections and carbonates may determine Fe and Mn content in plants (Table 4).

The percentage share of chemical forms of Pb occurrence in soil of examined habitats is presented in Fig. 2.

The research results regarding the change of particular metal content in the total fallout of water-soluble and water-insoluble fractions were presented in Table 5. The percentage share of dissoluble metal fraction was for Cd 6%, Ni 2%, Pb 8%, Cu 22%, Zn 20%, Mn 13%, and Fe 39%.

Discussion

There is a diversity in the contamination of plants with Pb, Cd, and Ni in the range of industrial emission influence [15].

It turns out that in the example of Pb, Cd, and Ni content examination in 27 plant species, those amounts were significantly higher in comparison with the average content in the places located away from this area [15, 16]. The effect of the mill in Trinec on occurrence of Pb, Cd, and Ni in many plant species is proved by calculated enrichment coefficients for the air-soil system. For example, the level of metal carbonate content in soil on Cieszyn terrain was much higher in comparison with geochemical Cd, Ni, and Pb content.

The higher than geochemically characteristic metal contents show the role of long-range dust emission. Those differences may prove the effect of transboundary emission of selected elements. Emited dusts contain soluble salts or potentially bioavailable compounds of selected metals.

Therefore, the range of transboundary emission, as well as its meaning for the environment in Wisła (which is separated from the Trinec-Ostrava industrial area by the massif of the Czantoria-Soszów-Stożek mountains at an altitude of 900 m above sea level) might be described by the results of speciational analysis in soil. Specific amounts of individual chemical forms of metals and their dissolved compounds in the total fallout can determine the real exposure of plants (i.e. stinging nettle). For this fact we point to the research of Mirosławski et al. regarding Cieszyn, about 10 km from the area source of imission (Trinec, Ostrava), located in Czech Republic [16].

Cd levels are 10-fold higher in all the pockets of Wisła (Table 2) than those declared in the literature of geochemi-

Table 5. Statistical characteristics of metal occurrence in water-soluble (1) and water-insoluble (2) fraction in dust fallout (mg·kg^{-1}).

Metal	Fraction	Geometric Mean	Percentile		Coefficient		
			10	95	Excess	Kurtosis	Variability [%]
Cd	1	7.94	1.53	34.67	1.57	2.66	96
	2	126.40	15.70	520.83	0.99	-0.03	92
Ni	1	5.15	1.62	14.03	0.29	-0.50	69
	2	295.77	20.94	2,546.84	2.12	4.69	137
Cr	1	15.44	4.86	42.09	0.29	-0.50	69
Pb	1	104.00	28.27	336.70	1.32	2.26	79
	2	1,354.64	9.31	7,575.76	1.01	-0.29	104
Cu	1	85.01	13.88	368.19	0.72	-0.70	92
	2	309.11	35.89	1,190.48	1.39	2.49	85
Zn	1	565.58	194.36	1,599.33	0.92	0.05	72
	2	2,832.83	213.60	19,615.38	1.64	2.79	117
Mn	1	182.86	30.83	1,568.37	2.16	4.88	142
	2	1,412.99	156	5364	1.06	1.51	83
Fe	1	376.99	112.03	1,028.32	0.76	-0.73	72
	2	964.01	340.83	28,250.00	1.25	1.69	108

cal levels of element occurrence in soil. Maximum Ni contents in Wisła soil are comparable with a minimum of Ni geochemical background contents. The range of Cr levels (41-100 mg·kg^{-1}) in Wisła soil are within the range given by Państwowy Instytut Geologiczny [17]. The soil from the examined stands in Wisła are much higher Pb content than those from the geochemical background (25-50 mg·kg^{-1}). Zn levels in the soil from Wisła have higher when compared to those observed in natural geochemical conditions in the Western Beskid. Fe levels in the soil are much higher than the levels determined by geochemical conditions of the examined area. Mn levels are below the levels determined by geochemical conditions. However, the maximum Mn levels are within the lowest levels determined by geochemical background.

Recapitulating this part of the discussion, it can be accepted that Cd, Pb, Fe, and Zn, as elements characteristic of mill dust emissions, are the elements of long-range emissions, that enhance bioavailability of selected elements in the soil.

Another argument toward the effect of a transboundary emission involve dust on leaves [18]. It has been shown that the metal levels in a soluble form found in dust settled on leaves of common coltsfoot are as follows (mg·kg^{-1}): Cd – 8.0, Ni – 32.5, Cr – 0.05, Pb – 163.1, Cu – 103.1, Zn – 542.7, Mn – 151.9, and Fe – 2120.0. These levels in the case of Cd, Pb, Cu, Zn, and Fe are much higher than those determined by geochemical characteristics of the ground. A common phenomenon in the case of dry soils is occurrence of the secondary dust rising. It draws from this, that long-range dust emission has a stronger effect on the mineral content of dust settled on the leaves than dusts flowing with the winds from above the surface of soils not changed antropogenically.

In accordance with literature [19, 20] in the interpretation of results, it was recognized that content equivalent of 10th percentile characterizes environmental element concentration, determined by geochemical conditions of the ground and secondary emission from soil at the examined area. Whereas the content equivalent of 95th percentile reflects incidental levels of occurrence of the examined metals, it is a result of its industrial imission (total fallout of a particular element) on the surface soil layer. It should be emphasized that this content is the evidence of level of risk for plants, e.g. medicinal plants that grow in such habitat conditions. Both geochemical environmental concentrations (10th percentile) as well as bothersome anthropogenic influences (95th percentile) that are subject to area changes, have a specific area characteristic of the occurrence frequency of chosen concentrations of given elements (and are additionally diversified by the variation coefficient) (Table 2). The difference between contents equivalent to 95th percentile and 10th percentile shows the possibility of intoxication of plants as a result of permanent transboundary industrial dust emission. It should be added that a complex impact of the industrial emission from Czech Republic takes place, because in the area of Wisła natural gas is used for heating in 90% of cases. That is why the areas situated

Table 6. Reaction and content of organic matter in soil on the examined sites.

Site	Height above sea level (m)	pH	SD	Organic matter %	SD
Bukowa	700	5.55	0.48	11.11	0.11
Czarne	600	4.48	0.52	17.63	0.47
Głębce	600	4.55	0.35	7.13	0.14
Jawornik	570	5.11	0.15	8.70	0.16
Kubalonka	760	5.77	0.31	7.73	0.28
Malinka	600	5.48	0.36	9.13	0.64
Kobyla	800	5.30	0.17	10.81	0.49
Salmopol	934	5.20	0.42	11.25	0.35

above the valley of the Wisła River contain lower amounts of those elements, e.g. on Kubalonka (open area). The stand in Bukowa located not so much lower (700 m above sea level) was an exception and showed the highest contents of Pb (99.77 mg·kg^{-1}) as well as Zn (480.64 mg·kg^{-1}) and Cu (27.16 mg·kg^{-1}) (Table 3). In Kubalonka soils two times lower contents of Cr, Cu, and Fe were observed and 3-4 times less of Mn. It was also interesting that the content of Cd on the stand on Kubalonka was seven times higher in comparison with stands on Kobyla and Salmopol.

The works of Karczewska regarding another boundary area – Western Sudetes – are an indirect argument for the influence of transboundary emission [21]. Dust imission can vary depending on the area [18]. Regional diversity of Pb and Cd content in the dust settled on the leaves of coltsfoot has been proven by speciacic investigation of the soil related to Pb, Cd, Mn, Cu, Cr, Ni, Fe, and Zn. On the basis of Pb and Cd occurrence on the leaves of coltsfoot, the following regional diversity can be observed (mg·kg^{-1}):

Pb: Malinka 37.1 < Kubalonka 90.0 < Jawornik 92.0 < Czarne 96.0 < Bukowa 97.3 < Głębce 140.4

Cd: Głębce 3.8 < Malinka 4.5 < Kubalonka 8.8 < Bukowa 9.9 < Jawornik 10.3 < Czarne 10.8

Diversified results of metal speciation in soil in area grasp, as well as mentioned contents of Pb and Cd in particular districts of Wisła in dust settled on leaves, indicates the influence of transboundary emissions from the Czech Republic. However, on the mountain areas the diverse temperature distribution can be noticed, which results in specific convection of air masses. The final deposition of many metals through precipitation is determined by the amount of transboundary emission. This problem is complex because the characteristic physiography of the mountain area allows for keeping relatively high contents of examined metals when the wind speed is relatively low and turbulence is weak. Our own research results regarding the content in soil in particular occurrence forms as well as amounts of dissoluble metal forms in dust settled on leaves prove this. During this complex imission process of transboundary pollution in the Wisła area, occurrence of successive averaging of imission is reflected and in some measure it might be impacted by the occurrence of secondary dusting of local forests. The results representing the habitat in the area of the Wisła-Bukowa district might be an example.

The accumulation through a root system of bioavailable chemical forms of element occurrence in soil that is characteristic for plants and distinguishes particular plant habitats is the source of metal occurrence in plants. Directly bioavailable chemical forms of a given element for plants are exchangeable in adsorptive forms. In the case of the pH change towards acidity, also organic connections and carbonates of particular elements are bioavailable, which are included as potentially bioavailable.

The problem of the long-range emission on the examined area is multiplied by the fact that on this area both soils as well as rainfalls (Table 6), have an acid reaction that additionally results in the fact that sources of directly bioavailable forms of particular metals, e.g. Pb (13.01-20.63 mg·kg^{-1}), and Zn (2.92-59.07 mg·kg^{-1}), are increased by potential bioavailable sources, e.g. Pb (12.41-35.47 mg·kg^{-1}), and Zn (31.11-33.45 mg·kg^{-1}).

It draws attention to the fact that relatively high content of Pb is present in Wisła soils in directly bioavailable forms (33.64 mg·kg^{-1}), as well as potentially bioavailable for plants (47.88 mg·kg^{-1}) as a result of the transboundary emission and emission car (Table 5). Information regarding Pb content in soil is especially important because the Wisła area is considered a semi-recreational area where medicinal plants may be collected and which is a source of valuable herbal material. In the case of an increase of Pb content in soil environment, especially in the most mobile forms, the higher content of that element should be expected in particular morphological portions of plants.

The interest of particular metals in dust fallout resulted from the necessity of answering the question how the directly bioavailable amounts of elements in soil can change, as well as potentially bioavailable amounts of particular metals can change during the plant vegetation period.

Metals present in the dust fallout are the direct additional source of its supplement from sources in surface layer of soil. They may be subject to direct sorption on the plant surface in dissoluble fraction, mainly through the laminae.

It should be added that, as a result of microbiological processes or soil pH changes, during the acid rain falls a plant may also gain some amounts of metals from insoluble fraction in the total fallout which are relatively high. For example: cadmium in insoluble fraction is 126.4 mg·kg^{-1} and in dissoluble fraction 104.00 mg·kg^{-1} (Table 5). Cd, Ni, Pb, and Zn had the highest content in insoluble fraction in July and October. The most intensive growth of plants in June was accompanied by the biggest amounts of Cd-33.67, Ni-14.03, Pb-336.70, Zn-1599.33, and Mn-1,568.37 (mg·kg^{-1}) in bioavailable fraction.

Comparing the results of speciational analysis of metal content in soil and contents of metals in the dust fallout on the examined six stands representing characteristic physiographic districts of Wisła, as the result of the above-described metal imission process, its much higher contents in given habitat element might be observed as the difference between background values (10th percentile) and incidental values (95th percentile). This problem is particularly important because the occurrence of bioavailable elements with toxic features in a relatively large amount was presented in the paper in comparison with background amounts (10th percentile). This problem was indicated by Ernst and Fairbrother [22, 23].

The problem of a transboundary emission influence on the examined area is even more important regarding the fact that on this area it is very popular to collect medicinal plants for herbal prevention purposes.

Conclusions

1. Cd, Pb, Zn, Fe contents in soil above the geochemical background (as well as in fallout dust) show the influence of transboudary emission on the Wisła environment.
2. The long-range emission of Pb, Cd, Zn, Ni, Cr, Cu, Mn, and Fe to the Wisła area and acid reaction of soil results in an increase of their mobility and bioavailability for plants.
3. The bioavailability of chemical forms of metals in soil (exchangeable and adsorbed form) is a basic source of these contents in stinging nettle.

References

1. SALEMAA M., DEROME J., HELMISAARI H., NIEMINEN T., VANHA-MAJAMAA I. Element accumulation in boreal bryophytes, lichenes and vascular plants exposed to heavy metal and sulphur deposition in Finland. Sci. Total Environ. **324**, 141, **2004**.
2. PARPAN V.I., SHPARYK Y.S. Heavy metal pollution and forest healt in the Ukrainian Carpathians. Environ. Pollut. **130**, 55, **2004**.
3. J.L. No. 60, item 311, **1985** [In Polish].
4. GRODZIŃSKA-JURCZAK M., GODZIK B. Air pollution and atmospheric precipitation chemistry in Poland – a review. Environ. Rev. **7**, (2), 69, **1999**.
5. MILL W. Transboudary air pollution with acidogenic substances with special regard to Silesia. Problemy Ekologii **8**, 296, **2004** [In Polish].
6. HATTORI H. Decomposition of organic matter with previous cadmium adsorption in soil. Soil Sci. Plant Nutr. **42**, 745, **1996**.
7. CHŁOPECKA A. Forms of trace elements from inorganic sources in soil and amounts found in spring barley. Water, Air, Soil Pollut. **69**, 127, **1993**.
8. YONG R.N., GALVEZ-CLOUTIER R., PHADUNGCHEWIT Y. Selective sequential extraction analysis of heavy metals retention in soil. Can. Geoch. J. **30**, 834, **1993**.
9. IIN Q., ZI-JIAN W., XIAO-QUAN S., QIANG T., BEI W., BIN C. Evaluation of plant availability of soil trace metals by chemical fractionation and multiple regression analysis. Environ. Pollut. **91**, 309, **1996**.
10. TEMPLETON D. M., ARIESE F., CORNELIS R., DANIELSSON L. G., MUNTAU H., VAN LEEUWEN H. P., ŁOBIŃSKI R. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000). Pure Appl. Chem. **72**, 1453, **2000.**
11. HLAVAY J., PROHASKA T., WEISZL M. WALTER W. W., STRINGEDER J. G. Determination of trace elements bound to soil and sediment fraction. Pure Appl. Chem. **76**, 415, **2004**.
12. RUDD T., LAKE D.L., MEHROTRA J., STERRITT R.M., KIRK P.W.W., CAMPBELL J.A., LESTER J.N. Characterisation of metal forms in sewage sludge by chemical extraction and progressive acidification. Sci. Total Environ. **74**, 149, **1988**.
13. SALMINEN R., BATISTA M.J., BIDOVEC M. Geochemical Atlas of Europe, Part 1 – Background Information, Methodology and Maps. Geological Survey of Finland, Espoo. http//gtk/publ/foregsatlas, **2005**.
14. IUSS Working Group WRB. World reference base for soil resources 2006. World Soil Resources Reports 103, FAO, Rome, **2006**.
15. BURCZYK J., WIECHUŁA D., MIROSŁAWSKI J., DORDA E., PAUKSZTO A., ROCHEL R., KWAPULIŃSKI J. The plants' contamination in range of industrial emission on example of Cieszyn. Ochr. Pow. i Probl. Odpadów **4**, 124, **1996** [In Polish].
16. MIROSŁAWSKI J., KWAPULIŃSKI J., KOWOL J., WIECHUŁA D., PAUKSZTO A., ROCHEL R. Speciation of Pb in soil. Zesz. Nauk. Komitetu "Człowiek i Środowisko PAN **21**, 79, **1998** [In Polish].
17. LIS J., PASIECZNA A. Geochemical Atlas of Upper Silesia. Państwowy Instytut Geologiczny, Warszawa, **1995** [In Polish].
18. KOWOL J., KWAPULIŃSKI J., PAUKSZTO A., GROMULSKA E., GOSZYK E. Concentration of heavy metals in the dust deposited on the coltsfoot and stinging nettle leaves in the Vistula area Pol. J. Environ. Stud. **15**, (2A), 381, **2006**.
19. REIMANN C., GARRETT R.G. Geochemical background – concept and reality. Sci. Tot. Environ. **350**, 12, **2005**.
20. GAŁUSZKA A. A review of geochemical background concept and an example using data from Poland. Environ. Geol. **52**, 861, **2007**.

21. KARCZEWSKA A., SZOPKA K., KABAŁA C., BOGACZ A. Zinc and lead in forest soil of Karkonosze National Park – data for assessment of environmental pollution and soil monitoring. Pol. J. Environ. Stud. **15**, (2A), 336, **2006**.
22. ERNST W.H.O. Bioavailability of heavy metals and decontamination of soil by plants Appl. Geochem. **11**, 163, **1996**.
23. FAIRBROTHER A., WENSTEL R., SAPPINGTON K., WOOD W. Framework for Metals Risk Assessment. Ecotox. Environ. Safe. **68**, 145, **2007**.