

## The concentrations of trace metals in plants from phosphogypsum waste heap in Wiślinka, northern Poland

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**Abstract.** The aim of this work was determination of trace metals (Pb, Zn, Ni, Cu and Fe) in different plants collected in the vicinity of phosphogypsum waste heap in Wiślinka (northern Poland). The concentrations of trace metals were determined by two methods: AAS (atomic absorption spectrometry) and OES-ICP (atomic emission spectrometry with inductively coupled plasma). Enhanced levels of iron were observed in all the analyzed samples. This fact can be explained by the higher content of iron in the groundwaters of Żuławy Wiślane, where concentration of iron was 60 mg/l. The trace metals concentrations in plant samples from phosphogypsum waste heap recorded in this study are generally higher than in control sites. In this study the relationship is shown between atmospheric trace metals deposition and elevated trace metals element concentrations in plants and topsoils, especially in the vicinity of phosphogypsum waste heap.

**Keywords:** trace metals, plants, phosphogypsum waste heap, Wiślink (northern Poland)

### Introduction

Trace metals may be defined as metals occurring at 1000  $\mu\text{g g}^{-1}$  or less in the earth's crust and may be classified as heavy or light with respect to density. Trace heavy metals have densities greater than 5  $\text{g cm}^{-3}$  whereas light metals less than 5  $\text{g cm}^{-3}$  (Duffus, 1980; Osuji and Onjuke, 2004). We can divide them into four groups: elements of a very high degree of potential threat to the environment (Cd, Hg, Zn, Pb, Cr, Ag, Au, Sb, Sn, Tl), elements with a high degree of potential threat to the environment (Mn, Fe, Se, Mo), elements of moderate potential threat to the environment (Ni, Co, V), and elements with a low degree of potential threat to the environment (Zr, Ta, Nb, La) (PIOŚ, 1995). Trace metals in the environment are the result of natural geochemical processes, as well as of numerous anthropogenic sources (Allowey and Ayres, 1999). To the natural geochemical processes belong: weathering of rocks, evaporation of the oceans, volcanic eruptions, forest fires and soil processes (PIOŚ, 1995). The anthropogenic sources include mining and smelting of metal ores, agricultural materials (fertilizers and waste used for fertilizing, food preservatives, waste from intensive farming); energy based on burning coal and lignite, metallurgy, electronics, waste disposal and chemical industry (Allowey and Ayres, 1999). The natural content of heavy metals in the environment is very differentiated, because of the large diversity of properties of environmental media (air, soil, plants, or

water) (Wolak et al, 1995). Content excess of heavy metals in plants can be negative on their development. In contaminated areas bodies of plants produced adaptation and defense mechanisms which involves precipitation of excess metal in crystalline forms or salt deposition on the tips of the leaves. This effect can explain improper size and form of plants in comparison with those grown on uncontaminated areas (Kabata-Pendias and Pendias, 1993).

### Materials and Methods

The crop and meadow plant samples were collected from a private household I and II, which were situated at a distance of a 900 and 400 meters from the phosphogypsum waste in Wiślinka (northern Poland), respectively, in April 2009 and 2010 (Fig. 1). For comparison the same crop and meadow plants were collected in Osiek. The analyzed plants were separated into green parts and root. Obtained results of trace metals concentration in analyzed plants are given as an average of three experiments conducted for each sample. The concentrations of trace metals (Fe, Pb, Ni, Zn, Cu) were determined by two methods: AAS (atomic absorption spectrometry) and OES-ICP (atomic emission spectrometry with inductively coupled plasma). The detection limit for all analyzed trace metals was 0.005  $\text{mg L}^{-1}$ .

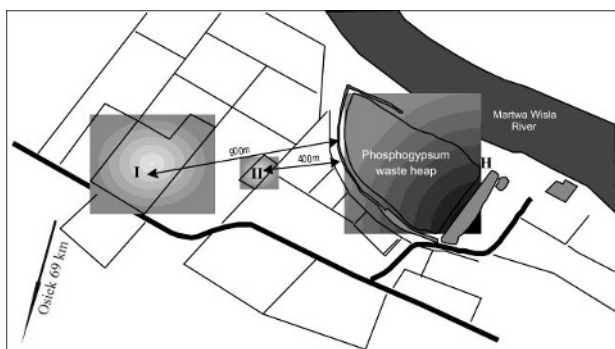


Fig.1 The places of analyzed plants samples collected

## Results and Discussion

The obtained results of trace metals in crop and meadow plant samples are given in Tables 1–3. The uptake of metals concentrations by roots depends on speciation of metals and soil characteristic and type of plants species. Atmospheric metals are deposited on plant surfaces by rain and dust, too (Srinivas et al., 2009). The lead contents in analyzed crop plants vary from 1.9 d. wt.  $\mu\text{g g}^{-1}$  to 29.4  $\mu\text{g g}^{-1}$  d. wt. for green parts and from 13.7 d. wt.  $\mu\text{g g}^{-1}$  to 77.0  $\mu\text{g g}^{-1}$  d. wt. for root. The values of zinc concentrations in analyzed plants were between 33.8–89.8  $\mu\text{g g}^{-1}$  d. wt. in green parts and between 43.5–185.5  $\mu\text{g g}^{-1}$  d. wt. in root. Nickel concentrations in analyzed samples range from 4  $\mu\text{g g}^{-1}$  to 28.2  $\mu\text{g g}^{-1}$  d. wt. in green parts and from 2.8  $\mu\text{g g}^{-1}$  d. wt. to 57.4  $\mu\text{g g}^{-1}$  d. wt. in root. Copper concentration in green parts of cultivated plants ranged between 0.5  $\mu\text{g g}^{-1}$  d. wt. and 27.5  $\mu\text{g g}^{-1}$  d. wt., while values in root were between 2.8  $\mu\text{g g}^{-1}$  d. wt. and 107.0  $\mu\text{g g}^{-1}$  d. wt. The iron concentrations in cultivated plants are between 75.8  $\mu\text{g g}^{-1}$  d. wt. and 568.4  $\mu\text{g g}^{-1}$  d. wt. for green parts and between 476.5  $\mu\text{g g}^{-1}$  d. wt. and 897.4  $\mu\text{g g}^{-1}$  d. wt. for root (Tab. 1). The remarkable high trace metals concentrations in root of analyzed samples may be related to kind of root. The higher concentrations were estimated in storage root system than fibrous root system. The diverse structures of analyzed plant roots (elongated taproots for garden radish and red beet, taproot system for carrot and parsley (Mowszowicz, 1986; Szafer et al., 1953), fibrous root systems for garden lettuce, onion, and leek) fundamentally influence the intake amounts of trace metals forms (Boryło and Skwarzec, 2011). The data stated that the transfer of trace metals into plants via roots is higher than transfer from atmospheric fallout. The leaves of vegetables such as red beet, garden radish and onion shows the highest concentrations of trace metals, because their leaves are most exposed part of plant to the environmental pollution due to the their large surface areas. Among meadow plants the highest contents of trace metals were noticed for plants which were collected in the vicinity of phosphogypsum waste heap.

The lowest trace metals contents were calculated for weeds, which were collected from uncontaminated area. Moreover, the highest trace metals concentrations were estimated for iron in root of plants (between 437.5  $\mu\text{g g}^{-1}$  d. wt. and 6642.9  $\mu\text{g g}^{-1}$  d. wt.), the lowest for copper (between 22.5  $\mu\text{g g}^{-1}$  d. wt. and 59.1  $\mu\text{g g}^{-1}$  d. wt.)

(Tab. 2 and 3). Among green parts of analyzed meadow plants the highest contents of trace metals were measured for iron, too (between 420.6  $\mu\text{g g}^{-1}$  d. wt. and 657.0  $\mu\text{g g}^{-1}$  d. wt.), the lowest for nickel (between 35.3  $\mu\text{g g}^{-1}$  d. wt. and 83.8  $\mu\text{g g}^{-1}$  d. wt.) (Tab. 2 and 3). The higher concentrations of trace metals were observed in root and green parts for *Potentilla anserina* in comparison to *Taraxacum officinal*, although *Taraxacum officinal* is used in the investigation of trace metals pollution. The higher content of trace metals in silverweed (*Potentilla anserina*) is probably associated with the silvery hairy character of leaves as opposed to the shiny and smooth character of dandelion leaves. These hairy surfaces could adsorb higher concentrations of trace metals from fallout unlike the smooth surface of leaves (Boryło and Skwarzec, 2011). Among the weeds the concentrations of trace metals were differences. Generally, the higher contents of trace metals in green parts were measured for Ni and Cu, but in roots of analyzed plants were estimated higher concentrations of Pb, Fe and Zn. The results shows that the vegetables and weeds studied appears to be rich in iron, too. The amount of metal accumulated by a plant is species-dependent and refers decisively to its morphological structure (Chiarenzelli et al., 2001, Rosamilia et al., 2004). The numerous studies show the increase of metal content in plants samples in the surroundings of contaminated areas (smelters, steelworks, power stations, mining sites or mixed industrial centres) (Boryło et al, 2011; Jeran et al, 1995). On the basis of values of trace metals concentrations in edible plants from phosphogypsum waste zone and uncontaminated area from Osiek, it was calculated that contaminations of vegetables from private household are much higher, varied considerable and range from 2.1 for Pb, 3.7 for Zn, 2.8 for Ni and 3.2 for Fe in green parts to 11.8 for Pb, 12.2 for Zn, 9.4 for Ni and 5.5 for Fe in root times higher in comparison to non-contaminated vegetables (control samples). Much higher concentrations of heavy metals in the samples of analyzed crops and grassland, which were obtained in Wiślinka compared to values measured in uncontaminated area indicate that another source of pollution is also the phosphogypsum waste heap.

## Conclusion

In this study the trace metals concentration in plants samples was considered as a means to get insight into the pollution of environment around the phosphogypsum waste heap in Wiślinka (northern Poland). In the phosphogypsum waste heap area the trace metals were reported for all the plants samples in higher concentrations compared with control area. The content of trace elements in analyzed plants samples varied widely, depending upon the composition of the soil, which was enriched with phosphogypsum particles and other environmental factors, but the detailed mechanisms are still unknown. This study shows that industrial pollutions around phosphogypsum waste heap in Wiślinka are an important source of trace metals in crop and meadow plants. The analyzed cultivated plants from Wiślinka area may provide larger amounts of trace metals to our body.

Tab.1 Average trace metals concentration in crop plants collected in April 2009 from private household II and Osiek (\*) (n=3)

Samples	Pb	Zn	Ni	Cu	Fe
carrot (green parts)	12.4±9.0	35.0±6.0	5.9±0.8	14.5±1.2	375.5±6.2
carrot (root)	13.7±9.0	b.d.l.	57.4±3.7	89.6±5.1	546.0±7.8
parsley (green parts)	1.9±0.1	35.8±6.0	2.9±2.1	15.1±3.3	580.8±6.4
parsley (root)	14.1±8.0	43.5±7.1	2.8±2.0	2.8±0.6	897.4±19.1
red beet (green parts)	19.8±12.0	60.4±4.6	9.4±0.6	18.1±0.5	346.2±7.3
red beet (root)	77.0±9.6	185.5±16.5	48.5±5.1	107.0±7.9	476.5±3.5
onion (green parts)	29.4±12.8	66.0±32.6	28.2±3.3	27.5±3.8	568.4±28.3
onion (root)	56.9±29.1	133.1±19.1	51.3±5.3	71.8±1.9	761.9±9.5
leek (green parts)	11.2±8.3	33.8±5.8	4.0±1.1	9.6±0.4	116.1±2.5
leek (root)	38.1±7.7	56.1±10.1	9.7±1.0	b.d.l.	420.3±2.6
garden radish (green parts)	b.d.l.	57.7±30.6	b.d.l.	b.d.l.	75.8±16.3
garden radish (root)	73.0±6.4	78.2±4.3	16.7±1.4	b.d.l.	199.7±3.5
garden lettuce (green parts)	27.9±2.8	89.8±6.0	15.0±0.4	0.5±0.1	341.4±3.9
garden lettuce (root)	b.d.l.	177.1±10.8	b.d.l.	b.d.l.	777.1±9.8
carrot (green parts)*	14.9±2.6	33.0±0.1	5.0±1.2	b.d.l.	153.8±4.5
carrot (root)*	4.9±1.2	23.5±3.0	7.7±1.2	b.d.l.	62.1±2.2
parsley (green parts)*	12.0±8.8	33.4±3.9	4.7±0.9	b.d.l.	262.5±7.4
parsley (root)*	b.d.l.	b.d.l.	b.d.l.	b.d.l.	60.3±2.7
onion (green part)*	13.1±5.6	b.d.l.	8.2±2.1	b.d.l.	130.8±3.3
onion (root)*	6.0±3.1	10.1±5.4	4.9±0.6	b.d.l.	69.4±1.9
garden lettuce (green parts)*	9.9±4.5	36.5±4.3	5.8±1.8	b.d.l.	208.3±3.1
garden lettuce (root)*	12.2±4.6	21.7±3.6	7.2±1.0	b.d.l.	544.3±5.7

b.d.l. – below the detection limit; n – number of individuals

Tab.2 Average trace metals concentration in *Taraxacum officinale* samples collected in April 2009 from the area around the phosphogypsum waste heap and Osiek (n=3)

Samples	Pb	Zn	Ni	Cu	Fe
green parts (*)	174.5±30.4	69.1±19.1	35.3±2.5	38.2±2.5	420.6±7.4
root (*)	204.4±29.5	133.7±20.8	56.9±10.9	52.5±3.5	477.0±5.8
green parts (**)	416.1±28.8	330.4±7.4	83.8±14.9	90.8±4.0	546.1±13.4
root (**)	108.8±28.9	1888.6±29.8	53.2±5.5	22.5±1.7	437.5±13.2
green parts (*)	36.0±5.2	86.0±2.6	b.d.l.	b.d.l.	527.5±13.0
root (*)	39.2±3.3	84.5±1.2	b.d.l.	b.d.l.	1080.7±26.8
green parts (***)	b.d.l.	89.9±21.2	b.d.l.	35.9±4.3	107.7±8.2
root (***)	b.d.l.	111.6±3.2	b.d.l.	64.2±2.8	424.8±7.6

(\*) private household I, (\*\*) area around retention reservoir, (\*\*\*) control plant, b.d.l. – below the detection limit; n – number of individuals

Tab.3 Average trace metals concentration in *Potentilla anserina* samples collected in April 2009 from the area around the phosphogypsum waste heap and Osiek (n=3)

Samples	Pb	Zn	Ni	Cu	Fe
green parts (*)	186.0±30.0	637.3±23.1	88.6±6.9	206.2±3.0	627.9±11.8
root (*)	185.6±22.3	86.7±14.1	58.1±4.8	42.2±1.9	2903.1±42.2
green parts (**)	158.0±14.3	523.1±24.6	66.4±3.9	165.4±3.4	657.0±12.3
root (**)	398.7±32.5	207.4±13.1	79.5±7.8	59.1±1.9	6642.9±79.0
green parts (*)	27.3±8.1	90.6±5.0	b.d.l.	b.d.l.	639.2±7.4
root (*)	20.0±5.6	53.6±3.5	b.d.l.	b.d.l.	881.6±9.5
green parts (***)	9.6±2.9	60.2±2.6	b.d.l.	b.d.l.	436.5±8.8
root (***)	27.1±8.1	89.9±4.9	b.d.l.	b.d.l.	639.8±7.4

(\*) private household I, (\*\*) private household II, (\*\*\*) control plant, b.d.l. – below the detection limit; n – number of individuals

## Acknowledgments

The authors would like to thank the Ministry of Science and Higher Education for the financial support under grant DS/8120-4-0176-12.

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