Pol. J. Environ. Stud. Vol. 22, No. 2 (2013), 347-356

Original Research

The Concentration of Trace Metals in Selected Cultivated and Meadow Plants Collected from the Vicinity of a Phosphogypsum Stack in Northern Poland

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Received: 26 April 2012
Accepted: 21 November 2012

Abstract

The aim of this work was the determination of trace metals (Pb, Zn, Ni, Cu, and Fe) concentrations in different plants collected in the vicinity of a phosphogypsum stack in Wiślinka (northern Poland). The measurements 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 and can be explained by the higher content of this element in the groundwaters of Żuławy Wiślane. The trace metal concentrations in plant samples from the phosphogypsum stack recorded in this study are significantly higher than in control sites. The relationship between atmospheric trace metals deposition and elevated trace metals concentrations in plants and top soil layers, especially in the vicinity of the phoshpogypsum stack, was shown in this study, as well as the discharge of trace metals and other pollutants from the phosphogypsum stack, resulting from industrial human activity. The considerably high concentrations of select trace metals in vegetables collected from the vicinity of the phosphogypsum stack obtained in this study can lead to the conclusion that consumption of these vegetables for a longer period of time can harm and adversely affect human health.

Keywords: trace metals, plants, phosphogypsum stack, Wiślinka, northern Poland

Introduction

Trace metals can be defined as metals occurring at 1,000 $\mu g \cdot g^{-1}$ 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 $g \cdot cm^{-3}$, whereas light metals are less than 5 $g \cdot cm^{-3}$ [1, 2]. 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) [3].

Trace metals in the environment are the result of natural geochemical processes, as well as of numerous anthropogenic sources [4]. The natural geochemical processes are: weathering of rocks, evaporation of the oceans, volcanic eruptions, forest fires, and soil processes [3]. 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, automobile exhaust, heavy-duty electric power gen-

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erators, electronics, waste disposal, and chemical industry, irrigation with wastewater, adjacent industrial activity, and use of pesticides in agriculture [4-6]. The natural content of heavy metals in the environment is differentiated because of the large diversity of properties of environmental media (air, soil, plants, or water) [7]. Plants intake trace metals from the environment through air, water, and food. Excessive content of heavy metals in plants can have a negative influence on their development. In the contaminated areas, plants produced adaptive and defensive mechanisms that involve precipitation of excess metal in crystalline form or salt deposition on the tips of the leaves. This effect can be explained by the improper size and form of plants in comparison with those grown in uncontaminated areas [8]. The plants growing in a polluted environment can accumulate trace metals at high concentrations, causing a serious risk to human health [9-11]. The main sources of trace metals in plants are the air from which the metals were absorbed by leaves and soil from which metals were taken up by roots. The metal contents in soils are divided into four degrees:

I degree of contamination – soils of elevated content of heavy metals;
II degree of contamination – soils slightly polluted with heavy metals;
III degree of contamination – soils of average content of heavy metals;
IV degree of contamination – soils heavily polluted with heavy metals [12].

Phosphogypsum is a primary by-product of the wet-acid process for producing phosphoric acid from phosphate rock. Phosphate production generates a large quantity of phosphogypsum, which is stored in huge piles called "stacks." The production of each ton of phosphoric acid is accompanied by the production of 4½ tons of phosphogypsum [13]. The phosphogypsum waste heap in Wiślinka is permanently integrated into the landscape of Żuławy Gdańskie (northern Poland) and is the result of deposition of the by-product produced by the Phosphoric Fertilizers Industry in Gdańsk. In the Wiślinka stack the estimated activity in 16 mln ton of phosphogypsum contains about $10.5 \cdot 10^9$ Bq for ^{210}Po and $1.6 \cdot 10^9$ Bq for $^{234+238}$U [14].

According to the ordinance of the Polish Ministry of Environmental Protection, phosphogypsum is not a hazardous waste but it is treated as production waste. The phosphorites (the main components in production) were transported to Gdańsk by the Phosphoric Fertilizers Industry from North Africa (Morocco). Phosphate rock, which is processed to make phosphoric acid, contains naturally occurring radionuclides, a large number of impurities, such as calcium fluoride, chlorides, chromium, elements of rare earth, and also some trace metals in such concentrations which, according to the U.S. EPA, may pose a chemical hazard to human health and the environment.

Analysis of samples from various places shows that the phosphogypsym contained arsenic, lead, cadmium, chromium, fluoride, zinc, antimony, and copper at concentrations that may pose significant health risks. These trace metals may also be leached from phosphogypsum and migrate to nearby surface and groundwater resources [13]. Based on total concentration and element transfer factors (TF) as criteria for examining the potential environmental risk of waste with respect to ores, it was observed that most trace elements are only transferred into phosphogypsum at rates of 2-12%. However, Pérez-López and collaborators, based on those studies, suggest that phosphogypsum is a higher emission source of contaminants than the unprocessed rock [15].

The main aim of this study was to investigate the level of trace metals in different vegetables and weeds collected from the area around the phosphogypsum stack in Wiślinka (northern Poland), where their higher concentrations, as well as the concentration of radionuclides, are consequences of anthropogenic emissions from industrial areas (refineries, fertilizers) in the vicinity [11, 16-18]. The determination of metal concentration in vegetables is very important from the point of view of crop yield technology, food nutrition, and health impact [5]. Some authors even suggest that planting crops in industrialized area should be prohibited to avoid health risks to humans [19].

Materials and Methods

Crop plants (garden lettuce *Lactuca capitata*, onion *Allium cepa*, carrot *Daucus carota*, parsley *Petroselinum sativum*, garden radish *Raphanus radicula*, leek *Allium porrum*, and red beet *Beta vulgaris esculenta*) were collected in September 2009 from a private household II situated 400 meters from the phosphogypsum stack. The meadow plant samples [silverweed (*Potentilla anserina*), and dandelion (*Taraxacum officinale*)] were collected in September 2009 and 2010 from a private household I, situated 900 meters from the phosphogypsum stack and around the retention reservoir in the vicinity of the stockpile. The crop plants were sown in a household II in April 2009. For comparison the same crop and meadow plants (control plants) were collected in Osiek (69 km from the phosphogypsum stack in Wiślinka). The collection sites of the analyzed plant samples are shown in Fig. 1.

The analyzed plants were separated into green parts and roots. Obtained results of trace metals concentrations in analyzed plants are given as an average of three experiments

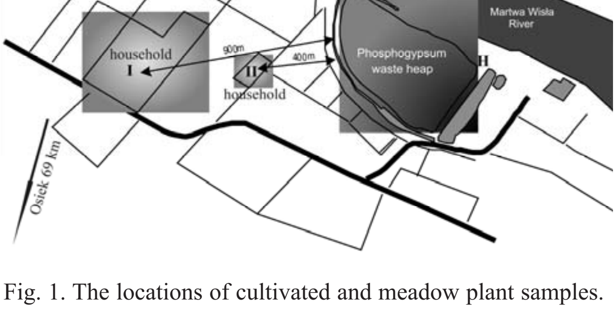

Fig. 1. The locations of cultivated and meadow plant samples.

Table 1. Average values of trace metals concentrations in crop plants collected in April 2009 from garden private II and Osiek (*).

Samples	Pb	Zn	Ni	Cu	Fe
	[μg·g^{-1} d. wt.]				
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 (n = 3)

conducted for each sample. The selected green parts and roots were dried by air in a well ventilated area. The material was then placed in bags for storage of histopathological materials and the process of drying was continued until the samples were air-dried. The dried material was crushed in agate mortar, and samples were packed and stored until analysis in sealed polyethylene bags. Dry plant samples (about 0.5 g) were mineralized using 30 mL mixture of concentrated acids HNO_3 and H_2SO_4 in a volume ratio of 2:1. After mineralization, the samples were diluted with deionized water to 100 mL. The same procedure was used to process the blank reagent, which was obtained from the same reagents and in the same quantities. 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). In the present study we show only the data acquired using the OES-ICP method, for which the detection limit for all analyzed trace metals was 0.005 mg·L^{-1}.

The accuracy and precision of the ICP methods were within 10% based on an international laboratory comparison using International Atomic Energy Agency reference materials (IAEA-359 *Cabbage Leaves*, IAEA-338 *Proficiency Test of Trace Elements in Lichen*) and reference materials INCT-TLI *Tea Leaves* from the Institute of Nuclear Chemistry and Technology in Warsaw.

The reliability of mercury determination method based on international laboratory comparison using reference materials CS-M-1 *Suillus bovinus,* also known as the Jersey cow mushroom. The certified content was 0.174±0.018 μg·g^{-1} d.wt, whereas in the present study the mercury content was 0.190±0.002 and 0.185±0.010 μg·g^{-1} d.wt for I and II series, respectively (n=3).

Results and Discussion

The obtained results of trace metal concentrations in crop and meadow plant samples are given in Tables 1-3 and

Table 2. Average values of trace metals concentrations in dandelion *Taraxacum officinale* samples collected in September 2009 from the area around the phosphogypsum waste heap and Osiek.

Samples	Pb	Zn	Ni	Cu	Fe
	[µg·g^{-1} d. wt.]				
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	1889±30	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.	1081±27
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 (n = 3).

Table 3. Average values of trace metals concentrations in silverweed *Potentilla anserina* samples collected in September 2009 from the area around the phosphogypsum waste heap and Osiek.

Samples	Pb	Zn	Ni	Cu	Fe
	[µg·g^{-1} d. wt.]				
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±42
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	6643±79
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 (n = 3).

presented in Figs. 2-4. The obtained results are differentiated, and remarkable differences were observed between the trace metal concentrations in vegetables and weeds with industrial area around phosphogypsum stack and uncontaminated area (control plants). Slightly higher levels were noticed in plant samples collected from Wiślinka, which indicates that the air near the phosphogypsum stack is enriched with Pb, Zn, Ni, Cu, and Fe. Higher concentrations of trace metals were measured in roots of cultivated plants collected from Wiślinka. Among the analyzed cultivated plants, higher concentrations were observed in storage root systems than in the fibrous root systems. The diverse structures of analyzed plant roots (elongated taproots for garden radish and red beet, taproot system for carrot and parsley, fibrous root systems for garden lettuce, onion, and leek) [20, 21], fundamentally influence the intake amounts of trace metals form [22]. The uptake of metals by roots depends on speciation of metals, soil characteristics and of plants species. The obtained data stated that the transfer of trace metals into plants via roots is higher than intake from atmospheric fallout. The soil and plant samples from the area around the phosphogypsum stack in Wiślinka are enriched in higher amounts of radionuclides of polonium and uranium [14, 22, 23]. Besides, the root and leaves of common chicory *Cichorium Intybus* collected from the area around the phosphogypsum stack accumulated high concentrations of Cd exceeding recommended tolerable levels and thus signifying potential health threats through contaminated crop plants [24]. Unfortunately, the content of trace metals in soil samples were not analyzed, but by analyses of radionuclide concentrations we suggest that the heavy metal content in soil also will be high. The concentrations of trace metals in phosphogypsum are differentiated. Al-Hwaiti [25] suggests that the amounts of heavy metals released into the environment, connected with phosphogypsum stockpiled wastes, seems not to be worrying from the point of view of environmental and human health protection, all the analyzed samples are relatively unpolluted to moderately polluted. Among trace metals, Hg, Cu, and Pb are considered in normal abundance in phosphogypsum, while Ni and Zn had the highest enrichment factors. For example in phosphogypsum from Aqaba and Eshidiya fertilizers plants in Jordania the levels were as follows: 1.17 µg·g^{-1} and 1.15 µg·g^{-1} for Cu, 0.06 µg·g^{-1} and 0.07 µg·g^{-1} for Hg, 18.24 µg·g^{-1} and 17.61 µg·g^{-1} for Ni, 5.58 µg·g^{-1} and 6.50 µg·g^{-1} for Pb, and 78.46 µg·g^{-1} and 69.48 µg·g^{-1} for Zn [25]. The concentration of copper in phosphogypsum samples from Syria was 51.7 µg·g^{-1} [26], but mobility of Cu and Zn in phosphogypsum is classified into degrees: elements with high mobility (Cu) and with moderate mobility (Zn). This suggests that Zn and Cu elements were not only uniformly distributed in the stack, and they are not leached from the phosphogypsum stacks in any significant amount, and then they are not easily transferred to the surrounding aquatic environment and/or soils [27]. Changes in mobility of toxic elements during the production of phosphoric acid are connected with effective transferration of trace metals from the phosphate rock to phosphogypsum waste, as indicated by the element transfer factors, phosphogypsum concentration of the metals in the mobile fraction is higher than phosphate rock and most of these metals in phosphogypsum are bound to organic matter (i.e. oxidizable fraction), unlike phosphate rock, which does not contain metals associated with this fraction [28]. During phosphoric acid production, between 2% and 12% of each trace element in phosphate rock is transferred to phosphogypsum, except for Sr (66%), Ce (56%), Y (41%), and Pb (27%). From the mobile contaminants about 60-100% of the V, Zn, As and U, 10-40% of the Ti, Cr, Cu, Cd, Fe, and Ni, and 2-10% of the Y, Pb, Ce, and Sr would be water-soluble, and hence, potentially bio-available through soil for plants that grow in the vicinity [15]. Among Cd, Cu, Cr, Pb, V, As, and Zn, the

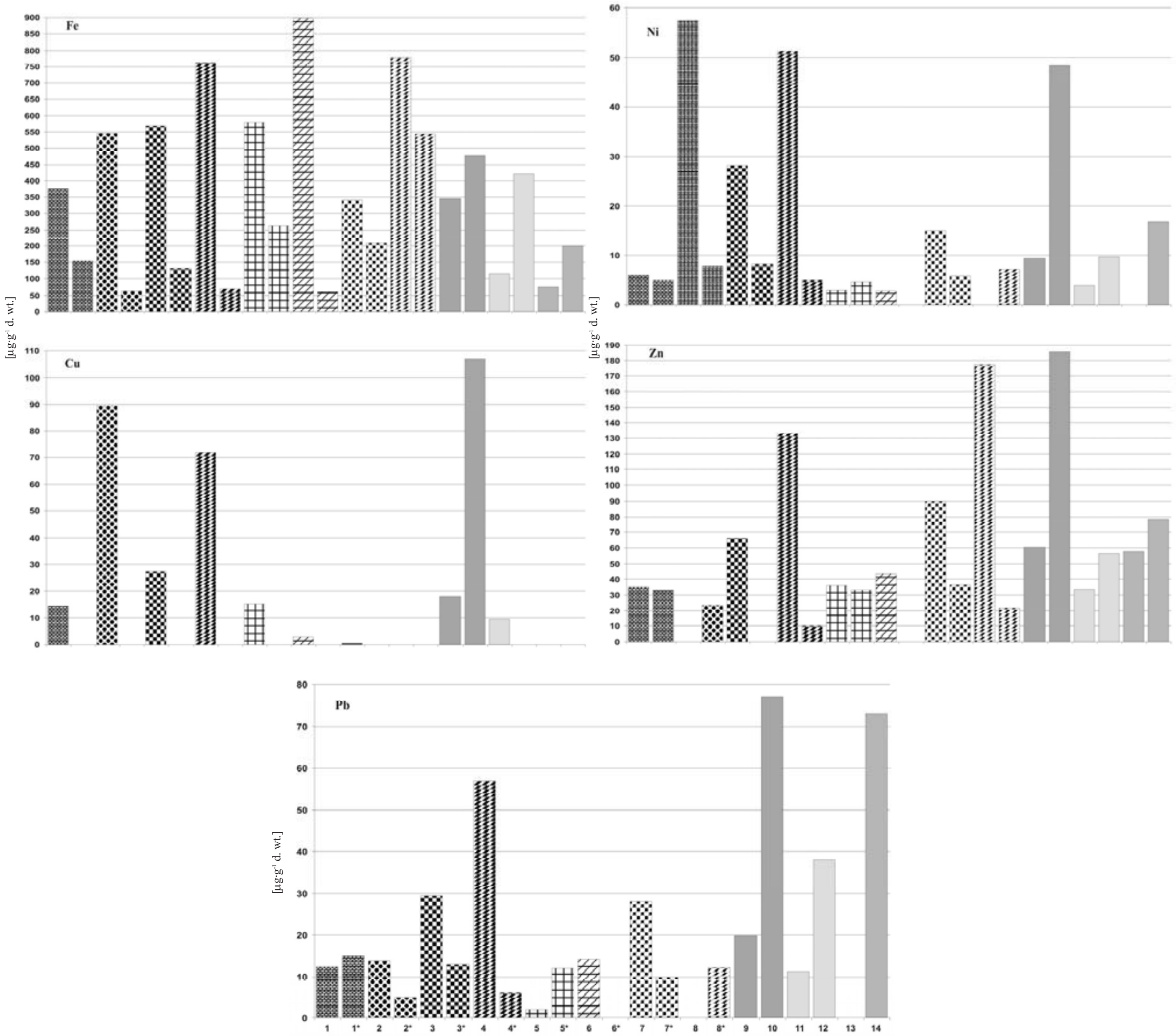

Fig. 2. The average values of lead, zinc, nickel, copper, and iron concentrations in analyzed vegetables collected around the phosphogypsum stack and in Osiek (*); 1 – carrot (green parts), 2 – carrot (root), 3 – onion (green parts), 4 – onion (root), 5 – parsley (green parts), 6 – parsley (root), 7 garden lettuce (green parts), 8 – garden lettuce (root), 9 – red beet (green parts), 10 – red beet (root), 11 – leek (green parts), 12 – leek (root), 13 – garden radish (green parts), 14 – garden radish (root).

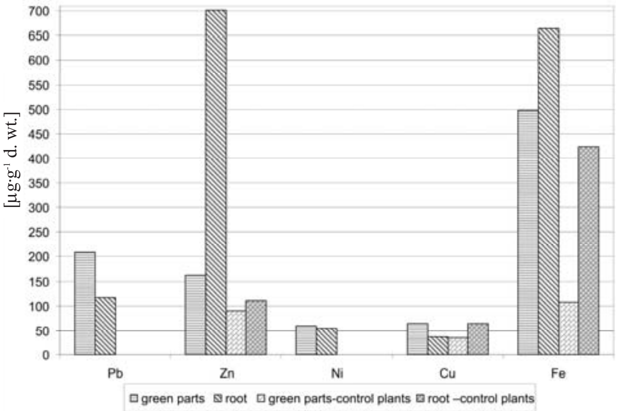

Fig. 3. The average values of trace metals concentration in dandelion collected around the phosphogypsum stack and in Osiek.

all elements, without As, are enriched in phosphoric acid. Assessment of the availability of toxic elements to plants showed that Cd and Cr are not available for plant uptake, whereas Cu, Pb, V, and Zn will be available in direct application of phosphate to soil [29].

On the other hand, among the control-cultivated plants slightly higher concentrations were observed in green parts. The similar effect was noticed in vegetables from the area around the Dabaoshan mine, South China [30], which is probably due to emissions, atmospheric transport, and the deposition process. Large leaves of cultivated plants will be more exposed to environmental pollution because of their surface area. Atmospheric metals are deposited on plant surfaces by rain and dust. Among the weeds the values of trace metals concentrations were variable. Higher contents were measured for Ni and Cu, but in roots of analyzed plants were estimated higher concentrations of Pb, Fe, and Zn. The result shows that the vegetables and weeds studied appear to be rich in iron, too.

Lead

The lead contents in analyzed crop plants vary from 1.9 $\mu g \cdot g^{-1}$ to 29.4 $\mu g \cdot g^{-1}$ for green parts and from 13.7 $\mu g \cdot g^{-1}$ to 77.0 $\mu g \cdot g^{-1}$ for roots. The lead concentrations in vegetables from uncontaminated areas (control samples) (Osiek) are between 9.9 $\mu g \cdot g^{-1}$ and 14.9 $\mu g \cdot g^{-1}$ for green parts and from 4.9 $\mu g \cdot g^{-1}$ to 12.2 $\mu g \cdot g^{-1}$ for roots (Table 1, Fig. 2). The higher lead concentrations were measured in roots of analyzed crop plants from contaminated areas, the lower in green parts. In the control plants the higher contents of lead were observed in green parts. The obtained results of lead content in analyzed samples of crop plants were higher than the content in vegetables from independent agricultural production from the Łódź region in Poland, where its concentration was 0.19 $\mu g \cdot g^{-1}$ d. wt. for garden lettuce, 0.04 $\mu g \cdot g^{-1}$ d. wt. for red beet and carrot [31]. The smaller content of lead in edible parts of plants growing in industrial and semi-urban areas (Visakhapatnam) and uncontaminated areas was observed in India, too (the average 3.55 $\mu g \cdot g^{-1}$ d. wt. and from 0.05 to 3.0 $\mu g \cdot g^{-1}$ d. wt., respectively) [11] and in the edible shoots of vegetables from East Africa (e.g. 0.21 $mg \cdot kg^{-1}$ for leek) [6]. The values, as confirmed by the authors, were below EU and UK statutory limits and the maximum concentration limit in leafy vegetables recommended by the joint FAO/WHO Food Standards Program of 0.3 $mg \cdot kg^{-1}$ fw [6]. According to Europe Commission Regulations (WE) the permissible levels of lead content in garden lettuce, red beet and carrot were estimated at 0.30 $\mu g \cdot g^{-1}$ d. wt. 0.10 $\mu g \cdot g^{-1}$ d. wt. 0.10 $\mu g \cdot g^{-1}$ d. wt., respectively [32]. The permissible limit of lead in vegetables for human consumption is 2.0-2.5 $\mu g \cdot g^{-1}$ d. wt. [33]. In the case of lead, its contents were higher than permissible limits. As numerous authors have suggested, the application of fertilizers and sewage sludge increase the level of Pb in crop plants [34].

Zinc

The values of zinc concentrations in analyzed plants were between 33.8-89.8 $\mu g \cdot g^{-1}$ in green parts and between

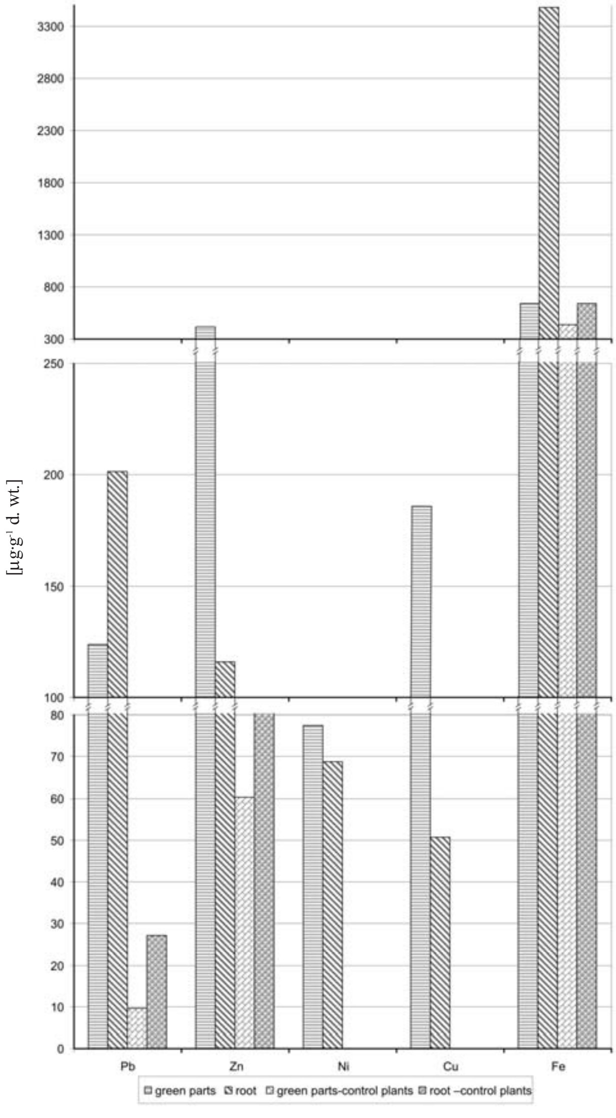

Fig. 4. The average values of trace metals concentration in silverweed collected around the phosphogypsum stack and in Osiek.

43.5-185.5 µg·g^{-1} in roots, but in control plants from Osiek they range from 33.0 µg·g^{-1} to 36.5 µg·g^{-1} for green parts and from 10.1 µg·g^{-1} to 23.5 µg·g^{-1} for roots (Table 1, Fig. 2). The higher zinc concentrations were measured in roots of analyzed crop plants from contaminated areas, the lower in green parts. In the control plants from Osiek the higher content of zinc was characterized for green parts. The obtained results are higher than the content of this metals in crop plants from industrial parts of India (19.93-41.46 µg·g^{-1} d. wt.) [11] and in the edible parts of tropical vegetables from Africa (between 13.7 and 95.3 mg·kg^{-1}) [6]. The obtained results of zinc concentration in the analyzed plants from Wiślinka are higher than the permissible limit of zinc content in edible parts of vegetables for human consumption (the mean is 10-50 µg·g^{-1} d. wt.) [33]. Recommended daily dietary intake of this element is 15 mg, the permissible limit is 10-50 µg·g^{-1} [5, 35, 33]. According to Hashmi [5] a normal body contains from 1.4 to 2.3 g of zinc and it is present in all body cells.

Nickel

Nickel concentrations in analyzed samples occupy a wide range, from 4 µg·g^{-1} to 28.2 µg·g^{-1} in green parts and from 2.8 µg·g^{-1} to 57.4 µg·g^{-1} in roots, but in control samples from Osiek were distinctly lower (4.7-8.2 µg·g^{-1} in green parts, 4.9-7.7 µg·g^{-1} in root) (Table 1, Fig. 4). The obtained results for the analyzed cultivated plant samples from contaminated and uncontaminated areas of northern Poland are distinctly higher than the results collected from Visakhapatnam city (India), where the majority of industries such as refineries and fertilizers are located (1.29-2.62 µg·g^{-1} d. wt.) [11] and the results in vegetables from Baghdad city markets (0.028 µg·g^{-1} for onion, 0.031 µg·g^{-1} for leek, 0.038 µg·g^{-1} for parsley) [34]. The average levels of Ni in selected vegetables purchased in the Tricity area in Northern Poland also are lower. For example, the contents of nickel were as follows: 0.03-0.04 µg·g^{-1} for red beet; 0.03 µg·g^{-1} for onion; 0.02-0.04 µg·g^{-1} for carrot; 0.01 µg·g^{-1} for leek, garden lettuce and garden radish; and 0.3-0.4 µg·g^{-1} and 0.5 µg·g^{-1} for green parts and root of parsley, respectively [36]. The results, according to WHO [37], show nickel concentrations in vegetable in the range of 0.02 to 2.7 µg·g^{-1} d. wt.

Copper

The remarkable differences of copper concentration in green parts and roots of the analyzed cultivated plants were observed and results ranged between 0.5 µg·g^{-1} and 27.5 µg·g^{-1}, and between 2.8 µg·g^{-1} and 107.0 µg·g^{-1}, respectively. The copper concentrations in all the analyzed control plants from Osiek were below the detection limit (Table 1, Fig. 2). Our results are slightly higher than the results from industrial area of Pakistan, where the concentration of iron in vegetables purchased randomly from markets of Karachi (Pakistan) was estimated at 0.8 µg·g^{-1} for stem of onion, 1.9 µg·g^{-1} for root of red beet, 1.0 µg·g^{-1} for root of radish, and 1.2 µg·g^{-1} for root of carrot [5]. As indicated by Pandey, the atmospheric depositions as well as wastewater irrigation have significantly elevated the levels of trace metals (e.g. 5.942 µg·g^{-1} for Ni, 27.462 µg·g^{-1} for Cu, 19.272 µg·g^{-1} for Pb) [38]. The maximum permissible limit for copper in vegetables is 50 µg·g^{-1} [33]. A daily dietary intake of 2 to 3 mg of this element is recommended for humans [5, 35]. In the present study the uptake concentrations of copper in vegetables were within the limits, except the roots of carrot, red beet, and onion, where the contents were higher than permissible limits.

Iron

The iron concentrations in cultivated plants lie between 75.8 µg·g^{-1} and 568.4 µg·g^{-1} for green parts and between 476.5 µg·g^{-1} and 897.4 µg·g^{-1} for roots (Table 1). Much smaller amounts of iron were measured in the analyzed control cultivated plant samples from Osiek (130.8-262.5 µg·g^{-1} for green parts and 60.3-544.3 µg·g^{-1} for roots) (Table 1, Fig. 2). The results obtained in this study are distinctly higher than the results obtained for Łódź agglomeration, where the average concentrations of iron in the edible parts of vegetables, which were purchased at marketplaces, were estimated at 0.0039 µg·g^{-1} for garden lettuce, 0.0013 µg·g^{-1} for red beet, and 0.0011 µg·g^{-1} for carrot [31]. Higher iron concentrations were observed in vegetables from the Pakistan area (13.4 µg·g^{-1} for onion stem, 12.7 µg·g^{-1} for red beet root, 15.5 µg·g^{-1} for radish root, and 11.4 µg·g^{-1} for carrot root) [5], but the values were slightly lower than for the analyzed cultivated plants.

Among meadow plants the highest concentrations of trace metals were noticed for plants collected in the vicinity of the phosphogypsum stack (area of retention reservoir and private household I, which is situated at a distance of 900 m). The higher concentrations of trace metals were measured in the area around retention reservoir, the lower were calculated for weeds, which were collected from the area of private household I (Tables 2, 3, Figs. 3, 4). The concentration of trace metals in green parts of dandelion ranges 36.6-416.1 µg·g^{-1} for Pb, 69.1-330.4 µg·g^{-1} for Zn, 35.3-83.8 µg·g^{-1} for Ni, 38.2-90.8 µg·g^{-1} for Cu, and 420.6-546.1 µg·g^{-1} for Fe. Distinctly higher concentrations were observed in roots of this sample: 39.2-204.4 µg·g^{-1} for Pb, 84.5-1,889 µg·g^{-1} for Zn, 53.2-56.9 µg·g^{-1} for Ni, 22.5-52.5 µg·g^{-1} for Cu, and 437.5-1,081 µg·g^{-1} for Fe (Table 2). The concentrations of select trace metals in green parts of silverweed were between 27.3-186 µg·g^{-1} for Pb, 90.6-637.3 µg·g^{-1} for Zn, 66.4-88.6 µg·g^{-1} for Ni, 165.4-206.2 µg·g^{-1} for Cu, and 627.9-657 µg·g^{-1} for Fe. Different concentrations also were measured in roots: 20.0-398.7 µg·g^{-1} for Pb, 53.6-207.4 µg·g^{-1} for Zn, 58.1-79.5 µg·g^{-1} for Ni, 42.2-59.1 µg·g^{-1} for Cu, and 881.6-6,643 µg·g^{-1} for Fe (Table 3).

For most of the analyzed meadow samples the higher concentrations of trace metals were observed in silverweed *Potentilla anserina* in comparison to dandelion *Taraxacum officinale*, although dandelion is used in the investigation of trace metals pollution (Figs. 3, 4) [39, 40]. Among phytoindicators, dandelion (*Taraxacum officinale*) fulfills most of the requirements as a useful plant in the investigation of trace metal pollution. Relative accumulation (CSRA) values clearly indicate significantly greater uptake of Cd, Cu, Mn, Pb, Zn, and Fe by dandelion than by other plants [39-41]. 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. A similar effect was noticed for polonium (^{210}Po) and uranium isotopes (^{234}U, ^{238}U) [22].

The content of trace metals in leaves and root of dandelion is 20-110 mg·kg^{-1} and 10-60 mg·kg^{-1} for Zn, 1.6-6.5 mg·kg^{-1} and 0.2-5 mg·kg^{-1} for Pb, 5-20 Cu mg·kg^{-1} and 5-25 mg·kg^{-1} for Cu [41]. The content of all analyzed trace metals in plants collected in the area of the phosphogypsum stack significantly exceeded the background levels, but in Osiek area these values insignificantly exceeded the background values. Therefore, the content of some elements found for the dandelion from contaminated and uncontaminated areas in Wiślinka is regarded as noxious according to the data presented in the literature, because as reported Kabata-Pendias and Hemphill the copper content with 100 mg/kg and the zinc content with 400 mg·kg^{-1} is noxious and toxic [42, 43].

Although relatively high concentrations of Zn, Cu, and Pb in dandelion were recorded in the sample from Upper Silesia (Ruda Śląska nad Bytom) in Poland, where the coking plant and steel mill are located (between 186.3 and 213.9 mg·kg^{-1} for Zn, from 25.9 to 64.8 mg·kg^{-1} for Cu and between 110.2 and 37.3 mg·kg^{-1} for Pb) [40], dandelion from the area of the phosphogypsum stack is slightly enriched in trace metals.

The amount of metals accumulated by a plant is species-dependent and refers decisively to its morphological structure [44, 45]. Numerous studies show the increase of metal content in plant samples in the surroundings of contaminated areas (smelters, steelworks, power stations, mining sites, or mixed industrial centers) [18, 46]. On the basis of values of trace metals concentrations in edible plants from the vicinity of the phosphogypsum stack and uncontaminated area from Osiek, it was calculated that the factor of contamination for vegetables from private households is much higher, varied considerably and ranged 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). It is worth noting that the analyzed samples of vegetables from the Osiek area were also very enriched in significant amounts of heavy metals in comparison with other uncontaminated areas. This allows us to conclude that the soil from Osiek can be fertilized with mineral fertilizers. Much higher concentrations of heavy metals in the samples of analyzed crops and grassland (obtained in Wiślinka) compared to values measured in an uncontaminated area (Osiek) indicate that the main source of pollution is also the phosphogypsum stack.

Conclusion

In this study the trace metals concentrations in plant samples were considered as a means to get insight into the pollution of the environment around the phosphogypsum stack in Wiślinka (northern Poland). The assimilability of heavy metals by plants depends on many factors: contents of elements in soil, interactions between metals and soil, their content on the form available for plants (which is dependend on soil reaction), and the ability of the plants itself to absorb certain metals selectively.

The mean metal content in the leaves and root of cultivated plants and weeds in the Wiślinka area significantly exceeded background values, while in the Osiek area they were within the range of concentrations assumed as background. The content of trace elements in analyzed plant samples varied widely, depending on 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 the phosphogypsum stack in Wiślinka are an important source of trace metals in crop and meadow plants.

The analyzed cultivated plants from the Wiślinka area are an important source of essential trace metals and may provide larger amounts of trace metals to the human body than cultivated plants from non-industrial areas. On the basis of values of trace metals concentrations in edible plants from the phosphogypsum stack and uncontaminated area from Osiek, it was calculated that the factor contaminations of vegetables from a private household are much higher, varied considerably, 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). The levels of analyzed trace metals in chosen vegetables were higher than the permissible FAO levels in food. Heavy metal contamination of crops grown around the phosphogypsym stack in Wiślinka may be a health risk to the local population through the consumption of these vegetables.

Acknowledgements

The authors would like to thank the Ministry of Science and Higher Education for financial support under grant No. DS/530-8120-D196-12. The authors would like to thank the Research Group of Environmental Chemistry, Ecotoxicology and Food Toxicology (Dorota Danisiewicz and Leszek Bielawski) under the direction of Professor Falandysz from the Institute of Environmental Sciences & Public Health, University of Gdansk, for their help in performing some of the analyse.

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