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Letters to Editor

Monitoring of Selected Heavy Metals Uptake by Plants and Soils in the Area of Toruń, Poland

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Abstract

Environmental monitoring of selected metals was performed using biota and soil samples. Sampling was carried out during the period March-May and October-November. For the isolation of these analytes, conventional extraction and microwave mineralization techniques were applied. Atomic Absorption Spectroscopy (AAS) equipped with Graphite Furnace (GF) was used to determine heavy metals and macroelements. The obtained data were compared with the respective values recommended by the Polish Standards. Popular bioindicators were used to estimate the level of pollution by heavy metals of Torun, Poland. Application of the established sampling procedures for environmental samples and determination methods for xenobiotics can be successfully applied for the purpose of routine analyses in biomonitoring.

Keywords: biomonitoring, heavy metals, soil, plants

Introduction

The high concentration of heavy metals in soils is reflected by higher concentrations of metals in plants, and consequently in animal and human bodies. The ability of some plants to absorb and accumulate xenobiotics makes them useful as indicators of environmental pollution. The study of excessive concentrations of pollutants in biological matrices has been reported in numerous publications [1-8]. Pine and spruce needles, mosses and grasses are widely used as a specific indicator in the study of a geographical and temporal pattern of pollutants [9-12].

Streit and Strumm [13] classified the exchange of chemicals between soil and plants. They divided the most common methods of assessing metal toxicity to plants from soil into three categories in the conditions closed system:

(i) monitoring of the presence or absence of specific plant ecotypes and/or plant species (indicator plant),

(ii) measurements of metal concentration in tissues of selected species (accumulative bioindicators),

(iii) recording of physiological and biochemical responses (biomarkers) in sensitive bioindicators.

The aim of the present work was to investigate relations between contents of metals in soil and their accumulation in different morphological parts of plants. For this purpose, the concentrations of Pb, Zn, Cd, Cu, Fe, Ca, Mg in these matrices were measured. Popular bioindicators including grasses, mosses, pine needles were used for the estimation of heavy metals pollution of Torun.

Experimental

Reagents and Apparatus

Potassium chloride (POCh, Gliwice, Poland) was used for soil acidity determination. Nitric acid 0.5 M (POCh, Gliwice, Poland) was used for the extraction of metals

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from soil. Solutions of 65% nitric acid, 30% hydrogen peroxide purchased from J.T. Baker (Deventer, the Netherlands) were used for microwave digestion of tissue. Atomic absorption spectroscopy (AAS) analysis results for the extracts were compared with certificate reference soil and plant (Panalytica, Warsaw, Poland). Calibration standards for AAS analysis were purchased from Aldrich-Chemie (Steinheim, Germany).

Instrumental analysis was carried out using the following apparatus:

(i) A set for microwave digestion consisting of a rotor MDR 1000/6/100/110 (MDR Technology, Bergamo, Italy) and a Samsung microwave oven of RE 1200 type (Seoul, Korea);

(ii) A PU 9100x atomic absorption spectrophotometer with a graphite cuvete and autosampler (Philips, Cambridge, England);

(iii) pH meter N5170E (Teleko, Warsaw, Poland).

Sample Collection Procedure

Soil and plant samples (needles *Pinus silvestris L.*, grass *Festuca protensis L.*, moss *Pleurozium schreberi)*

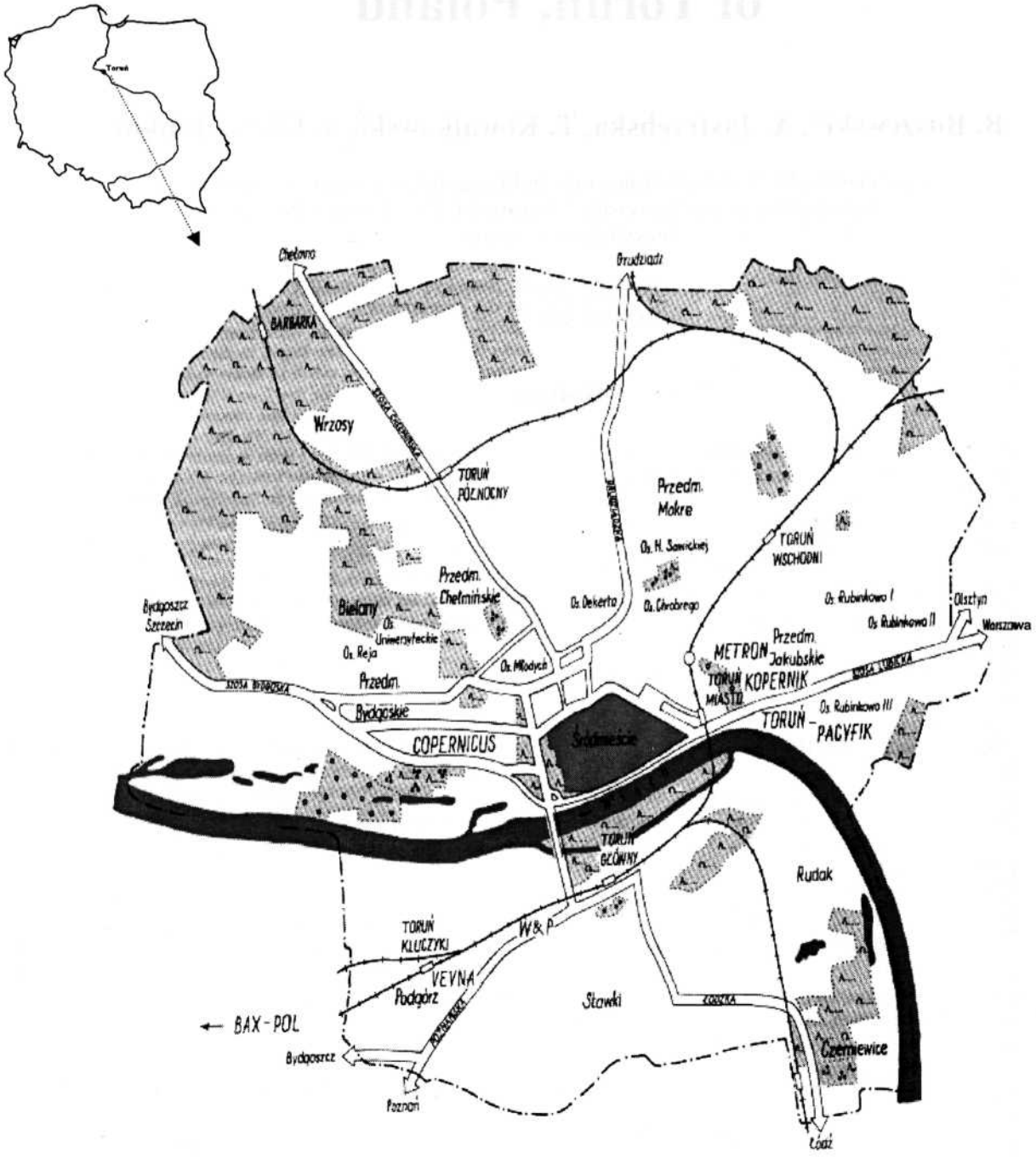


Fig. 1. Localization of the sampling points of plants and soil.

were collected from different sites (Fig. 1) during a few years every March-April and October-November. Totally, thirty samples were taken out from the chosen and marked rectangles 50x100 m. The surface soil samples were from 0-20 cm depth. Clark's procedure [14] for evaluation of homogenity of environmental samples has been used to find out the optimal number at sampling sites to characterize the investigated area. Precision of the analytical results was calculated as the coefficients of variation.

Sample Preparation

The soil samples were dried at a room temperature for 7 days and sieved (2 mm sieve). The dried samples were subjected to a cool extraction with 0.5 M HNO_3 for 30 minutes [15-16]. Pb, Zn, Cu, Mg, Fe and Ca were determined by acetylene-air flame atomic absorption spectrophotomectry and Cd was determined by graphite furnace atomic absorption spectrophotometry. The pH levels of soil layers were also measured.

Samples of grasses, mosses and pine needles were dried for 14 days at room temperature. Experimental plant material was not washed. The needles from different years were first segregated. The samples were microwave digested and the determination of selected heavy metals was done using AAS, FG/AAS [17-18]. The oxidizing medium was 65% HNO_3 (3 ml) and 30% H_2O_2 (1 ml). The mineralization conditions are presented in Table 1 [19].

All results obtained were statistically analyzed and calculated as a dry mass.

Table 1. The procedure of microwave mineralization [19].

Stage	I	II	III	IV	V
Power (W)	240	0	240	400	560
Time (min)	0.5-1	2-7	5	5	5
% of power	30	0	30	50	70

Results and Discussion

The results of the heavy metal concentrations determined in plant tissues and in top layers of soils are presented in Tables 2-4.

Table 2. Concentration of selected metals (mg/kg soil) in soil collected in 1999 year in Torun (n - number of sampling)

	pH_{KCl}	Pb	Cu	Cd	Zn	Fe	Ca	Mg
Autumn (n=54)								
Mean	**4.75**	**16.43**	**9.69**	**0.54**	**19.88**	**234.88**	**309.41**	**35.64**
	± 0.14	± 1.78	± 1.42	± 0.09	± 1.09	± 50.38	± 90.09	± 2.9
Min	4.09	4.60	0.18	1.02	1.60	63.75	9.30	5.00
Max	5.81	60.25	68.75	0.21	120.87	663.12	694.10	134.37
Spring (n=54)								
Mean	**4.25**	**13.70**	**5.03**	**0.51**	**13.52**	**206.99**	**122.66**	**18.16**
	±0.12	± 1.24	± 0.40	± 0.10	± 1.28	± 97.31	± 31.82	± 2.56
Min	4.80	0.50	3.75	1.09	71.25	1.28	3.75	12.50
Max	34.85	15.45	37.15	0.20	375.00	488.75	37.50	65.08

Table 3. Concentration of selected metals in plants collected in 1999 during autumn in Toruń (mg/kg dry mass)

	Pb	Cu	Zn	Fe	Ca	Mg
Grasses (n=32)						
Mean	**21.39**	**20.77**	**79.12**	**325.73**	**5294.15**	**1620.75**
	± 2.30	± 1.39	± 10.48	± 52.52	± 101.63	± 302.51
Min	9.01	5.16	41.48	155.12	2481.50	632.84
Max	45.07	40.40	116.84	654.83	8097.40	2948.40
Mosses (n=31)						
Mean	**12.56**	**4.60**	**39.60**	**335.34**	**441.27**	**287.78**
	± 6.46	± 0.36	± 10.39	± 79.64	± 46.71	± 100.40
Min	9.13	2.62	24.53	233.29	179.38	206.76
Max	18.72	7.15	51.69	484.33	1651.40	437.91
Pine needles (I — III years) (n=33)						
Mean	**8.73**	**7.33**	**63.26**	**241.53**	**1070.70**	**727.95**
	± 0.27	± 0.94	± 20.60	± 54.42	± 195.72	± 114.66
Min	5.80	7.00	48.72	165.92	915.31	559.80
Max	11.51	7.68	79.60	298.13	1275.30	1091.00

The pH values of soils presented in Table 2 classified them as acidic. The pH of spring samples is often higher than the autumn samples. The amount of acid accumulated in soil can be explained by the liberation of acids by plant at the beginning of the vegetation cycle and starting soil-decomposition process.

The concentration of analyzed metals shows some diversity in the studied area. The highest concentrations were observed for macroelements (Fe, Ca, Mg). These result from physicochemical properties of the investigated soils. In case of trace heavy metals, the highest difference between the minimum and maximum value noticed was for Zn (119 mg/kg dry mass in autumn samples and 33 mg/kg in spring sample). The small difference for the spring samples can be explained by an intensive cumulating of the elements by biota. The decrease in heavy metals concentration in soil samples from spring samples was observed.

The concentration of heavy metals in the examined soils did not exceed the limited values for agricultural soils (according to Polish Norms) [20].

The applied acidic extraction allows for the determination of total metal concentrations in soil. The values of total concentration of heavy metals were related to its uptake by plants [16].

The metal concentrations in biosensors, *i.e.* grasses, mosses and pine needles, similarly to soil, show differences (Table 4). The observed differences between minimum and maximum values (for example: grasses Pb - 3, Cu - 35, Zn - 75, Fe - 499, Ca - 5615, Mg - 2315 mg/kg dry mass) are related to a different pollution level of the examined places. The highest concentration of heavy metals were found in plants collected during springtime (Fig. 2) and from the areas localised near high traffic streets, and residential and commercial area with a heavy use of heating appliances (Fig. 1).

Generally, the concentrations of selected metals in plants are in the range of values recommended by the Polish Norms [20]. Only in the case of lead does the mean concentration exceed the admissible standard (limited value - 10 mg/kg dry mass). Special attention should be given to a considerable accumulation of Pb in grasses. The maximum detected concentration was four times higher than the permitted value. It is important to notice that this element negatively influences the physiological processes of plants.

Analysis of metal uptake by plants serving as biosensors permits us evaluation of pollution in the studied area. The concentration of metals in grasses was proportional to those in soil (Fig. 3). A variance analysis (Scheffe's test) was performed to evaluate correlations in plant <=> soil system using StatSoft Statistica 5.0 [21]. Linear correlation coefficients show a distinct dependence between content of heavy metals in plants and soils (Table 4).

Correlation and regularities in the accumulation of selected metals in biota (results from years 1995 - 1998) are presented (Fig. 4).

It can be noticed that the metal contents in grasses were almost unchanged during the study period. The mean concentrations of these elements were as follows: Pb - 25, Cu - 20, Zn - 83 mg/kg dry mass. The small differences of values can be caused by changes of

Table 4. Linear correlation coefficients (R^2) for comparison of the total content of heavy metals in plants and soils (n=31), p = 0.05

Heavy metals	Soil ⇔ grasses	Soil ⇔ pine needles	Soil ⇔ mosses
Pb	0.9520	0.064	0.059
Cu	0.7335	0.035	0.024
Zn	0.4664	0.009	0.095

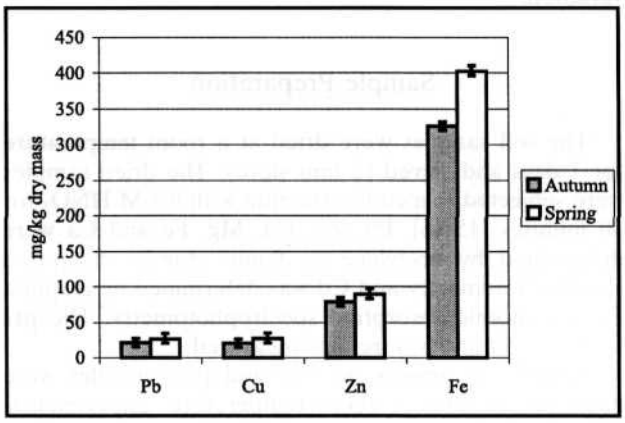
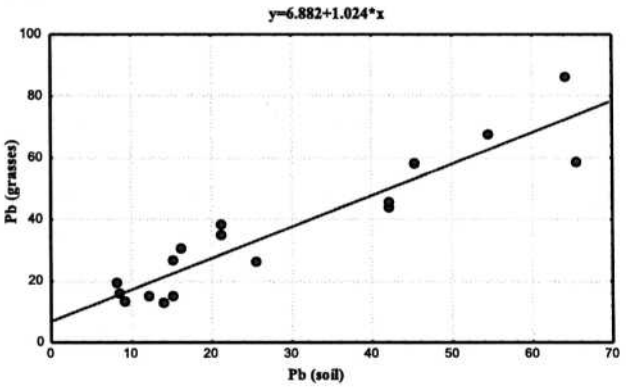


Fig. 2. Concentration of heavy metals in grasses (number of samples, n = 36) sampled in autumn and spring.

Fig. 3. Comparison of Pb concentration in soil and in grass



samples collected in Torun (p=0.02), R^2 = 0.9520.

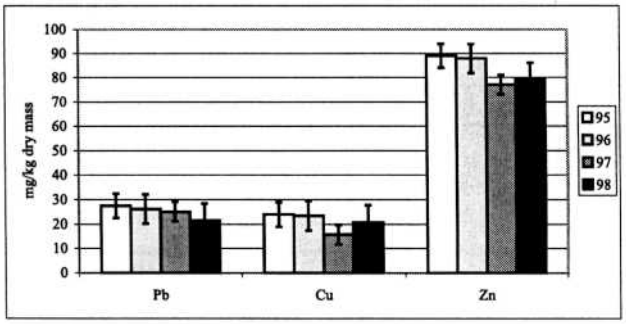


Fig. 4. Comparison of the content of heavy metals in grasses in 1995-1998.

environmental, and atmospheric conditions as well as pollution levels (traffic intensity and conditions in a given area).

Conclusions

Our study proves that plants selected by us accumulate metals (heavy metals and macroelements) in assimilation organs and roots. Thus, they can be recommended as indicators for determination of pollution levels of the environment.

The metal concentrations in soils of the measured area (Toruii, Poland) did not exceed the limited values recommended by the Polish Standards for agricultural soils [22]. Lower amounts of heavy metals in soil samples taken in spring were observed.

The contents of metals in examined plants (grasses, mosses, pine needles) were lower than permitted concentrations, except lead in grasses and mosses. Generally, the concentration of metals decreased with increasing distance from the pollutant emission sources.

Grasses do absorb the contaminants during their relatively short vegetation period, *i.e.* spring-autumn. The concentrations of heavy metals in grasses were proportional to those in soil. For that reason they are very good instruments - biosensors - for observation of the trends in soil composition of pollutants.

The results of investigation were optimization of sampling methods for biological samples and determination methods for xenobiotics in soil and plants. Application of the established sampling procedures and determination methods for xenobiotics in environmental samples can be successfully applied for the purpose of routine analyses in biomonitoring.

This result will serve as a pilot study for further investigation of plant species in bioindication of environmental pollution. We will continue this trend of investigations in our future work.

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References

1. MCCRADY J. K., MAGGARD S. P., Uptake and photodegradation of 2,3,7,8-tetra chlorodibenzeno-p-dioxin sorbed to grass foliage, Environ. Sci. Techol., **27,** 343, **1993.**
2. A. JASTRZEBSKA, B. BUSZEWSKI, Zastosowanie biomonitoringu w ekoanalityce, Chemia i Inzynieria Ekologiczna, **11,** 1097, **1999.**
3. HAUK H., UMLAUF G, MCLACHLAN S., Uptake of gas eous DDE in spruce needles, Environ. Sci. Technol., **28,** 2372, **1994.**
4. FARAGO M. E., Plants as indicators of mineralisation and pollution, in: Plants and the Chemical Elements, VCH, Wienheim, 221, **1994.**
5. GORNA-BINKUL A., KEYMEULEN R., VAN LANGENHOVE H., BUSZEWSKI B., Determination of monocyclic aromatic hydrocarbons in fruit and vegetables by gas chromatography-mass spectrometry, J. Chromatogr. A, **734,** 297, **1996.**
6. PANDOLFINI T., GREMIGNI P., GABBRIELLI R., Bi omonitoring of Soil Health by Plants, in: Biological Indicator of Soil Health and Sustainable Productivity, CAB Interna tional, 325, **1997.**
7. BERTHELSEN B.O, STEINNES E., SOLBERG W., JINGSEN L., Heavy metals concentrations in plants relation to atmospheric heavy metals deposition, J. Environ. Qual., **24,** 1018, **1995.**
8. NAMIESNIK J., WARDENCKI W, Wykorzystanie roslinnosci w biomonitoringu srodowiska, Chemia i Inzynieria Ekologiczna **3,** 189, **2000.**
9. RICHARDSON D. H. S., Metal Uptake in Lichens, Symbio sis, **18,**119, **1995.**
10. BARGAGLI R., BROWN D. H., NELLI L., Metal bi omonitoring with mosses: procedures for correcting for soil contamination, Environ. Pollut., **89,** 169, **1995.**
11. JASTRZEBSKA A., KOWALKOWSKI T., GORNA-BINKUL A., BUSZEWSKI B., Biowskazniki w ocenie stopnia skazenia srodowiska. Modele sorpcji zanieczyszczen, in: Zwiazki organiczne w srodowisku i metody ich oznaczania, BMS, Warszawa, 135, **1998.**
12. JENSEN S., ERIKSSON G., KYLIN H. Atmospheric by persistent organic compounds: monitoring with pine needles, Chemosphere, **24,** 229, **1992.**
13. STREIT B., STRUMM W., Chemical properties of metals and the process of bioaccumulation in terrestrial plants, in Plants as Biomonitors, in: Indicators for Heavy Metals in the Terrestial Environment, VCH, Weinheim, 381, **1993.**
14. SIENKIEWICZ J., Forest site bioindications with plant chemistry representatives of plant material sampling, Ochrona srodowiska i zasobow naturalnych, **14,** 43, **1998.**
15. RAUTER G., Extraction procedures for the determination of heavy metals in contamined soil and sediment, Talanta, **46,** 449, **1998.**
16. NOVOZAMSKY I, LEXMOND T. H. M., HOUBA V. J. G., A single extraction procedure of soil for evaluation of uptake of some heavy metals by plants, J. Environ. Anal. Chem., **55,** 47, **1993.**
17. BROOKS R.R., Plants that Hyperaccumulate Heavy Metals, CAB International, 95, **1997.**
18. GZYL J., Lead and cadmium contaminations of soil and vegetables in the upper region of Poland, Sci. Total Environm., **96,** 199, **1990.**
19. SZABLEWSKI L., JASTRZEBSKA A., BUSZEWSKI B., Microwave methods of sample preparation for the purposes of environmental analysis, Polish J. Environ. Studies, **5,** 13, **1997.**
20. Monitor Polski nr 22 (11.05.1993).
21. SIENKIEWICZ J., Assessment of indicatory role of bilberry (Vaccinium myrtillus L.) in bioindication of site pollution, Ochrona srodowiska i zasobow naturalnych **15,** 29, **1998.**
22. KABATA-PENDIAS A., PENDIAS H, Biogeochemia pierwiastkow sladowych, PWN, Warszawa, 53, **1995.**