Polish J. of Environ. Stud. Vol. 17, No. 1 (2008), 121-128

Original Research

A Preliminary Investigation in Using *Pohlia Nutans* and *Larix Decidua* as Biomonitors of Air Pollution by the Coke Industry in Wałbrzych (SW Poland)

A. Samecka-Cymerman[1]*, K. Kolon[1], A.J. Kempers[2]

[1]Department of Ecology, Biogeochemistry and Environmental Protection, Wrocław University, ul. Kanonia 6/8, 50-328 Wrocław, Poland
[2]Department of Environmental Science, Radboud University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received: June 15, 2007
Accepted: November 6, 2007

Abstract

Concentrations of accumulated heavy metals were compared between the terrestrial bryophyte *Pohlia nutans* and needles and bark of *Larix decidua* collected on a dump situated in the vicinity of coke- and sulphuric acid-producing factories and a municipal thermal-electric power station. The dump consisted of heavily polluted mine and smelter wastes located near Walbrzych (southwestern Poland). The plant samples were compared with material of the same species from the control site. In the examined area needles and bark can be considered as suitable biomonitors for atmospheric pollution for Co, Cu, Ni and Pb. Bioaccumulation abilities of Pb in *P. nutans* and *L. decidua* needles and Ni in *P. nutans* and *L. decidua* bark were similar. Compared to each other needles were better accumulators of Ni and the moss *P. nutans* was a better accumulator of Co and Cu. *P. nutans* was a better accumulator of Co, Cu and Pb compared to bark.

Keywords: bioindication, heavy metal, major axis regression, *Larix*, *Pohlia*

Introduction

Knowledge of the spatial and temporal deposition patterns and concentration levels of trace elements in wild plants should be useful for environmental management and will at least provide information on the ecological impact of human activities and on xenobiotics in natural ecosystems [1]. Plants have been widely used for assessing and monitoring environmental pollution. Among them Bryophytes have been described in literature as being able to intercept, retain and accumulate pollutants. The technique, of analyzing the contents of contaminants in native mosses is known as passive biomonitoring and was first used by Ruhling and Tyler [2]. Also, trees are very efficient at trapping atmospheric particles, which is especially important for urban areas and in the surroundings of industrial facilities so their leaves have been used as indicators and/or monitors of trace metal pollution [3, 4].

Several authors used bark samples to illustrate heavy metal distribution trends in the investigated areas [5-7]. Their use was recommended for larger scale surveys because of their greater availability compared to lichens and mosses [8, 9].

European larch (*Larix decidua* Mill.) grows on slightly acid soils, tolerates soil and air pollution and is frequently used for recultivation of dumps [10, 11]. On older trees of this species the bark is very flaky and heavily ridged with wide fissures, so may be very convenient for biomonitoring purposes [10]. No literature could be

*e-mail: sameckaa@biol.uni.wroc.pl

found comparing the accumulation abilities of bark with those of *Larix decidua* needles of the same tree collected in the investigated heavily polluted area. Based on the assumption that the terrestrial moss *Pohlia nutans* (Hedw.) Lindb. is adequate for biomonitoring purposes [12, 13] and has a tendency to high accumulation of a number of elements, this moss can serve as a base comparing the accumulation and biomonitoring abilities of *Larix decidua* needles and bark.

In this investigation, the hypotheses to be tested are:

1. Atmospheric deposition is the main contribution to the levels of metals in *Pohlia nutans* and in bark and needles of *Larix decidua* investigated in the coke factory in Walbrzych in SW Poland.
2. Larix needles and bark are suitable for biomonitoring pollution.

Materials and Methods

Study Area

The study area consists of a dump in the western part of Walbrzych (southwestern Poland) about 200 m from coke and sulphuric acid producing factories. The dump, abandoned in the early 1980s and not recultivated, consists of material excavated from a nearby black coal mine and ash from a nearby coke factory (working since 1886) and a municipal thermal-electric power station. The investigated dump forms in some parts green, blue, red, white or brown precipitates caused by atmospheric deposition of exhausts of neighbouring factories. Daily gas exhausts of yellow-green breathtaking acrid smoke form in times of mist persistent smog and in times of rain acid deposits. Typical composition of these exhausts may consist of 25% CO, 5-8% CO_2, 0.5-15% methane, 45-56% nitrogen and sulphur oxides in amounts dependent on the quality of coal used for the production of coke [14]. The dump is limited by a forest to the west and a coke factory to the east. The nearby coke factory produces considerable amounts of dust and gaseous pollution which is considered the highest in industrial Lower Silesia [14]. The predominant tree on the dump is *L. decidua* and the predominant moss is *P. nutans.*

Sample Collection and Preparation

At the dump near Walbrzych (N 50° 47', E 16°17') five sampling sites (five square areas of 50 m x 50 m in which both moss and trees occurred) were selected randomly. These sampling sites were at equal distance from the emission sources as they were situated on the top of the dump. In each of the five square areas 5 samples (each sample consisted of a mixture of 3 subsamples mixed and treated as one replicate giving a total of N=25 samples) of the moss *P. nutans* (only the green parts) were collected. Also at the dump five trees per square (50 m x 50 m) area (*L. decidua,* 25 years old) were selected randomly and sampled as follows: a total of three branches from three sides of the outside of the tree crown were cut from each tree at a height of 1.6 m and needles from the three branches were collected and mixed (resulting in one mixed sample per tree) giving a total of N=25 samples. From the same trees, bark flakes of about five mm thickness were cut at 1.2 m above ground level from three sides around the tree, (resulting in one mixed sample per tree), giving a total N=25 samples [8].

In each of the five square areas (50x50 m^2) 5 samples of the topsoil (0-5 cm for mosses and 0-30 cm for trees, each sample consisted of a mixture of three subsamples) were collected, total N=25. Plant remains and stones were removed from the soil samples before transporting them to the laboratory.

The pattern of sampling collection was dependent on the presence of all investigated plants at the same sampling site. Control samples of *P. nutans* and needles and bark of *L. decidua* were collected (according to the same procedure) from a forested control site in the Sowie Mountains (N 50° 44', E 16° 28') at a distance of 14 km E from the dump. According to Vázquez et al. [15], background or reference levels are only applicable if calculated from samples from the region, since they reflect the natural characteristics (especially the climate conditions) of the area where the species occurs. Based on this statement, reference values for the study area were calculated as approximate values for *P. nutans* and *L. decidua* of the control site. The control site consisted of a shallow acid soil which was collected, together with plants giving a total of 5 replicates of soil and plant samples.

As required by the rules set by the Environmental Monitoring and Data Group [16] and within the European Heavy Metal Survey [17] patches of *P. nutans* from the control site and dump mosses had not been exposed directly to canopy throughfall and well exposed to wind. Dead material, soil particles and litter were manually removed from the moss samples. Since the purpose of this study was to estimate the ability of mosses, needles and bark to reflect atmospheric heavy metal deposition, they were not washed prior to analysis [18]. Needles and bark samples were cleaned of debris.

Soil, Dump Substrate and Plant Analyses

Fresh soil samples were used for determination of pH_{H_20} and pH_{KCl} (potentiometrically).

Plant and soil material was dried at 50°C for 48 hours and homogenized. Plant samples were homogenized in a laboratory mill. Soil samples were homogenized with mortar and pestle and coarse material was removed using a 2 mm sieve. Samples (200 mg, in duplicate) were digested with nitric acid (*pro analysi*, 67%) and hydrogen peroxide (*pro analysi*, 35%), during which temperatures were raised to about 95°C until the evolution of nitrous gas stopped and the digest became clear. After dilution to 10 ml, the plant, bark and soil digests were analyzed for Al, Cr, Fe, Mn, Ni, Pb and Zn with Simultaneous Sequential Inductively Coupled Plasma Emission Spectrophotometry SIMSEQ. Co, Cu and Cd were analyzed with a Furnace Atomic Absorption Spectrophotometer Philips PU 9200X.

All elements were determined against standards (BDH Chemicals Ltd, pro analysis quality) and blanks prepared in 0.5 M nitric acid. Blanks and standards contained the same matrix as the samples. All results for soil and plants were calculated on a dry weight basis.

The recovery rates, relative to the results of an interlaboratory study on digesting and analyzing reference materials (Wageningen Evaluating Programmes for Analytical Laboratories, WEPAL), were as follows for each of the investigated elements (percentages with SD): Al (98±4), Cd (94±5), Co (101±4), Cr (104±4), Cu (99±5), Fe (96±5), Mn (105±3), Ni (103±4), Pb (94±5), Zn (102±4). The reference material consisted of pine needles (IPE 761), leaves of *Nymphaea alba* (not coded) and soil (RTH907).

Statistical Analysis

Differences between sampling sites in terms of concentrations of elements in soil, dump substrate, *P. nutans* and *L. decidua* were evaluated by ANOVA on log transformed data to obtain a normal distribution of features according to Zar [19]. The normality of the analyzed features was checked by means of Shapiro-Wilk's W test and the homogeneity of variances was checked by means of Bartlett's test [19, 20].

T-test was applied on log transformed data to compare the concentration of elements in soil, *P. nutans*, *L. decidua* needles and bark between dump and control sites.

In order to remove fluctuations of absolute values and to give clue sources of metals found in the moss, needles and bark, raw data of concentrations were normalized to the soil crustal abundance pattern by calculating the Enrichment Factor (EF) defined as [21]:

$$\mathrm{EF} = \frac{\left(\frac{X}{Al}\right)_{Moss}}{\left(\frac{X}{Al}\right)_{Soil}}$$

The differences in bioconcentration (EF) in *P. nutans*, *L. decidua* needles and bark samples were compared by means of regression analysis. The metal concentrations in the tissues of these plants and bark are not independent because they are related to the location of the site and the amount of metal deposition. ANOVA or other simple tests for comparison of means are therefore not applicable [22]. According to these authors, in the regression analysis, if the null hypothesis is true, when the pairs of values (*P. nutans* and *L. decidua* needles; *P. nutans* and *L. decidua* bark samples) are plotted, a straight line with a slope equal to 1 should be obtained. To conclude if there are differences between the species, a test is done if the slope of the regression line that relates bioconcentrations in *P. nutans* (considered as a good bioaccumulator) and *L. decidua* needles or bark is significantly different from a slope equal to 1. We compared the slopes using the method of Zar [19] suggested by Fernández et al. [22]. An independent variable was not possible to be distinguished so the regression was calculated as a major axis regression [20, 22].

Table 1. Range, mean and SD of pH and concentration (mg kg^{-1}) of elements in soil of dump and control sites; $t_{0.05}$ tabular= 2.01. The data in the column Unpolluted Soils are from Ministerie van VROM [24].

	Dump soil range	mean	SD	Control soil range	mean	SD	t-test	p level	Unpolluted Soils
pH_{H_20}	3.0-5.2	3.9	0.5	5.1-5.3	5.2	0.1	-7.8	<0.001	
pH_{KCl}	2.2-4.8	2.9	0.4	4.1-4.3	4.2	0.1	-4.5	<0.001	
Al	7026-8139	9610	344	3310-4390	3650	32	7.54	<0.001	
Cd	0.56-0.65	0.60	0.03	0.05-0.08	0.07	0.01	-14.2	<0.001	0.8
Co	14.2-19.8	16.3	1.3	2.0-2.9	2.5	0.3	7.86	<0.001	20
Cr	37-49	42	3.1	13-19	16	1.2	14.5	<0.001	100
Cu	40-48	43	2.4	6-14	10	1.4	10.5	<0.001	36
Fe	2284-2380	2336	31	618-639	627	8.0	12.1	<0.001	
Mn	472-531	498	19	137-184	157	8.2	13.3	<0.001	
Ni	2.1-7.0	5.9	1.3	0.39-0.47	0.4	0.03	3.7	<0.001	35
Pb	140-189	159	12	19-31	27	0.6	11.1	<0.001	85
Zn	328-338	332	3.2	21-33	28	3.4	12.8	<0.001	140

Table 2. Range, mean and SD of concentration (mg kg^{-1}) of elements in *Pohlia nutans* from dump and control sites; t $_{0.05}$ tabular= 2.01. The data in the column Unpolluted Mosses are from Djingova et al. [26] and Bykowszczenko et al. [27] for terrestrial mosses from unpolluted areas.

	Native range	mean	SD	Control range	mean	SD	t-test	p level	Unpolluted Mosses
Al	470-636	559	23	281-321	297	12	21.78	<0.001	322-385
Cd	0.4-0.5	0.44	0.02	0.11-0.2	0.14	0.02	-16.18	<0.01	<0.2
Co	3.9-5.6	4.7	0.2	0.07-0.09	0.08	0.01	2.59	<0.001	<1.0
Cr	13-28	19	3.2	1.7-1.9	1.8	0.05	6.71	<0.001	0.9-3.0
Cu	45-50	47	0.9	5.0-7.0	5.9	0.6	8.51	<0.001	4.5
Fe	5708-5840	5785	40	210-420	290	9.2	15.12	<0.001	233-1250
Mn	361-371	366	2.5	121-232	129	3.1	8.14	<0.001	110
Ni	6.1-8.9	7.8	0.5	0.9-2.1	1.4	0.5	6.62	<0.001	0.9-3.5
Pb	71-79	74	2.4	3.0-8.1	5.1	0.6	7.96	<0.001	5.7
Zn	42-50	46	2.9	17-19	17.8	0.7	14.82	<0.001	25

Table 3. Range, mean and SD of concentration (mg kg^{-1}) of elements in needles of *Larix decidua* from dump and control sites; t $_{0.05}$ tabular= 2.01. The data in the column Terrestrial Plants are from Kabata-Pendias [25]

	Dump sites range	mean	SD	Control sites range	mean	SD	t-test	p level	Terrestrial Plants
Al	427-499	464	25	107-279	178	47	15.14	<0.001	10-900
Cd	0.25-0.49	0.44	0.05	0.08-0.16	0.14	0.02	-16.08	<0.001	<0.2
Co	1.3-2.5	2.3	0.3	0.10-0.22	0.2	0.04	-9.71	<0.001	<1.0
Cr	3.7-5.1	4.2	0.4	0.3-0.9	0.7	0.1	3.51	<0.01	1-2
Cu	24-39	27	1.7	5.1-8.0	6.7	1.2	10.48	<0.001	4-5
Fe	633-752	674	34	218-278	244	18	12.11	<0.001	42-352
Mn	420-487	457	21	334-391	375	12	13.31	<0.001	15-160
Ni	1.2-2.3	2.0	0.4	0.4-0.9	0.57	0.2	-9.71	<0.001	<1
Pb	19-36	27	3.1	1.2-1.9	1.6	0.23	7.06	<0.001	0.4-2.5
Zn	86-99	92	4.3	33-42	38	2.7	12.80	<0.001	15-30

All calculations were done with the program CSS Statistica 7.1 [23].

Results and Discussion

Ranges of mean concentration of elements in soil, moss, bark and needles of dump and control sites are presented in Tables 1-4.

The dump substrate (Table 1) was very acid and contained elevated levels of Cu, Pb and Zn [24]. *P. nutans and L. decidua* needles from the dump contained elevated levels of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (Table 2 and 3) and *P. nutans* contained additionally Al [25, 26, 27]. Concentrations of Al, Cr, Cu, Fe, Mn, Ni and Pb in *L. decidua* bark samples from the examined dump (Table 4) were higher than the background values for heavy metal contents of Scots pine bark samples collected by Gałuszka [28] in an unpolluted area in the Holy Cross Mountains. Compared to the control values the concentrations of all investigated metals were significantly higher in soil, *L. decidua* needles and bark and *P. nutans* from the dump sites (Table 1-4).

To discriminate between anthropogenic and natural sources of heavy metals measured in *P. nutans*, *L.decidua* needles and bark enrichment factors were calculated using Al as the normalizing element because it likely reflects the amount of silicate in aerosols [29]. According to Dongarra and Varrica [30], Fernández and Carballeira [31] elements were considered to be enriched when the average Enrich-

Table 4. Range, mean and SD of concentration (mg kg^{-1}) of elements in bark of *L. decidua,* from dump and control sites; $t_{0.05}$ tabular= 2.01. The data in the column Scotch pine bark are from Galuszka [28], a clean area in the Holy Cross Mountains.

	Dump sites range	mean	SD	Control sites range	mean	SD	t-test	p level	Scotch pine bark
Al	1494-1717	1631	67	178-272	212	7.9	9.05	<0.001	312-456
Cd	0.57-0.66	0.61	0.03	0.18-0.28	0.23	0.03	-14.10	<0.001	0.5-0.7
Co	7.6-8.0	7.7	0.03	0.03-0.10	0.05	0.01	-4.17	<0.001	1-9
Cr	28-30	29	0.6	0.3-0.4	0.32	0.04	6.10	<0. 01	1-4
Cu	22-26	24	1.3	4.8-7.0	6.0	0.7	10.18	<0.001	4-10
Fe	1059-1299	1163	56	55-81	67	6.1	7.78	<0.001	254-470
Mn	440-483	457	14	115-197	155	27	13.95	<0.001	21-44
Ni	3.2-27.4	21	2.1	1.0-2.8	1.7	0.5	6.49	<0.001	1-23
Pb	59-63	60.3	0.7	1.1-1.5	1.3	0.1	6.61	<0.01	10-28
Zn	61-76	66	9.0	20-24	22	1.1	13.36	<0.001	23-104

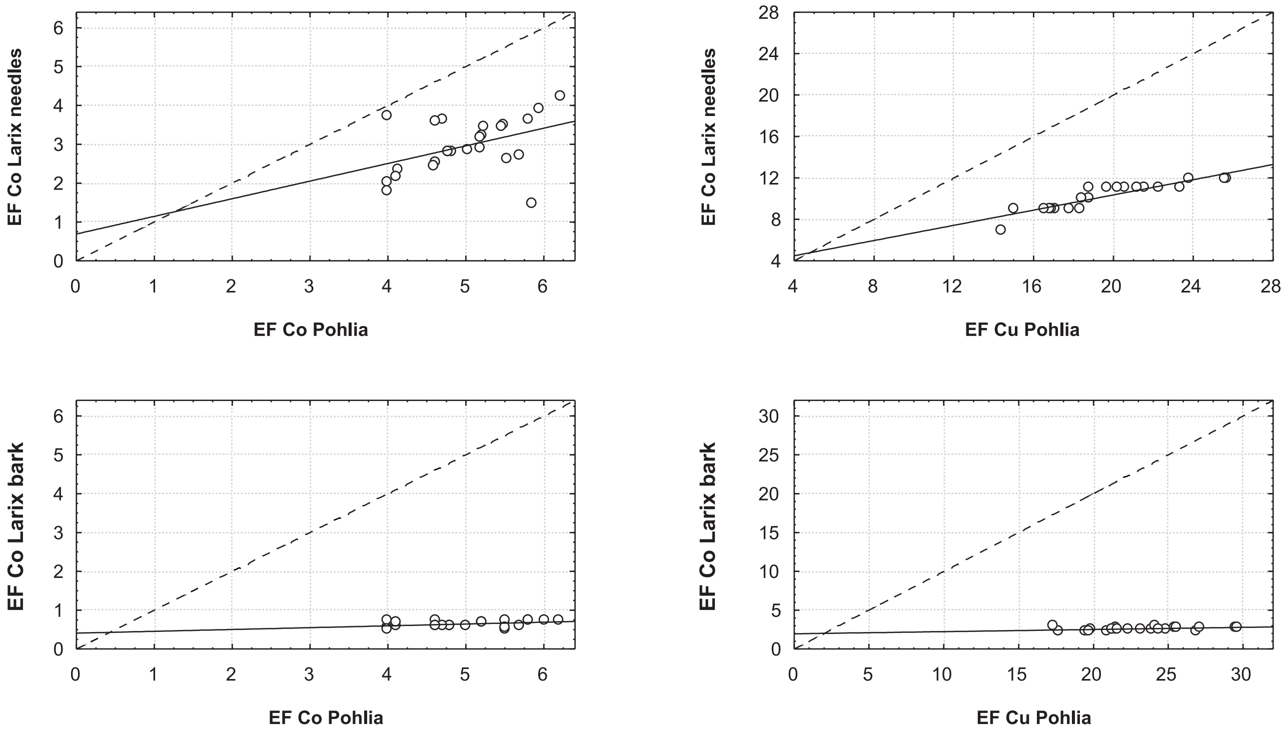

Fig. 1. Plots showing the results of the interspecies comparison between *P. nutans* (Pohlia) and the needles and bark of *L.decidua*. The black line is the regression line and the dashed line is the line of slope equal to 1.

ment Factor (EF, see Material and Methods section) was larger than 3 and for a higher degree of certainty, at least 30% of the samples should have EF>3. Table 5 shows some descriptive statistics of the EF for *P. nutans, L. decidua* needles and bark as well as the percentage of samples with EF>3. The results suggest that for Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb in case of moss and Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in case of needles and all elements in case of bark there are other sources of contamination apart from the soil. The calculated enrichment factors revealed a high metal excess in mosses, needles and bark [29]. Major sources of pollution with these elements are mainly burning of biolites and exhausts of metal smelters and black coal power plants [25]. So the coke and sulphuric acid producing factories and the nearby municipal thermal-electric power station were the main sources of pollution with these elements for plants growing on the dump.

Zn was the only element in *P. nutans* with EF<3. Čeburnis and Valiulis [32] state that some metals such as Zn enter the moss also from non atmospheric sources. Ac-

Table 5. Assessment of mean values, standard deviation (SD) and range of enrichment factors (EFs) of different metals in *P. nutans* (Pn), needles (n) and bark of *L. decidua* growing on the dump relative to the total metal content of the soils and the percentage of each metal with EF >3% (see text).

Element	Mean EF	Minimum	Maximum	S.D.	%
Cd Pn	14	11	25	3.4	100
Co Pn	4.9	3.9	6.2	0.3	100
Cr Pn	7.8	5.0	11	1.1	100
Cu Pn	19	14	26	2.3	100
Fe Pn	43	37	52	1.5	100
Mn Pn	13	11	15	0.9	100
Ni Pn	5.5	3.6	8.9	0.7	100
Pb Pn	3.7	2.9	4.6	1.2	96
Zn Pn	0.4	0.3	0.5	0.1	0
Cd n	15	9.1	19	2.3	100
Co n	3.0	1.5	4.4	0.2	48
Cr n	2.1	1.8	3.1	0.2	12
Cu n	10	7.4	12	1.4	100
Fe n	5.9	5.0	6.9	0.5	100
Mn n	19	16	22	0.9	100
Ni n	10	5.9	16	1.5	100
Pb n	3.9	2.4	5.1	0.6	96
Zn n	3.7	3.0	4.5	0.4	100
Cd bark	5.8	5.2	6.5	0.3	100
Co bark	2.8	2.2	3.4	0.3	48
Cr bark	4.1	3.6	4.7	0.3	100
Cu bark	3.3	2.8	3.7	0.4	80
Fe bark	2.9	2.4	3.2	0.3	48
Mn bark	5.4	4.9	6.0	0.5	100
Ni bark	5.5	3.1	8.9	0.6	100
Pb bark	2.7	2.9	3.6	0.2	60
Zn bark	4.3	3.4	4.9	0.4	100

cording to Szczepaniak and Biziuk [33] and Zechmeister et al. [34] mosses appear to be excellent deposition bioindicators for monitoring elements such as Cd, Co, Cr, Cu, Fe, Ni, Pb and only partly Zn. Chiarenzelli et al. [35] stated that Zn is accumulated by mosses and retained by other than via deposition of airborne particulates. According to the obtained EF results (Table 5) the concentration of elements in *P. nutans* reflected the atmospheric pollution of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb.

Regression analysis was used to compare the EFs of elements obtained for the two species: *P.nutans* and *L. decidua* needles; *P.nutans* and *L. decidua* bark samples. The regression lines corresponding the EF of elements analyzed in samples collected from sites where species occurred together, are shown in Figs. 1 and 2. The regression lines of the EF obtained for: *P. nutans* and needles for Cu, Ni and Pb were significant at $P<0.01$ and for Co at $p<0.05$, for *P. nutans* and bark for Co, Cu, Ni and Pb were significant at $P<0.01$. There were no relations between the EFs of *P. nutans* and needles and between *P. nutans* and bark for Cd, Cr, Fe, Mn, and Zn. So neither bark nor needles may be considered as biomonitors for these elements in the examined area. The presented regression analysis indicates that *L. decidua* needles and bark can be considered as environmental pollution biomonitors of Co, Cu, Ni and Pb in the examined area. The established relations in this investiga-

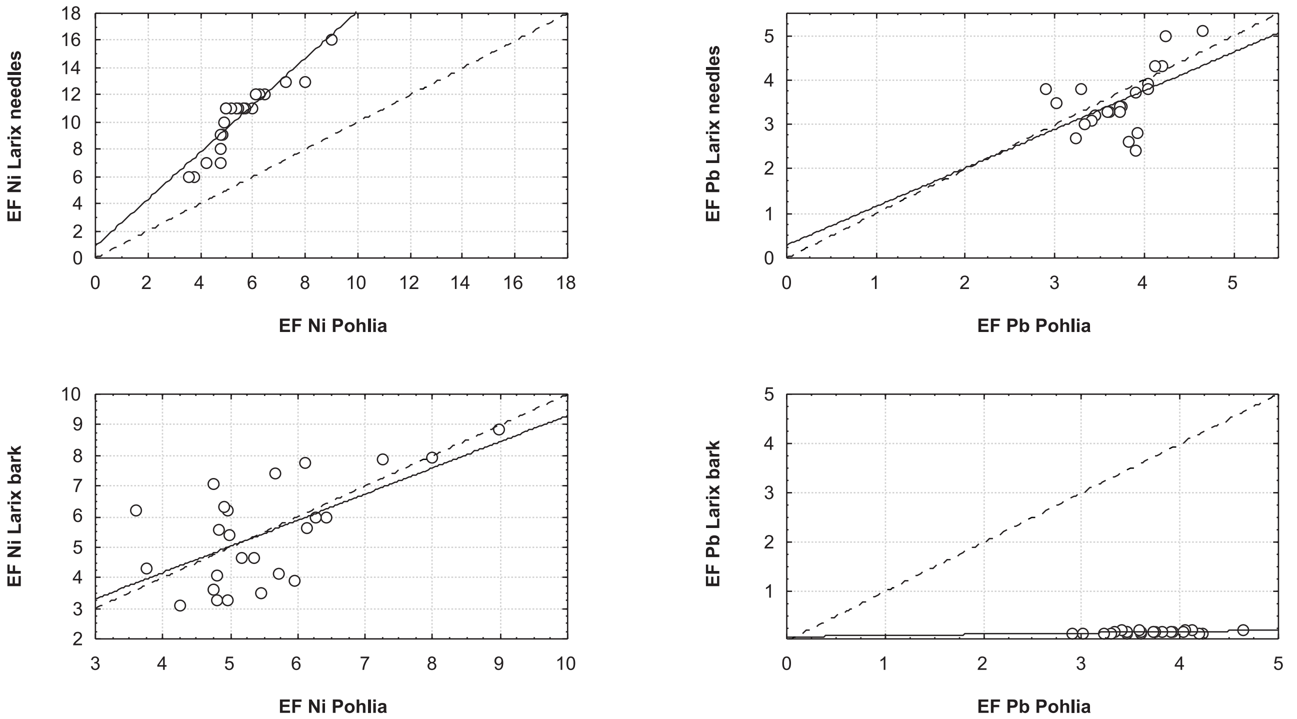

Fig. 2. Plots showing the results of the interspecies comparison between *P. nutans* (Pohlia) and the needles and bark of *L.decidua*. The black line is the regression line and the dashed line is the line of slope equal to 1.

tion between the EFs of *P. nutans* and *L. decidua* support Orlandi et al. [36] that *L. decidua* is a potentially powerful tracer for monitoring Co, Cu, Ni and Pb pollution.

The dashed lines (Fig. 1 and 2) represent the line of slope equal to 1, corresponding to the hypothetical regression lines that would be obtained if there were no differences in bioconcentration in *P. nutans* and *L. decidua* needles or bark. Comparison of the slopes of the regression lines obtained with the hypothetical lines showed that there were statistically significant differences for Co and Ni between *P. nutans* and *L. decidua* needles at $P<0.001$ and for Cu at $P<0.001$. Statistically significant differences also existed between *P. nutans* and *L. decidua* bark for Co at $P<0.05$ and for Cu and Pb at $P<0.001$. There was no significant difference between *P.nutans* and *L. decidua* needles for Pb and between *P.nutans* and *L. decidua* bark for Ni. The examined species therefore must take up Co, Cu, Ni (only needles) and Pb (only bark) in different ways, whereas uptake of Ni by moss and bark and Pb by moss and needles was similar.

In this investigation comparison of the slopes of the regression lines obtained with the hypothetical lines showed that needles were better accumulators of Ni and worse for Co and Cu compared to *P. nutans* (Fig. 1 and 2) and bark was a less good accumulator of Co, Cu and Pb than *P. nutans*. Uptake of Ni by *P. nutans* and *L. decidua* bark as well as uptake of Pb by *P. nutans* and *L. decidua* needles was similar.

Conclusions

1. Atmospheric deposition is the main contributor to the elevated levels of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb in moss and increased levels of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in *L.decidua* needles and increased levels of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in pine bark in the examined area.
2. *L.decidua* needles and bark can be considered as suitable biomonitors for environmental pollution by Co, Cu, Ni and Pb in the examined area.

References

1. SARDANS J., PEÑUELAS J. Trace element accumulation in the moss *Hypnum cupressiforme* Hedw. and the trees *Quercus ilex* L. and *Pinus halepensis* Mill. in Catalonia. Chemosphere **60**, 1293, **2005.**
2. RUHLING A., TYLER G. A ecological approach to the lead problem. Bot. Notiser **121**, 248, **1968.**
3. ABOAL J.R, FERNÁNDEZ J.A, CARBALLEIRA A. Oak leaves and pine needles as biomonitors of airborne trace elements pollution. Environ. Exp. Bot. **51**, 215, **2004.**
4. TOMAŠEVIĆ M., VUKMIROVIĆ Z., RAJŠIĆ S., TASIĆ M., STEVANOVIĆ B. Characterization of trace metal particles deposited on some deciduous tree leaves in an urban area. Chemosphere **61**, 753, **2005.**
5. HUHN G., SCHULZ H., STAERK HJ., TOELLE R., SCHEUERMANN G. Evaluation of regional heavy metal deposition by multivariate analysis of element contents in pine tree barks. Water Air and Soil Pollution **84**, 367, **1995.**
6. POIKOLAINEN J. Sulphur and heavy metal concentrations in Scots pine bark in northern Finland and the Kola Peninsula. Water Air and Soil Pollution **93**, 395, **1997.**
7. MIGASZEWSKI Z.M., GAŁUSZKA A., PASŁAWSKI P.

The use of barbell cluster ANOVA design for the assessment of environmental pollution: a case study, Wigierski National Park, NE Poland. Environ. Pollut. **133**, 213, **2005.**
8. KUIK P., WOLTERBEEK H.T. Factor analysis of trace-element data from tree-bark samples in the Netherlands. Environ. Monit. Assess. **32**, 207, **1994.**
9. PACHECO A.M.G., BARROS L.I.C., FREITAS M.C., REIS M.A., HIPOLITO C., OLIVEIRA O.R. An evaluation of olive-tree bark for the biological monitoring of airborne trace-elements at ground level Environ. Pollut. **120**, 79, **2002.**
10. VOGEL W.G. A guide for revegetating coal minesoils in the eastern United States. Gen. Tech. Rep. NE-68. Broomall, PA: U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, pp. 198, **1981.**
11. WENZEL W.W., JOCKWER F. Accumulation of heavy metals in plants grown on mineralised soils of the Austrian Alps. Environ. Pollut. **104**, 145, **1999.**
12. SHAW A.J. Metal tolerance in bryophytes. In: Shaw A.J. (ed) Heavy metal tolerance in plants: Evolutionary aspects. CRC Press, Boca Raton, FL pp. 133, **1990.**
13. SALEMAA M., DEROME J., HELMISAARI H.Y.S., NIEMINEN T., VANHA-MAJAMAA I. Element accumulation in boreal bryophytes, lichens and vascular plants exposed to heavy metal and sulfur deposition in Finland. Sci. of the Total Environ. **324**, 141, **2004.**
14. Wojewódzki Inspektorat Ochrony Środowiska WIOŚ (Provincial Inspectorate for Environmental Protection) Raport o stanie środowiska w województwie dolnośląskim (Report on the Environment Quality in Lower Silesia). Biblioteka Monitoringu Środowiska (Library of Environmental Monitoring), Wrocław, **2004** [In Polish].
15. VÁZQUEZ M.D., WAPPELHORST O., MARKERT B. Determination of 28 Elements in Aquatic Moss *Fontinalis antipyretica* Hedw. and Water from the Upper Reaches of the River Nysa (Cz, D), by ICP-MS, ICP-OES and AAS. Water and Soil Pollution **152**,153, **2004.**
16. MARKERT B., HERPIN U., SIEWERS U., BERLEKAMP J., LIETH H. The German heavy metal survey by means of mosses. Sci. of the Total Environ. **182**, 159, **1996.**
17. UNECE. Heavy metals in European mosses 2000/2001 survey. UNECE ICP Vegetation. Compiled by A. Buse and D. Norris and H. Harmens and P. Buker and T. Ashenden and G. Mills, Center for Ecology and Hydrology, Bangor University of Wales Bangor, UK. pp.45, **2003.**
18. ČEBURNIS D., STEINNES E. Conifer needles as biomonitors of atmospheric heavy metal deposition: comparison with mosses and precipitation role of the canopy. Atmos. Environ. **34**, 4265, **2000.**
19. ZAR H. Biostatistical analysis. Prentice Hall, Upper Saddle River, New Jersey, pp.931. **1999.**
20. SOKAL R.R., ROHLF F.J. Biometry. The principles and practice of statistics in biological research. Freeman and Company: New York, pp.859, **2003.**
21. BARGAGLI R., BROWN D.H., NELLI L. Metal biomonitoring with mosses: procedures for correcting for soil contamination of samples. Environ. Pollut. **89**, 169, **1995.**
22. FERNÁNDEZ J.A., EDERRA A., NÙÑEZ E., MARTÍNEZ–ABAIGAR J., INFANTE M., HERAS P., ELÍAS M.J., MAZIMPAKA A., CARBALLEIRA A. Biomonitoring of metal deposition in northern Spain by moss analysis. Sci. of the Total Environ. **300**, 115, **2002.**
23. STATSOFT, STATISTICA (data analysis software system), version 7.1, **2005** www.statsoft.com.
24. MINISTERIE VAN VROM Milieukwaliteitsdoelstellingen bodem en water. Environmental objectives for soil and water. Derde Nota Waterhuishouding. Third Announcement Water Management. Tweede Kamer Lower House, Vergaderjaar AssemblyYear 1991-1992, 21.990 en 21.250, No. 3, SDU, The Hague, The Netherlands.
25. KABATA-PENDIAS A. Trace Elements in Soils and Plants, CRC Press, Boca Raton, London, New York, Washington D.C., pp.413, **2001.**
26. DJINGOVA R., KULEFF I., MARKERT B. Chemical fingerprinting of plants. Biol. Res. **19**, 3, **2004.**
27. BYKOWSZCZENKO N., BARANOWSKA-BOSIACKA I., BOSIACKA B., KACZMAREK A., CHLUBEK D. Determination of Heavy metal Concentration in Mosses of Slowinski National Park Using Atomic Absorption Spectrometry and Neuron Activation Analysis Methods. Pol. J. Environ. Stud. **15**, 41, **2006.**
28. GAŁUSZKA A. The chemistry of soils, rocks and plant bioindicators in three ecosystems of the Holy Cross Mountains, Poland. Environ. Monit. Assess. **110**, 55, **2005.**
29. CLOQUET C., CARIGNAN J., LIBOUREL G. Atmospheric pollutant dispersion around an urban areaa using trace metal concentrations and Pb isotopic compositions in epiphytic lichens. Atmos. Environ. **40**, 574, **2006.**
30. DONGARRA G., VARRICA D. The presence of heavy metals in air particulate at Volcano Island (Italy). Sci. of the Total Environ. **212**, 1, **1998.**
31. FERNÁNDEZ J.A., CARBALLEIRA A. A. comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (northwest Spain). Environ. Pollut. **114**, 431, **2001.**
32. ČEBURNIS D., VALIULIS D. Investigation on absolute metal uptake efficiency from precipitation in moss. Sci. of the Total Environ. **226**, 247, **1999.**
33. SZCZEPANIAK K., BIZIUK M. Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. Environ. Res. **93**, 221, **2003.**
34. ZECHMEISTER H.G., HOHENWALLNER D., RISS A., HANUS-ILLNAR A. Variations in heavy metal concentrations in the moss species *Abietinella abietina* (Hedw.) Fleisch. according to sampling time, within site variability and increase in biomass. Sci. of the Total Environ. **301**, 55, **2003.**
35. CHIARENZELLI J., ASPLER L., DUNN C., COUSENS B., OZARKO D., POWIS K. Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the central Barrenlands, Nunavut, Canada. Appl. Geochem. **16**, 245, **2001.**
36. ORLANDI M., PELFINI M., PAVAN M., SANTILLI M., COLOMBINI M.P. Heavy metals variations in some conifers in Valle d'Aosta (Western Itlian Alps) from 1930 to 2000. Microchem J. **73**, 237, **2002.**