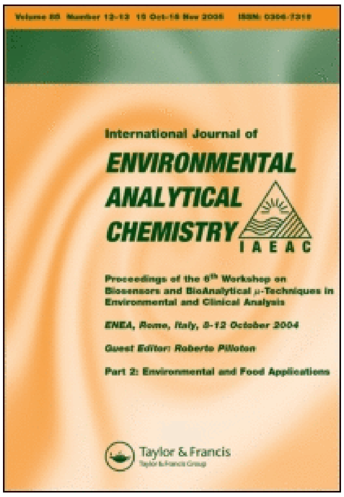

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Major and Trace Elements in Spruce Needles from Urban Areas: Some Aspects of Analysis in Environmental Studies

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MAJOR AND TRACE ELEMENTS IN SPRUCE NEEDLES FROM URBAN AREAS: SOME ASPECTS OF ANALYSIS IN ENVIRONMENTAL STUDIES

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Main and trace elements in samples of spruce needles from urban areas in Poland and Norway were analysed using the ICP-AES method. Concentrations of Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Sr, Ti, V and Zn were measured in needles from conifer trees growing in different locations. Two different procedures of laboratory sample preparation were compared and discussed. Different washing procedures were examined and compared. For quality control of analytical measurements, Standard Reference Material BCR CRM 101 (spruce needles from Europe) was used. Synergistic and antagonistic relationships between elements in spruce needles were investigated. Applicability of spruce needles in biomonitoring of environmental metal pollution was discussed.

Keywords: Spruce needles; Sample preparation; Major and trace elements; ICP-AES; Interelement correlations

INTRODUCTION

Recently, a great attention has been paid to monitoring of trace elements in the environment. One of the methods of environmental monitoring is assessment of the pollution based on chemical composition of plants. Mosses, lichen, grasses, cultivated plants, deciduous trees and conifers have been used for biomonitoring. Among evergreen trees most often Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) have been examined. Norway spruce as one of the dominant tree species of Middle Europe forest ecosystems became a subject of many environmental studies. Spruce tissues have been used in various monitoring programmes. In investigations of metal and organic pollution, needles have been applied most often. Norway spruce needles

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from trees growing in forests all over the Europe i.e. Great Britain [1–3], France [2,4], Germany [1,2,5–8], Switzerland [1,2,5,7], Austria [9], Norway [10], Sweden [11,12], Finland [11], Poland [13], Czech Republic [14], Lithuania [15] and Ukraine [10] have been analysed. Nowadays a special attention is paid to the quality of analytical measurements including those performed for environmental studies. Therefore, quality assurance became a very important task regarding analytical procedures and methods. Quality of trace element determinations depends on the choice of sampling strategy, sample pre-treatment and preparation procedures. For most of the commercially used analytical methods for plant materials, sample decomposition is usually necessary. Sample decomposition methods in analysis of coniferous tree foliage (i.e. pine, spruce and yew needles) prior to element determination by atomic emission spectrometry (ICP-AES) were investigated and discussed in our previous study [16].

Washing of conifer foliage can be a critical step in environmental studies. Different procedures reported in literature, as washing in deionized water [3,17,18], chloroform [1,2,19] or, as reported by Wyttenbach and co-workers, in a mixture of toluene and tetrahydrofuran (1 : 1) [20] have been used to remove adhering particles, accumulated particles and surface waxes. In some papers unwashed needles have been analysed [9,17,21,22,23].

In the analysis of coniferous tree needles two different strategies of sample preparation have been employed. In the first method, samples from individual trees of one location were analysed (see e.g. [18–20,24–26]). In the second procedure, one composite sample (characterizing one sampling site) was prepared by mixing of needles from each tree (as reported in [11,20,27]). So far no comparison of those procedures was reported, so such study seems to be interesting from the point of view of analytical practice.

Validation of analytical method is based on a series of experimental procedures to establish selectivity, sensitivity, repeatability, reproducibility, linearity of calibration graph, detection limit and robustness. It is argued that these headings become more difficult to apply as the complexity of analysis increases [28]. The one way to assess accuracy of the method is the analysis of the certified reference materials. The significant role of certified reference materials is underlined in many reports and guides for quality assurance. Reference material can be really useful only if the biological matrix is similar to the analysed sample and concentration of the analysed elements are comparable.

Nevertheless, in most of the papers on analysis of needles, reference materials have not been used, in others, the comparison between the concentrations certified and measured have not been reported in detail. It should be noticed that there are only two conifer needle (spruce only) materials commercially available. They are CRM 101 – Norway spruce needles collected in Europe and CLV 2 – from near Uranium mining in Canada. In the first material (CRM 101), certified concentration values for Al, Ca, Cl, Mg, Mn, N, P, S, Zn only are present. In CLV 2, concentration values for both radioactive fall out elements and trace metals (i.e. Al, Ba, Br, Ca, Cl, Co, Cu, Dy, I, Mn, Mg, Na, K, Sr, Th, Tl, V) are given.

Interelement correlations in human and animal tissues were the subject of many studies e.g. [29–32]. Such correlations were also examined for soil–plant systems [33]. Lately, interelement correlations in coniferous tree samples were studied. Relations between concentration of elements in needle samples of Norway spruce [34] and red spruce [35] and in Scots pine bark [36] have been investigated.

In the present study concentrations of elements in two species of spruce needles from different sampling sites at urban areas in Poland and Norway were measured and compared. A few problems of sample treatment (as laboratory sample preparation and washing procedures) were examined and discussed here.

EXPERIMENTAL

Sampling

Sampling of Norway spruce (*Picea abies*) and White spruce (*Picea galuca*) needles was carried out after the end of the vegetation period in Oława (industrial town in Lower Silesia; Poland – four sites) and in Trondheim (city in Norway – one location).

Samples were taken from 3–12 trees growing at one stand by cutting branches from the middle of the crown, as described in other studies (see e.g. ref. nos. 1,8,27 and 37).

Sample Pre-treatment

Two methods of analytical sample preparation were carried out:

1. needles of each tree were treated separately as individual samples;
2. one composite sample was prepared by mixing an equal amount of needles from each of the seven trees.

Dust and deposits were removed from the surface of needles by washing in tap and distilled water (see [37]). The cleaned needles were dried at room temperature (as in [18,39]) and removed from twig axis. Material prepared in such a way was used for study of material homogeneity and analysis of spruce needles sampled at urban areas.

To study different washing procedures we proceed as follows: fresh needles from trees of one survey, removed from shoots, were repeatedly agitated for 30 s in different washing solutions: (1) deionized water, (2) chloroform and (3) toluene/tetrahydrofuran (1 : 1).

Needles were dried at room temperature and in the oven (60°C for 24 h). All the dry samples were stored in bags until analysis.

Reagents

Aqueous standard solutions were prepared by dilution of the stock standard (SPEX Industries) solutions. The following chemicals of analytical grade were used for sample preparation: Chloroform, Toluene, Tetrahydrofuran – POCH Gliwice, Poland; 65% Nitric acid – Merck KGaA, Darmstad, Germany; 30% Hydrogen peroxide – PPH "Standard", Lublin, Poland; 35–38% Hydrochloric acid – Merck KGaA, Darmstad, Germany and PPH "Standard", Lublin, Poland.

Deionized water (specific resistivity – 18,3 MΩ cm) was prepared with the aid of an Easy pure RF (series 703, Barnstead, Thermolyne Corporation, USA) water purification system.

Glassware and plastic bottles were cleaned in ultrasound bath (in Extran MA 03, Merck, Darmstad, Germany) and rinsed with distilled and deionized water.

Microwave-assisted Digestion Procedure

About 500 mg of powdered spruce needles was accurately weighed into a Teflon digestion vessel. 6 ml of concentrated nitric acid and 1 ml of hydrogen peroxide (30%) were added. Decomposition of samples was carried out in microwave digestion system (Milestone, MLS-1200, MEGA). After cooling the sample solutions were quantitatively transferred into 25 ml volumetric flask and brought to volume with deionized water.

Measurements

In all samples, the following elements were determined: Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, Ti, V and Zn. The element concentrations in needles were measured using atomic emission spectrometry with inductively coupled argon plasma as the excitation source (ICP-AES). A Jobin-Yvon 38S spectrometer was working under conditions reported in the previous paper [16]. Blank sample solutions were simultaneously prepared and measured. The results from the blank were then applied as a correction to the sample measurements. Precision of the results was determined from duplicate measurements of five replicate samples. Accuracy was checked by analysis of the Standard Reference Material (CRM 101).

RESULTS AND DISCUSSION

Material Homogeneity

Homogeneity of whole and grounded needles was examined here. Concentration of 19 elements was three times measured in ten independent samples. Comparison of content of elements in 10 g of not grounded and 1 g of grounded samples digested with nitric acid and hydrogen peroxide on conventional hot plate was carried out. Some results are presented in Fig. 1. For most of the analysed elements, compatible data were obtained. Scatter of results for ungrounded samples were much higher than equivalent values for grounded needles (standard deviations were even threefold higher). Exceptions were chromium and nickel. In case of those elements, concentrations obtained in the grounded needles are higher than those in the ungrounded samples. It is assumed to be due to contamination from steel parts of mill. It should be mentioned that grounding leads to lower standard deviations.

Washing Procedures

The efficiencies of the washing procedures for spruce needles were examined here by analysis of unwashed needles and foliage washed in deionized water, chloroform and mixture of toluene and tetrahydrofuran (1 : 1). Concentrations of elements in washed and unwashed needles were compared. Selected results (for Ba, Ca, Cr, P, Ti and Zn) are showed in Fig. 2. Only for Ba, Ca, P and Zn differences were smaller than standard deviations. For the other elements, significant differences in concentrations in washed and unwashed needles were observed. As can be seen, each of the examined washing solutions is removing a part of element contents, from the sample. On the basis of our results, it cannot be unequivocally said, which solvent is removing

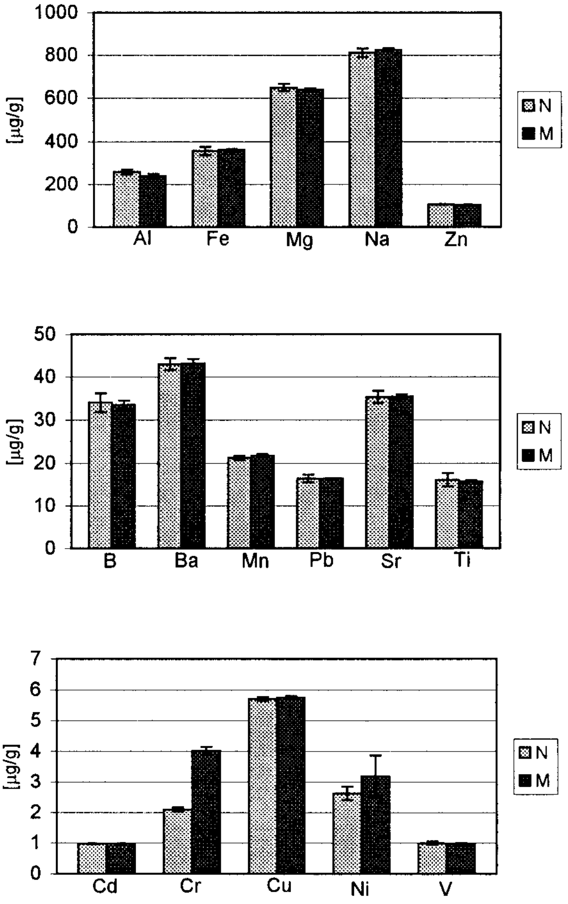

FIGURE 1 Homogeneity of spuce needle samples: *N* – not grounded, *M* – grounded.

only elements and particles adhering to the surface of needles, and which one is extracting metals from samples. It indicates difficulties in distribution of the examined elements to external (exogenous) and endogenous fractions, which is very important in biochemical and environmental studies.

Laboratory Sample Preparation

Concentrations of elements in the needle samples from individual trees and in the mixed sample were measured and compared. Taking into account small number of samples, results in Table I are presented as mean value ($\bar{x}$) and confidence interval (magnitude of interval around experimental mean value $\bar{x}$ that contains the population mean with probability of 95%, $p > 0.05$). As shown in Table I, arithmetic means of the element concentrations calculated for 7 samples treated separately are well consistent with the concentration values found for the mixed sample. As one could expect, the precision of concentrations calculated, as arithmetic means is considerably higher than, that for mixed sample.

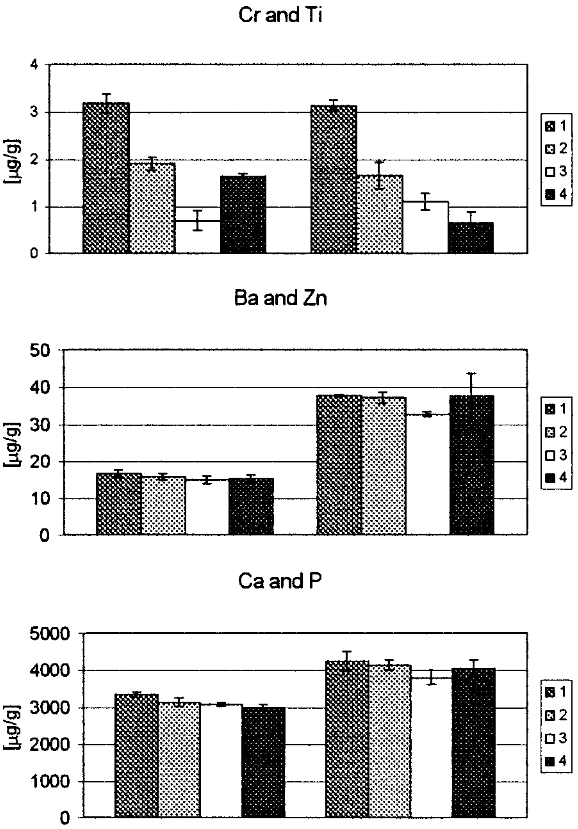

FIGURE 2 Comparison of different washing procedures: 1. unwashed needles, needles washed in: 2. deionized water, 3. chloroform, 4. toluene/tetrahydrofuran (1 : 1).

TABLE I Concentrations of selected elements measured in spruce needle samples [µg/g]

	Individual tree samples[a]							*Arithmetic mean*[b]	*Mixed sample*[c]
	Tree 1	*Tree 2*	*Tree 3*	*Tree 4*	*Tree 5*	*Tree 6*	*Tree 7*		
B	23.2	17.9	16.3	21.2	16.7	9.2	19.7	17.7 ± 4.2	16.2 ± 0.9
Ba	48.3	52.5	48.7	40.3	33.3	41.1	29.8	42.0 ± 7.8	39.4 ± 1.9
Cr	5.0	0.34	0.56	2.5	3.8	5.6	3.4	3.0 ± 1.9	3.6 ± 0.2
Cu	5.5	5.0	6.84	9.1	6.5	7.2	6.1	6.6 ± 1.2	5.4 ± 1.9
Fe	301	209	164	436	476	226	398	316 ± 113	309 ± 15
Mg	799	673	638	1130	1087	673	827	832 ± 186	894 ± 42
Mn	199	85.2	163	40.7	34.2	21.9	24.4	81.2 ± 66.7	83.7 ± 4.4
Ni	5.2	2.4	2.4	3.3	4.5	2.7	4.0	3.51 ± 1.01	3.8 ± 0.9
Pb	6.1	4.1	4.3	11.2	10.9	5.4	7.1	7.0 ± 2.7	5.9 ± 2.2
Sr	36.8	32.0	37.6	45.9	32.6	36.4	29.1	35.8 ± 5.0	33.6 ± 1.5
Ti	11.7	7.8	5.1	17.4	19.0	6.2	15.0	11.7 ± 5.2	11.2 ± 0.6
Zn	96.8	80.5	64.2	49.5	38.7	53.7	32.8	59.5 ± 21.2	58.5 ± 3.9

[a] needles sampled from individual trees treated separately.

[b] arithmetic mean calculated from samples of trees 1–7 (mean ± confidence interval).

[c] samples from trees of one location combined into one laboratory sample (mean ± confidence interval).

Standard Reference Material Analysis

In this work, analysis of SRM (CRM 101-Norway spruce needles collected in Europe) was performed for validation of sample preparation procedure and accuracy of determination method. Concentration of elements were measured in samples mineralised by mixture of nitric acid and hydrogen peroxide (as is commonly used) in closed system with the aid of microwave energy. Results of the measurements are presented in Table II. For most of the examined elements, a good agreement between obtained data and certified values is observed. Only for Al, Ca and Mg significant differences between measured concentrations and certified values were noticed. For those elements the obtained values were lower than certified (Al 39%, Ca 39%, Mg 9.5%). Also measured contents of Cr and Fe were lower than those reported for the SRM (CRM 101).

The same material was digested using procedure recommended by producer of the reference material, it is in the mixture of hydrofluoric and nitric acids. For Al, Ca, Mg, Pb and Ti, application of HF lead to acquire higher concentrations in comparison to the results for HNO_3. A good agreement between our results (for HF digestion) and concentration values presented in the BCR report for CRM is observed for Al, Cd, Cu, Fe, Mg and Zn. However precision of the results determined in samples digested with HF is meaningfully lower for Al, B, Ba, Ca, Fe, Mn, Sr and Zn. Unexpectedly, concentration of Pb, Sr and Ti is higher than value from the BCR report (about 53% for Pb, 10% for Sr and almost three times for Ti).

TABLE II Standard Reference Material analysis CRM 101 – spruce needles (*Picea abies*) from Europe

		Experimental results (this study)	
		$HNO_3 + H_2O_2$	*$HF + HNO_3$*
Certified values (BCR report)			
Al	173 ± 5	105 ± 4	160 ± 14
Ca	4280 ± 80	2620 ± 156	3610 ± 563
Mg	619 ± 9	560 ± 14	623 ± 14
Mn	915 ± 11	918 ± 23	858 ± 56
P	1690 ± 40	1697 ± 92	
Zn	35.3 ± 2.3	33.8 ± 1.8	34.8 ± 3.1
Not certified values (BCR report)			
B	23.6 ± 0.1	22.1 ± 0.7	15.9 ± 2.5
Ba		8.9 ± 0.3	10.1 ± 1.1
Cd	0.34 ± 0.01 0.35 ± 0.01	0.38 ± 0.07	0.31 ± 0.04
Co		0.4 ± 0.1	0.3 ± 0.1
Cr	2.62 ± 0.04 2.8 ± 0.3	2.1 ± 0.2	2.1 ± 0.3
Cu	4.9 ± 0.2	4.7 ± 0.7	5.0 ± 0.7
Fe	151 ± 7	143 ± 3	159 ± 10
Ni		6.2 ± 0.4	5.5 ± 0.5
Pb	2.4 ± 0.2 2.8 ± 0.1	3.4 ± 1.2	4.3 ± 1.0
Sr	5.2 ± 0.1	5.10 ± 0.35	5.74 ± 1.23
Ti	3.5 ± 0.1	3.70 ± 0.23	8.07 ± 0.50
V		0.6 ± 0.1	0.5 ± 0.1

Analysis of Spruce Needles Sampled at Urban Areas

Norway spruce and White spruce foliage from locations in Poland and Norway were analysed here. Results are presented in Table III. Concentration values achieved for elements composing inorganic matrix (i.e. Ca, Mg, and P) are similar in needle samples of both spruces from all sampling sites. Significant variances in contents of Al, B, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Ti are noticed. Concentrations of Al, Fe, Mg, Mn, Ni, Pb and Ti are higher in White spruce needles than in Norway spruce tissues sampled from trees growing at the same location (site 4). Metal concentrations are apparently lower in samples from clean (1) than in industrialized (2–5) sampling sites. Every monitoring programme is based on assumption that there is a relationship between quantity of accumulation in a bioindicator and effective biologically and ecologically available quantity of an element or other pollutant. Relation between needle elemental composition and sampling site was observed here and our results as well as data reported in literature (see Table III) suggest that spruce needles may serve as metal pollution indicators. Spruce needles can be good bioindicators especially for Al, Cd, Fe, Mn, Ni, Pb pollution monitoring.

Comparison of element concentrations in SRM (CRM 101) and those in the samples examined here (real spruce needle samples) show great differences especially for Ba, Fe, Mn, Ni and Sr (see Tables II and III). Therefore reliable information about accuracy can be obtained only for few elements.

Data obtained for Al, Ba, Ca, Mg, V and Zn are within the range of the values presented in literature [see 1,5,27,34,36,39] (Table III). Concentrations of B are lower than maximum value of those published in literature. Values determined for Cd, Co, Cr, Cu and Fe are higher than the experimental range reported in papers. The generally acceptable nutrient deficiency ranges for Norway spruce are Ca: 1000–2500 ppm, P: 1100–1120 ppm, Mg: 700–800 ppm, Zn: 18 ppm. In our samples for Ca, P and Zn concentrations were above the deficiency ranges. Only Mg concentration from two locations (2 and 4) was below deficiency level.

TABLE III Concentrations of elements in spruce needles in μg/g

	Norway spruce					*White spruce*	
	Site 1	*Site 2*	*Site 3*	*Site 4*	*Literature data*	*Site 4*	*Site 5*
Al	62.0	251	156	137	6.8–319	222	156
B	12.2	9.2	16.2	23.8	17–63	18.8	16.2
Ba	21.6	41.1	39.4	42.5	1.0–53.2	47.8	39.4
Ca	4390	3860	4180	3700	600–8078	3200	4182
Cd	2.2	4.7	0.3	0.5	0.064–0.19	0.5	0.3
Co	0.5	0.5	1.5	0.3	0.1–0.336	0.4	1.5
Cr	1.2	4.4	3.6	1.2	0.312–< 1.0	1.4	3.6
Cu	21.1	5.0	5.5	3.5	1.75–5.09	4.6	5.4
Fe	61.3	458	309	235	16.3–150	387	309
Mg	767	656	748	451	220–1500	533	894
Mn	327	50.2	83.7	17.7	33–3474	48.5	83.7
Ni	1.3	3.2	2.9	0.9	1.2–3.5	3.4	3.8
P	1250	1560	1720	1630	1500–1600	1720	1715
Pb	0.3	1.6	5.9	11.8	0.8–< 10	17.6	5.9
Sr	23.0	29.8	33.6	26.2	< 10–99	21.5	33.6
Ti	3.72	16.4	11.2	9.16	–	15.2	11.2
V	0.4	0.8	0.6	0.6	< 1	0.9	0.6
Zn	48.9	69.9	58.5	71.7	6.9–80	63.3	58.5

TABLE 4 Interelement correlation in spruce needles from trees of one location

	Al	*B*	*Ba*	*Ca*	*Cd*	*Cr*	*Cu*	*Fe*	*Mg*	*Mn*	*Ni*	*P*	*Pb*	*Sr*	*Ti*	*Zn*
Al	1															
B	0.25	1														
Ba	−0.78	0.06	1													
Ca	0.21	0.25	0.34	1												
Cd	*0.85*	0.67	−0.65	0.11	1											
Cr	0.45	−0.19	−0.43	0.35	0.29	1										
Cu	0.43	−0.12	−0.30	0.42	0.12	0.09	1									
Fe	*0.98*	0.38	−0.79	0.10	*0.92*	0.33	0.34	1								
Mg	*0.93*	0.40	−0.56	0.36	0.81	0.18	0.54	*0.92*	1							
Mn	−0.57	0.41	0.71	0.35	−0.24	−0.18	−0.39	−0.52	−0.41	1						
Ni	0.59	0.58	−0.38	0.32	0.79	0.38	−0.19	0.63	0.49	0.20	1					
P	0.52	0.21	−0.82	−0.62	0.61	−0.09	0.10	0.63	0.42	−0.47	0.23	1				
Pb	*0.95*	0.29	−0.64	0.33	0.77	0.25	0.60	*0.93*	*0.99*	−0.48	0.46	0.45	1			
Sr	0.13	0.15	0.26	0.79	−0.04	−0.01	0.80	0.03	0.36	0.14	−0.13	−0.39	0.35	1		
Ti	*0.95*	0.49	−0.69	0.14	0.14	0.23	0.30	*0.99*	*0.94*	−0.43	0.64	0.60	*0.92*	0.07	1	
Zn	−0.57	0.23	*0.87*	0.45	−0.37	−0.08	−0.53	−0.58	−0.45	0.81	0.03	−0.81	−0.54	0.08	−0.49	1

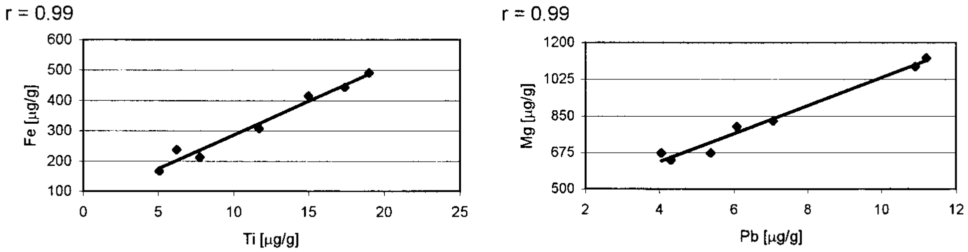

FIGURE 3 Correlations between selected elements.

Interelement Correlations

In spruce needle samples collected from individual trees of one-location relationships between elements were studied. Interelement correlation coefficients were calculated for the elements measured here and given in Table IV.

As can be seen in the table for the following pairs of elements significant positive correlations are observed: Al–Cd, Al–Fe, Al–Mg, Al–Pb, Al–Ti, Ba–Zn, Cd-Fe, Fe–Mg, Fe–Pb, Fe–Ti, Mg–Pb, Mg–Ti, and Pb–Ti. It indicates a synergism between these elements. High, positive correlation coefficients ($r > 0.87$; for $n = 7$ samples, at $p < 0.01$) suggest that both elements have the same origination. No negative correlation is noticed – any statistically significant coefficients were not obtained for elements studied. Figure 3 illustrates the relationship between selected elements.

CONCLUSIONS

Spruce needles from trees growing on urban areas have been analysed and element concentrations measured here were comparable with those found in needles from forest areas. For some elements the difference in concentrations were noticed to be insignificant. Considerable differences in contents of elements between

Norway spruce (*Picea abies*) and White spruce (*Picea galuca*) were observed for Al, Fe, Mg, Mn, Ni, Pb and Ti. For assurance of good quality of analytical measurements sampling and sample preparation steps are of great importance. No significant differences in results obtained for needles analysed as one composite sample and sampled from individual trees are observed, but the second procedure gives possibility to study interelement correlations. Comparison of various washing procedures used here showed meaningful differences in element concentrations removed from foliage material. The problem is essential in investigations of exogenous and endogenous metal contents. Therefore a development of one, standard washing procedure commonly accepted is indispensable. Very essential part of environmental analysis must be validation procedure by the use of reference materials. Unfortunately, only two SRM for needles (Norway spruce only) are commercially available and only for a few elements certified concentration values are given.

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