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PINE NEEDLES AS BIOINDICATOR OF POLLUTION BY TRACE ELEMENTS FROM CEMENT-LIMESTONE INDUSTRY IN CENTRAL-EASTERN POLAND

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Abstract: This article presents the results of studies on the pollution of atmospheric air by trace elements in the area of the so-called "Białe Zagłębie" located in the Świętokrzyskie Mountains. Bioindication studies involved two-year-old needles of Scots pine *Pinus silvestris* L., collected in 2016. Chemical analysis carried out at the Environmental Research Laboratory showed differences in pH and chemical composition of washed and unwashed needles. The largest differences in metal concentrations were found for Al – 95.33 $mg \cdot kg^{-1}$, Fe – 29.24 $mg \cdot kg^{-1}$ and Zn – 4.25 $mg \cdot kg^{-1}$. Scanning electron microscope (SEM) image of the needles' surface revealed changes resulting from pollution of stoma opening and closing by small solid particles of anthropogenic origins, mechanically disturbing a gas exchange. Analysis of the chemical composition showed that the largest share in the total weight of needle, apart from C and O, belonged to Pb, Si, Ca, Fe and Al.

Keywords: air pollution, biomonitoring, trace elements

1. INTRODUCTION

More than forty-year-old anthropogenic pressure of the cement and limestone industry in the study area causes its transformation towards alkalisation of the environment (Barga-Więcławska & Świercz, 2015, Kozłowski & Jóźwiak, 2017). Dust from the cement and limestone industry emitted to the atmosphere contains potentially toxic trace elements strongly affecting living organisms and their surroundings, including forests (Migaszewski et al., 2001, Filipović-Trajković et al., 2012). Structure, condition as well as elemental composition of trees' organic matter are subject to changes (Sawiols et al., 2011). Forest stands partly remove pollutants from the atmosphere due to deposition on assimilation organs and absorption of dust, aerosols and industrial gases (El-Khatib et al., 2017). Pollutants, including heavy metals, assimilated in this way may interfere with life processes (Barga-Więcławska & Świercz, 2015) and influence tree bioproduction (Ots & Mandre, 2012). Analysis of the chemical composition of assimilatory organs capable of bioaccumulating trace elements (Pöykiö & Heikki, 2001) and being responsible for a gas exchange allows for determining the air quality in areas strongly exposed to anthropogenic pressure (Alaimo et al., 2000). Apart from air pollution, the size of accumulation of contaminants in plants' biomass is also influenced by soil properties (Serbula et al., 2013), age of forest stand and climatic conditions (Varnagiryte-Kabasinskiene et al., 2014), as well as hybridisation within a given species (Juranović-Cindrić et al., 2018).

2. MATERIALS AND METHODS

Study area (Białe Zagłębie) is located in the Central Europe, in the south-eastern part of Poland, in the south-western part of the Świętokrzyskie Mountains (Fig. 1), in the area of the macroregion of Kielecka Upland. Due to the prevalence of Scots pine *Pinus silvestris* L. in the study area, forming dense complexes of upland and lowland forests with rich undergrowths and lower fir floors, two-year-old needles were selected for monitoring analyses (www.bdl.gov.pl). Samples were collected in 2016 from 22 sites (Table 1) in an amount of about 200 g for each site. Then, they were divided into two parts at the Environmental Research Laboratory of the Jan Kochanowski University. After drying at 65^{0}C for 24 h, one of these parts was directly ground with the IKA A-11 Basic organic matter grinder and subjected to further analyses, and the other one was washed three times with deionised water. After re-drying at 65°C for 24 h, it was ground.

In the ground samples, pH was analysed in solutions obtained by mixing the samples with water or a 1 N KCl solution in a ratio of 1:2.5. After 24 hours, the pH value was measured using a HACH HQ-40d multiparameter with an INTELLICAL electrode. A mixture of nitric acid (V) and hydrogen peroxide in a ratio of 2.5:1 was used for distributing dry samples of 0.1 g weighed amounts in polytetrafluoroethylene (PTFE) vessels. Material prepared in that way was subjected to microwave waves of 1400 W power and temperature of 200^{o}C for 40 minutes using the Multiwave 3000 Anton Paar mineraliser. After mineralisation, the samples were subjected to chemical analysis for the content of selected metals using the mass spectrometer ICP-MS-TOF OptiMass 9500. Results consisted of a mean value of three measurements. In order to control the quality of obtained results, such certified reference materials as ERM-CA713 produced by the Institute for Reference Materials and Measurements in Belgium were used. The obtained data was statistically elaborated using the Statistica 13.1 program. Before the analyses, the data were tested for compliance with a normal distribution using the W Shapiro-Wilk test. In the case of non-compliance with the normal distribution, further non-parametric tests were used, such as Spearman's rank-order correlation test and Mann-Whitney U test.

Table 1. GPS - geographical coordinates of sampling sites

No.	Longitude	Latitude
1	20.4630	50.8663
2	20.5269	51.0152
3	20.4838	51.0741
4	20.4608	51.0661
5	20.2844	50.9041
6	20.5030	50.8516
7	20.5022	50.9252
8	20.5913	50.9725
9	20.6450	50.9180
10	20.6025	50.9055
11	20.5252	50.8652
12	20.5488	50.8080
13	20.2324	50.9419
14	20.4561	50.8444
15	20.5327	50.9080
16	20.6783	50.8613
17	20.6638	50.9936
18	20.6780	51.0441
19	20.7727	50.8766
20	20.5992	50.8147
21	20.5109	50.7754
22	20.5121	50.7425

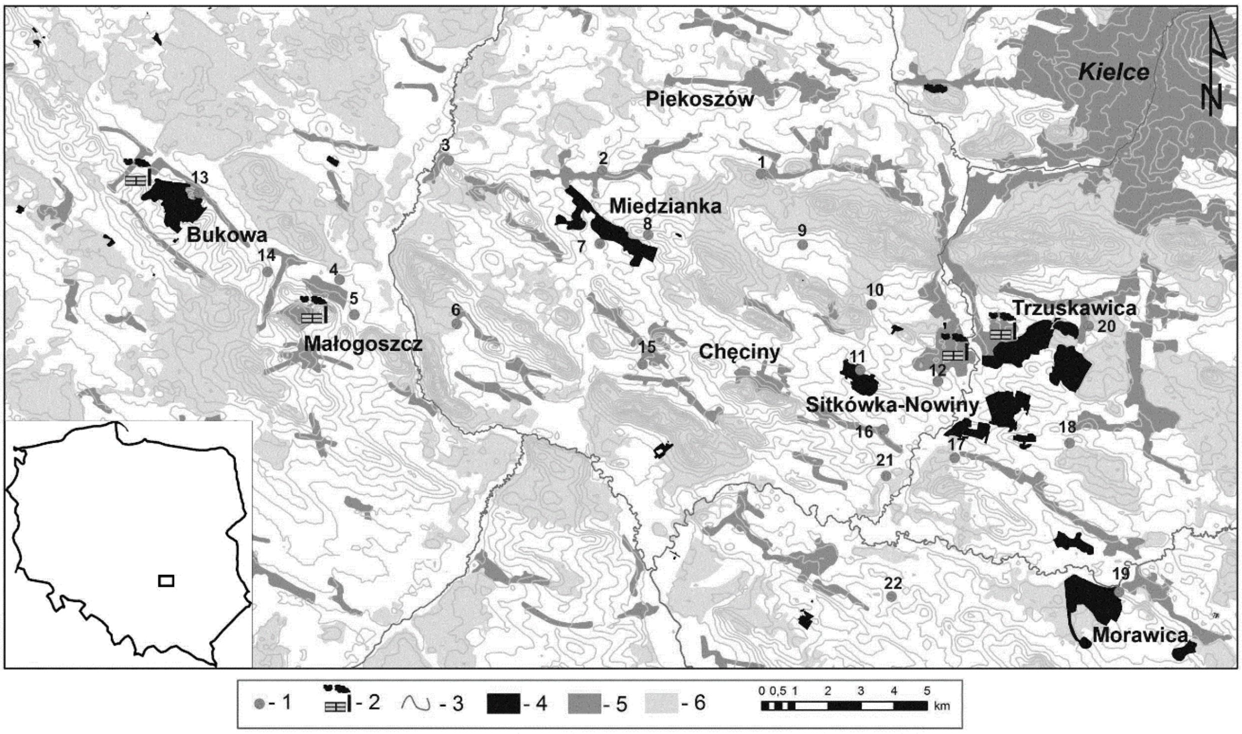

Figure 1. Location of study area (elaborated by M. Szwed on the basis of BDOT and CORINE Land Cover v.2012), 1-sampling spot, 2-cement and limestone plants, 3-rivers, 4-quarries, 5-buildings, 6-forests

Maps showing the spatial distribution of the analysed metals were plotted by means of the Surfer program using the kriging method. Meteorological data for the Kielce weather station was obtained from the Spanish OGIMET portal. The volume of emissions was elaborated basing on the data retrieved from the Regional Inspectorate of Environmental Protection in Kielce. Needle surface morphology was characterised by the method of scanning electron microscopy using a Hitachi TM3000 microscope (under full vacuum and with 15kV accelerating voltage) at the Institute of Inorganic Chemistry and Technology at the Cracow University of Technology.

3. RESULTS

Mean annual air temperature during the tests was 8.8°C, and the annual precipitation sum was 536.5 mm. The volume of emissions of cement and limestone dusts from plants operating in this area amounted in total to 263 300 kg in 2016 (Fig. 2). A cement plant in Małogoszcz had the largest share in cement dust emissions, i.e. approx. 98 000 kg, while a smaller plant in Bukowa – about 33 000 kg (unpublished data of Regional Inspectorate of Environmental Protection in Kielce).

Needles' pH determinations showed, on average, a value of pH_{H2O} amounting to 5.7 and pH_{KCl} amounting to 5.2 for unwashed samples, and pH_{H2O} amounting to 5.5 and pH_{KCl} amounting to 5.1 in the case of unwashed samples (Table 2). Conducted statistical testing procedure using the non-parametric U Mann-Whitney test showed a statistical significance level of "p" above 0.05, i.e. $p = 0.144$ for pH_{H2O} and $p = 0.107$ for pH_{KCl}. Obtained results were not statistically significant. The highest pH_{H2O} and pH_{KCl} values, i.e. 6.6 and 5.8, respectively, were recorded in the central part of the study area at a distance of about 1 km from a cement plant and quarry in Bolechowice (for unwashed needles) and in the vicinity of limestone plants, i.e. $pH_{H2O} = 6.3$ and $pH_{KCl} = 5.7$ (for washed needles).

Cement and limestone dusts coming from furnace and technological processes belong to one of the most important sources of metal emissions to the air in this area (Kozłowski, 2013). The content of trace elements in the dust composition results from production processes based on thermal treatment in furnaces using a specific fuel, i.e. coal, iron ore or waste (Stryczek et al., 2009). Precipitation of dusts

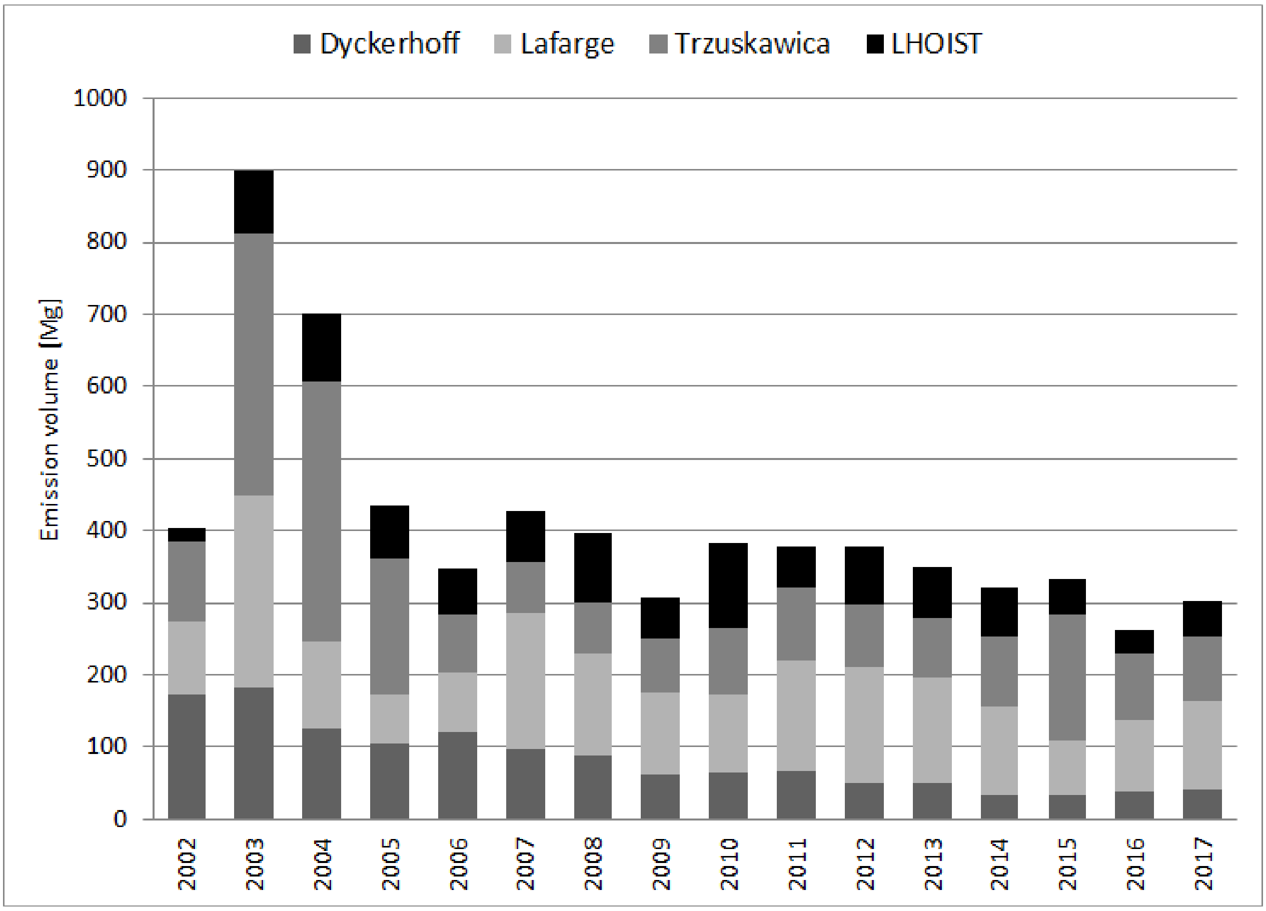

Figure 2. Volume of cement and limestone dust emissions in the Białe Zagłębie in the years 2002-2017 (data of Regional Inspectorate of Environmental Protection in Kielce)

containing significant quantities of chromium, lead, cadmium, and iron, present in the vicinity of cement plants poses a direct threat to the environment (Gołuchowska et al., 2012).

Mean content of the analysed metals in the samples of unwashed needles was the highest in the case of Al (over 400 $mg \cdot kg^{-1}$ d.m.), Fe (270 $mg \cdot kg^{-1}$ d.m.) and Zn (65 $mg \cdot kg^{-1}$ d.m.). Content of Pb, Cu, Ni and Sr did not exceed 10 $mg \cdot kg^{-1}$ d.m. Studies carried out on pine needles taken from the forests of the north-western part of Poland (Skonieczna et al., 2014), characterised by the lack of significant impact of industrial pressure on air quality, showed significantly lower concentrations of Fe (34 $mg \cdot kg^{-1}$ d.m.), Zn (48 $mg \cdot kg^{-1}$ d.m.), Cu (3 $mg \cdot kg^{-1}$ d.m.) and Cr (1 $mg \cdot kg^{-1}$ d.m.).

Content of iron and aluminium found in the air, apart from the emission from cement plants, is also associated with the weathering process of rocks and minerals (Kabata-Pendias & Pendias, 1999). Difference between the content of Al in the unwashed and washed needles was 100 $mg \cdot kg^{-1}$ d.m., 30 $mg \cdot kg^{-1}$ d.m. in the case of Fe and 4 $mg \cdot kg^{-1}$ d.m. for Zn. Differences among the concentrations of Pb, Cr, Cu and Ni slightly exceeded 0.1 $mg \cdot kg^{-1}$ d.m.; whereas, in the case of Co and Sr, they were close to zero. Observed differences may indicate deposition of some metals on the surface of needles (Al, Fe, Zn) and their accumulation inside a cell structure (Pb, Cr, Cu, Ni, Co and Sr).

Coefficient of variation of the needles' chemical properties and pH was varying from 8% (for pH) to 190%. Concentrations of Sr and Al (approx. 100%) were characterised by a large dispersion of values.

Except for Zn and Ni whose concentrations had almost a symmetric distribution, the other analysed characteristics of needles' chemical composition were characterised by a right-skewed distribution, as evidenced by the positive values of coefficient of skewness. Distribution of Pb, Co and Al was the most asymmetrical. In all cases, it was observed that the maximum measured value of the analysed coefficients was several times greater than the mean value. Samples characterised by the highest Pb, Co and Al concentrations were noted for needles' sampling sites located approx. 1 km from the cement plant in Nowiny and Małogoszcz.

Depending on the location, and above all, the distance from the emitter, the volume of accumulated elements by the pine needles varied considerably; while, the highest concentrations of Pb, Zn, Cr, Cu, Al and Fe were recorded in the control sites located within 1 km from the industrial plants and nearby quarries (Fig. 3).

There was a spatial pattern of concentrations of selected trace elements (Pb, Cu, Ni) observed in a latitudinal system, i.e. higher in the area of limestone and cement plants within 2 km from the emission source, and lower east of them, located in the vicinity of forest complexes within more than 2 km from rock processing plants.

Table 2. Pine needles' chemical composition and pH

Characteristics	**Pb**	**Cr**	**Co**	**Cu**	**Ni**	**Zn**	**Sr**	**Al**	**Fe**	**pH_{H20}**	**pH_{KCl}**
Unwashed needles ($mg \cdot kg^{-1}$ d.m.)											
Mean	1.3	3.1	0.03	5.1	0.93	65	6.1	420	270	5.7	5.2
Min	0.25	2.1	0.0	0.51	0.0	34	0.0	86	150	5.1	4.8
Max	6.2	5.5	0.21	9.5	2.3	95	27	1700	490	6.6	5.8
Coefficient of variation	104.5	25.0	158.4	45.9	83.4	29.3	100.0	92.9	34.4	8.3	7.6
Skewness	2.8	1.3	1.9	0.1	0.2	0.0	1.9	2.2	0.7	0.7	0.2
Kurtosis	9.4	2.9	3.6	-0.7	-1.4	-1.2	5.4	5.1	-0.2	-1.2	-1.5
Washed needles ($mg \cdot kg^{-1}$ d.m.)											
Mean	1.1	2.8	0.03	4.7	0.9	61	6.0	320	240	5.5	5.1
Min	0.17	2.2	0.0	0.47	0.0	29	0.47	70	12.8	5.0	4.9
Max	4.7	3.6	0.37	12.4	2.7	95	35.2	1300	400	6.3	5.7
Coefficient of variation	88.1	14.8	190.8	53.4	86.4	31.8	110.5	91.8	30.3	9.4	7.1
Skewness	2.5	-0.1	2.4	1.2	0.7	0.1	2.9	2.4	0.3	0.1	0.1
Kurtosis	7.8	-0.7	6.6	2.9	-0.4	-1.0	10.5	6.4	-0.7	-1.5	-1.6
Difference	0.1	0.4	0	0.4	0	4.3	0.0	95.3	29.2	0.1	0.2

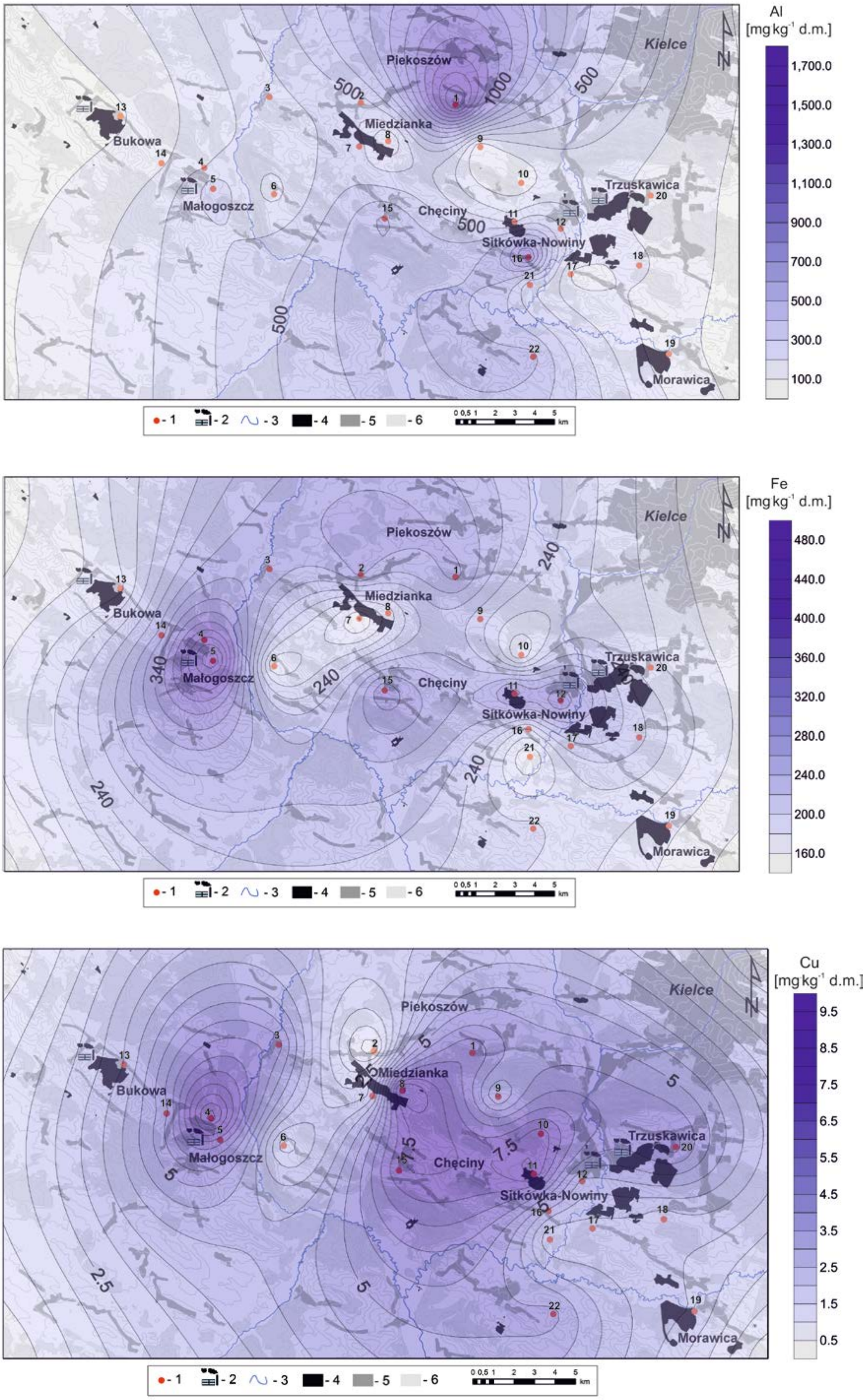

Figure 3. Spatial differentiation of concentrations of selected metals (Al, Fe, Cu)

Table 3. Spearman's rank-order correlation (significance level *p <0.01, **p <0.05)

Washed / Unwashed needles	Pb	Cr	Co	Cu	Ni	Zn	Sr	Al	Fe	pH H_20	pH KCl
Pb											
Cr	0.606* 0.143										
Co	0.200 0.454*	0.353 0.182									
Cu	0.475** 0.255	0.449** 0.310	0.141 0.445**								
Ni	0.325 0.676*	0.383 0.037	0.575* 0.653*	0.286 0.482**							
Zn	0.310 0.476**	0.328 0.138	0.430** 0.421	0.068 0.573*	0.652* 0.620*						
Sr	0.359 0.225	0.379 -0.041	0.137 0.637*	0.657* 0.766*	0.540* 0.582*	0.305 0.517*					
Al	0.153 0.613*	0.041 -0.254	0.384 0.481**	0.069 0.285	0.618* 0.529**	0.425** 0.287	0.366 0.345				
Fe	0.703* 0.702*	0.746* 0.268	0.530** 0.714*	0.442** 0.572*	0.732* 0.780*	0.741* 0.794**	0.466** 0.593*	0.340 0.502**			
pH H_20	0.386 0.508**	0.454** 0.482**	0.420 0.437**	0.193 0.556*	0.670* 0.525**	0.717* 0.755**	0.151 0.441**	0.252 0.286	0.800* 0.788*		
pH KCl	0.389 0.533**	0.476** 0.445**	0.517** 0.409	0.197 0.484**	0.619* 0.501**	0.690* 0.723**	0.106 0.360	0.271 0.311	0.812* 0.767*	0.957* 0.687*	

Statistical analysis showed a strong correlation of pH values both in water and KCl solution with the majority of analysed metals (except for Co, Cu, Sr and Al). In the case of unwashed needles, the strongest correlation was found among pH_{H2O} and Fe values as well as Cr and Fe values (r> 0.8). Fe and Ni as well as Fe and Zn were positively correlating with each other, as well. Relationship between Pb and Cr was also noted (only for unwashed needles). Similar relationships were found in the case of washed needles with a lower correlation coefficient (r<0.7) (Table 3).

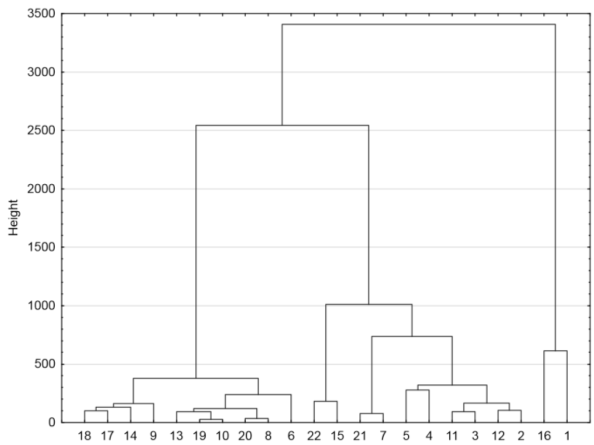

Figure 4. Agglomeration of unwashed needle samples from the Białe Zagłębie by the Ward's method (Manhattan distance).

The use of Ward's cluster analysis (Manhattan urban distance) allowed for separating 3 groups within washed and unwashed needles. The first one consisted of measurement sites located on the outskirts of the study area, whose needles accumulated the largest amounts of Fe and Al (sites no. 1, 15, 22 on the map). The second group comprised the locations of lichens with the highest accumulation of Cr, Co, Cu, Ni and Fe, situated in the immediate vicinity of the cement plants in Nowiny and Małogoszcz (2, 3, 7, 12). The third group was characterised by the increased accumulation of Zn, Sr and Pb; whereas, the location of measurement sites was within a short distance from the limestone plants in Trzuskawica (17, 18) and Bukowa. A source of trace elements in the vicinity of limestone plants in Bukowa may be the co-combustion of car tires in a process of lime production. Washing the dust layer of the surface of needles collected at four sites (11, 15, 16, 22) caused changes within the agglomeration (Figs. 4, 5).

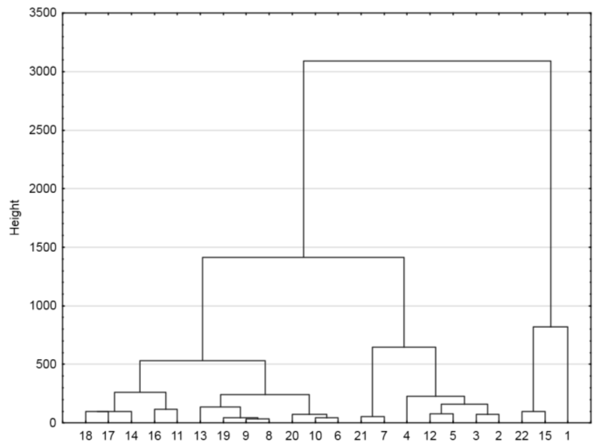

Figure 5. Agglomeration of washed needle samples from the Białe Zagłębie by the Ward's method (Manhattan distance).

A microscopic image of the surface of needles (Fig. 6), taken at a distance of 0.5 km east of the cement plant (site 4) and the limestone plant (13) confirmed the changes in the stomata. Deposited particles may penetrate the needles inside and thus cause their capping which disturbes a gas exchange (Parkhurst, 1986, Staszewski at al., 1994, Sensuła & Toroń, 2018). Analysis of the chemical composition confirmed the presence of metals (Pb, Fe and Al) as well as Ca, K and Mg (Fig. 7). Studies carried out by Kozłowski (2013) indicates that the most important elements included in cement and limestone dusts are Pb, Fe, Al and Ca. Therefore, it may be concluded that the limestone plants operating in this area are the direct source of emission of elements deposited on the surface of needles.

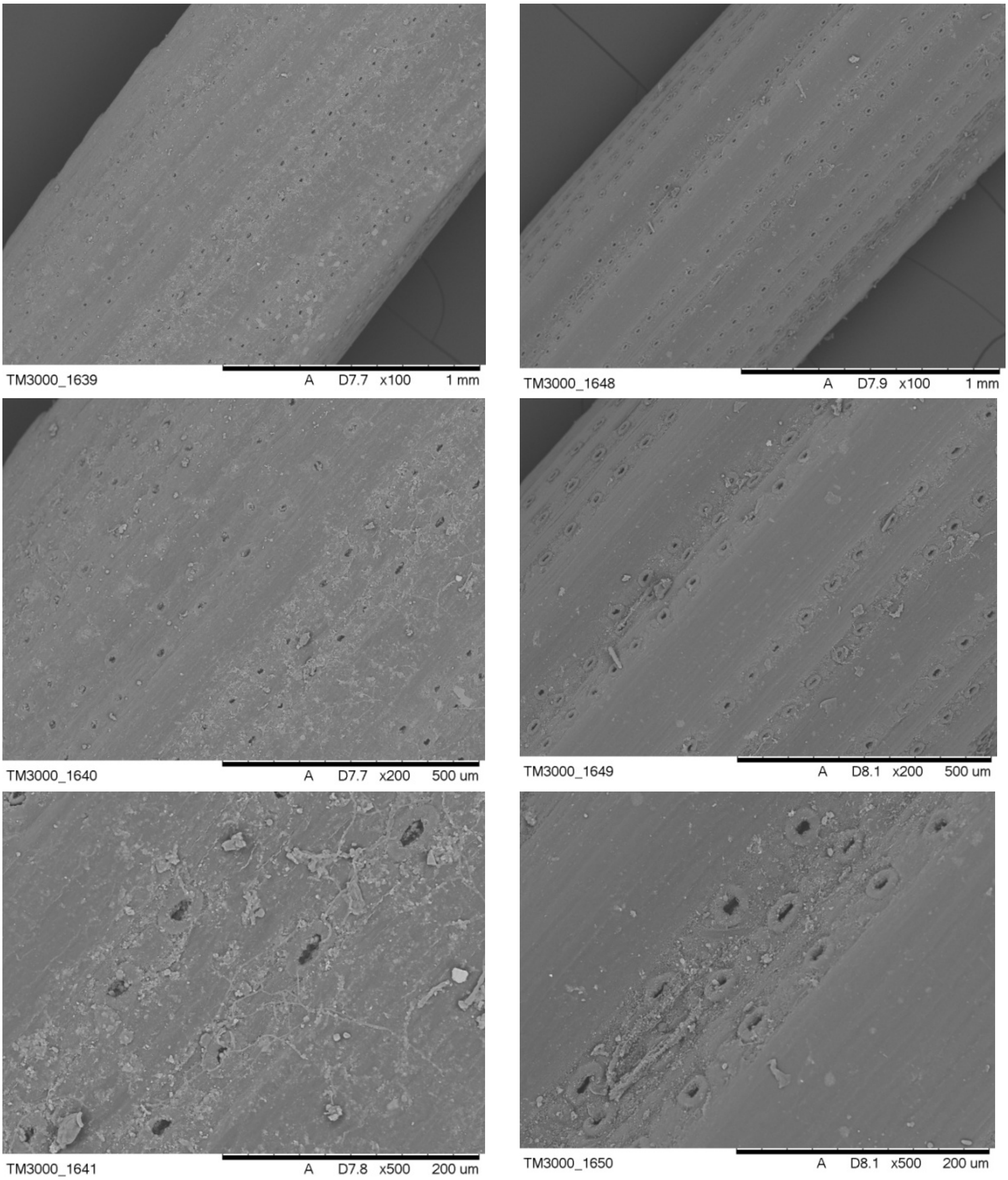

Figure 6. SEM photomicrograph of pine needles collected near the limestone plants in Małogoszcz - sample no. 4 (left column) and in Bukowa - sample no. 13 (right column)

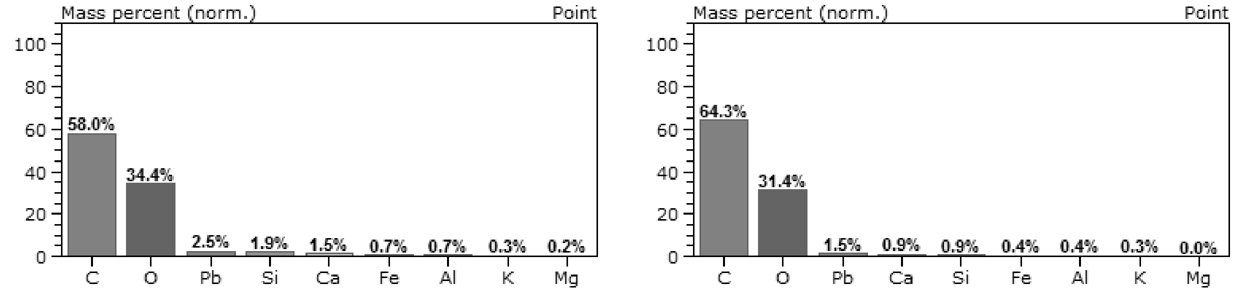

Figure 7. SEM/EDS surface analysis of pine needles from Małogoszcz - sample no. 4 (left column) and from Bukowa - sample no. 13 (right column)

4. DISCUSSION

Studies conducted in Słupsk in the northern part of Poland (Parzych & Jonczak, 2014) showed similar concentrations of Zn in washed needles to those in the study area, with a mean value of 66.8 mg·kg^{-1} d.m., and significantly higher concentrations in the case of Pb, amounting to 13.3 mg·kg^{-1} d.m. In Olsztyn, in turn, located in the north-eastern part of Poland, considered as the area with the lowest anthropopression (Kosiorek et al., 2016), concentrations of Pb in pine needles were almost 9 times lower (0.13 mg·kg^{-1} d.m.) and - in the case of Cr - 8 times lower (0.03 mg·kg^{-1} d.m.) than in the study area. Concentrations of Pb and Zn found in pine needles in the Upper Silesian conurbation, being the most industrialised part of Poland, reached a few hundred higher level (Kandziora-Ciupa et al., 2016) than in the study area. Studies conducted on the Kola Peninsula (Russia), in its industrialised part (Steinnes et al., 2000), showed comparable concentrations of Cr and Zn and much higher concentrations of Pb (7.4 times), Sr (2 times), Cu (8.6 times), Ni (63.4 times) and Fe (3 times) than in the study area. In the northern part of Estonia, being exposed to alkalisation by the cement plant (Mandre & Lukjanova, 2011, Ots & Mandre, 2012), concentrations of Cr, Pb, Fe, Zn and Cu were found to be about half as high as in the study area, but it should be noted that the authors did research on one-year-old needles. Studies conducted by Juranović-Cindrić et al. (2018) confirm the physiological changes of needles by demonstrating the relationship between mineral deficiency in soils and advanced alkalisation. Studies carried out by Barga-Wiecławska & Świercz (2015) in the Białe Zagłębie confirm the changes in the soil profile towards alkalisation resulting from more than forty-year-old emission of cement-lime dusts. As demonstrated by Kozłowski (2013), the increased concentrations of Pb in the topsoil within tree trunks were caused by deposition of dusts enriched in Pb by nearby cement plants.

5. CONCLUSIONS

Chemical composition of pine needles and pH were conditioned by deposition of cement and limestone dusts from the industrial plants and quarries located in the study area. The highest concentrations of trace elements were found in those samples which were collected up to 2 km from the cement plants in Nowiny and Małogoszcz (Cr, Co, Cu, Ni) and the limestone plants in Trzuskawica and Bukowa (Zn, Sr, Pb).

Studies on the content of selected trace elements confirmed the difference between the samples of unwashed and washed needles (the largest for Fe, Al, Zn), which resulted from deposition of dust from the atmosphere and their deposition on the surface of pine needles.

Analyses, including SEM photomicrographs, confirmed the effectiveness of capturing cement and limestone dusts, along with trace elements, by coniferous forest complexes within the area of Białe Zagłębie. In addition, it may be noted that fine dusts, regardless of their chemical composition, adversely affect the stomata, which may lead to gas exchange reduction. As a consequence, the reduction of gas exchange may lead to a decrease in the efficiency of photosynthesis and thus limit the development of the analysed forest stand.

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