

The SEM Studies and X-Ray Microanalysis – the Key for Understanding the Origin and Fate of Airborne Particulates

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Abstract

The occurrence of airborne particulates in the environment is a question that involves many implications in the environmental and biological sciences, toxicology and other related disciplines. Here we show that the mineralogical studies are the best method for determining the origin and pathways of airborne particulates in the environment, as well as for pinpointing industrial pollution sources. The brief historic context of different methods used for assessing environment quality is given in the Introduction section. Of the mineralogical methods, the X-ray microanalysis (SEM/EDS) used for studying particulates in Scots pine (*Pinus sylvestris* L.) needles is discussed in more detail. The SEM combined with EDS system enabled us to interpret the results of element determinations on the pine needles with the spectrometric (ICP-OES, AAS) methods.

Keywords: Scots pine needles, particulates, SEM/EDS method, forest ecosystems, Poland

Introduction

The impact of different air pollution sources on natural and seminatural ecosystems has been described in many publications since the onset of environmental studies [1]. A wide scope of methods has been used to trace the pathways of air pollutants from an emitter to the environment. Originally, only visual observations of plant appearance and growth around air pollution sources were made. The mid 19th century was the beginning of a wide use of plant bioindicators, e.g. lichens, mosses and conifers, for assessing environment quality [2]. At that time sulfur dioxide was regarded as the principal “culprit” responsible for destructive changes in the biosphere. Other potentially toxic pollutants were not considered due to the lack of sophisticated instrumental methods. All this changed in the early 20th century when emission and absorption spectroscopic techniques were devised and in-

roduced as a tool for determining the concentration of elements in plant ashes. This fact has enabled to compare visual changes in plants showing various toxicant levels. This approach is still a domain of different biogeochemical studies. By combining determinations of trace element concentrations in plant species with those in stack dusts, gases or feedstock material, it has been possible to find characteristic element associations. Many of the technogenic (industrial) dust emissions show a specific element signature (“fingerprint”), which is reflected in plant bioindicators, as well as in other media, i.e. soils, sediments, but especially in snow and ice [3, 4].

The development of mass spectrometry techniques has added a new tool to environmental studies. The sulfur and lead stable isotope “fingerprints” have commonly been used in solving different environmental issues, including localization of point- and non-point pollution sources [5-9]. In some of the case studies, isotope determinations have given far better results than chemical analyses [9]. However, it should be stressed that chemical and isotopic

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investigations are most successful when the element concentrations or isotope ratios of the point-source emissions are dramatically different from those naturally occurring in the receptors examined. Moreover, the presence of many pollution sources and/or distinctly raised pollutant concentrations make impossible to find a clear relationship between an emitter and a receptor. The chemical and isotopic ratios imprinted in biotic or abiotic media often represent a mean value originated from overlapping various anthropogenic (technogenic) and natural (geo- and biogenic) sources modified by different physical, chemical and biological factors. This is the main reason why the chemical and isotope methods give the best results in pristine areas impacted by one or two point-pollution sources.

With a gradual reduction of gas emissions, airborne particulates of different origin have become a great concern. Of the grain fractions, especially those below 0.5 μm in diameter are hazardous to animals and the humans, because like gases, they easily penetrate respiratory tract reaching directly circulatory system. Even insoluble minerals, when strongly disaggregated, show increased bioavailability or even toxicity (when enriched in heavy metals or hydrocarbons). Goyer [10] demonstrated that nearly 100% of lead contained in the fines is absorbed by organisms. With regards to plants, even bigger particulates (a few micrometers in size) can clog stomata making impossible proper gas-exchange.

Different methods and techniques are used in studying particulates, of which the mineralogical ones seem to be the most effective. These enable to determine mineral composition of solid phases found in different environmental media. Originally, mineralogical determinations of airborne dust samples collected from emitters and receptors were performed with a polarizing microscope and X-ray diffractometric (insoluble particulates) or infrared spectroscopic (soluble particulates) methods. The

shape of grains and grain aggregates was analyzed under scanning or transmitting electron microscopes, whereas element concentrations were determined with an X-ray fluorescence and/or atomic absorption spectrometry [11]. Recently, more sophisticated methods, *i.e.* an electron microprobe [12], an X-ray microanalysis coupled with a scanning electron microscope [13, 14], or a nuclear microprobe [15] have been used. The airborne dust samples have been analyzed for trace elements using different combined spectrometric methods, for example, inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES) or atomic absorption spectrometry (AAS). Of these methods, the Scanning Electron Microscopy (SEM) combined with EDS system was used in a few environmental projects conducted in different regions of northeastern, south-central and southeastern Poland, *i.e.* in Wigierski National Park, the Holy Cross Mountains including Świętokrzyski National Park, and Magurski National Park (Fig. 1A – C) [16 – 20]. This report presents the results derived from SEM/EDS, ICP-OES and AAS determinations made on Scots pine (*Pinus sylvestris* L.) needles.

Experimental Procedures

The mineralogical and geochemical studies encompassed Scots pine (*Pinus sylvestris* L.) needles, lichen [*Hypogymnia physodes* (L.) Nyl.] thalli, and partly moss [*Hylocomium splendens* (Hedw) B.S.G, *Pleurozium schreberi* (Brid) Mitt., *Hypnum cupressiforme* Hedw. S. Str.] tissues. Prior to the microscopic study, the unwashed plants were lyophilized and coated with a several-micrometer thick gold layer. The detailed studies of the plant parts and distribution of airborne particulate types were performed with a Surface Scanning Electron Microscopy

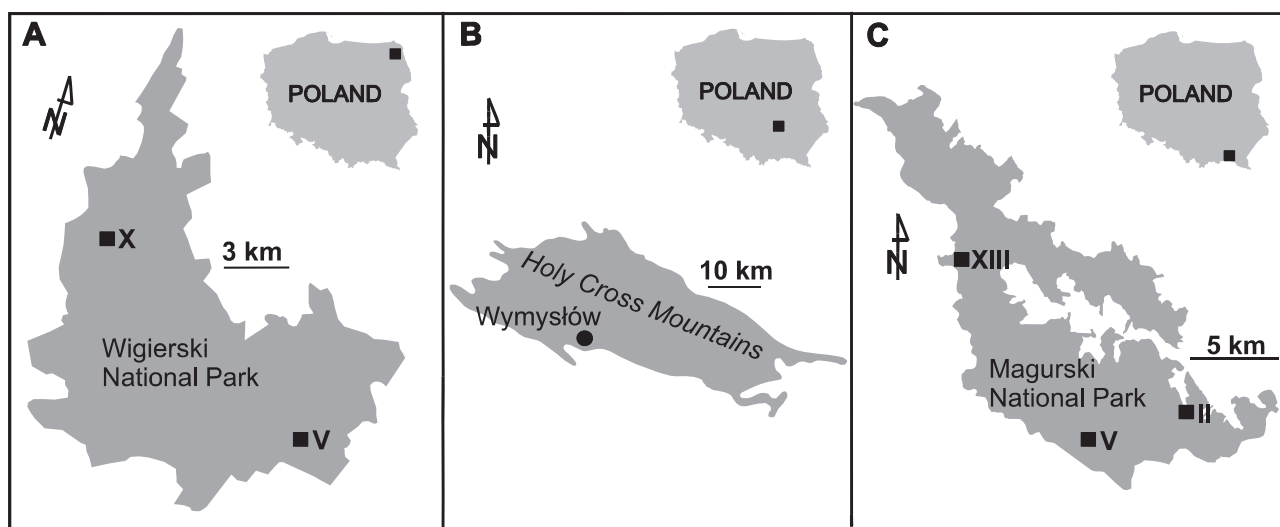


Fig. 1 Location of Wigierski National Park, the Holy Cross Mountains, and Magurski National Parks with sampling points given in Figs. 2 through 4 and Table 1.

SSEM) LEO 1430 (signal A = SE1, magn. = 50–15380×, EHT = 5.00–20.00 kV, WD = 8–36 mm) at the Electron Microscope Laboratory of the Polish Geological Institute in Warsaw. The semi-quantitative chemical composition of particulates was determined with an EDS ISIS Oxford Instruments Ltd. detector.

The chemical analyses were made according to methods and techniques used for environmental materials in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw. The pine needle material was placed in teflon beakers, washed briefly with deionized water, and dried. This latter procedure was repeated three times. As a result, outer contamination (pollen, cobwebs, dead insects, etc.) was removed. After air-drying, the pine needle samples were pulverized using a Retsch's blender. The fraction that passed a 0.5-mm sieve was digested with concentrated nitric acid in a closed microwave system (MDS 81, CEM Corp.). The pine needle samples were analyzed for 22 elements, *i.e.* Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sr, Ti, V and Zn, using inductively coupled plasma-optical emission spectrometry (ICP-OES; spectrometer Jobin-Yvon model JY 70 PLUS with vertical plasma), and by atomic absorption spectrometry (AAS; spectrometer PU 9100 X UNICAM). Mercury

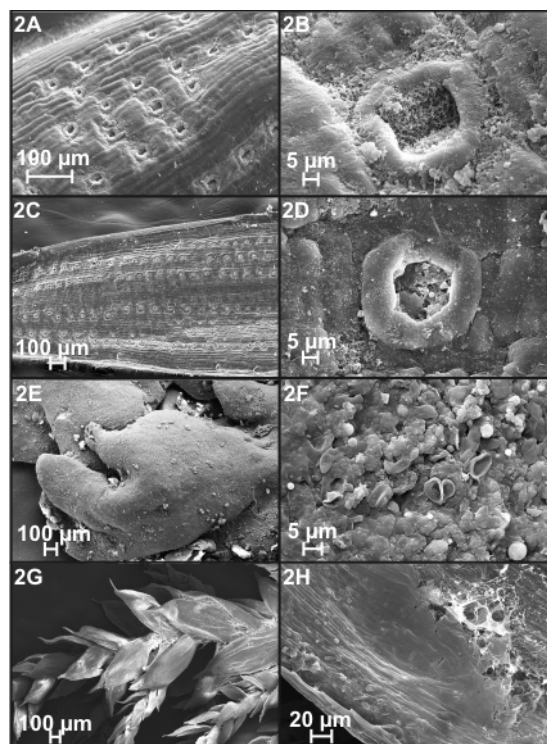


Fig. 2. SEM images: (A, B) Stomata in 1-year old (*i.e.* 2000) and (C, D) 3-year old (*i.e.* 1998) Scots pine (*P. sylvestris* L.) needles collected from the same branch. The minute spherical technogenic particulates (<1 μm) are scarce in 3-year pine needles. (E, F) Lichen (*H. physodes*) thalli with single technogenic particulates. (G, H) Moss (*H. splendens*) tissues with no distinctive particles. All samples collected at Wymysłów near Daleszyce (south-central part of the Holy Cross Mountains).

was determined using an atomic absorption spectroscopic method (AAS; Altec amalgam analyzer AMA 254). Of the total number of samples, 10% were randomly selected for routine replicate analyses, and international standards (Pine Needles 1575) were inserted at a frequency of 5%. These and other methods and techniques, as well as the sample collection and preparation, have been described in more detail in the separate reports [16–20].

Results

The SEM images show the state of preservation of *P. sylvestris* pine needles (Fig. 2A–D), *H. physodes* thalli (Fig. 2E–F) and *H. splendens* tissues (Fig. G–H), as well as the spatial distribution of different particulate types on pine needles (Fig. 3A–H). Moreover, Fig. 4A–B depicts both the SEM images of particulates and the selected X-ray patterns. The chemical analyses of the pine needle

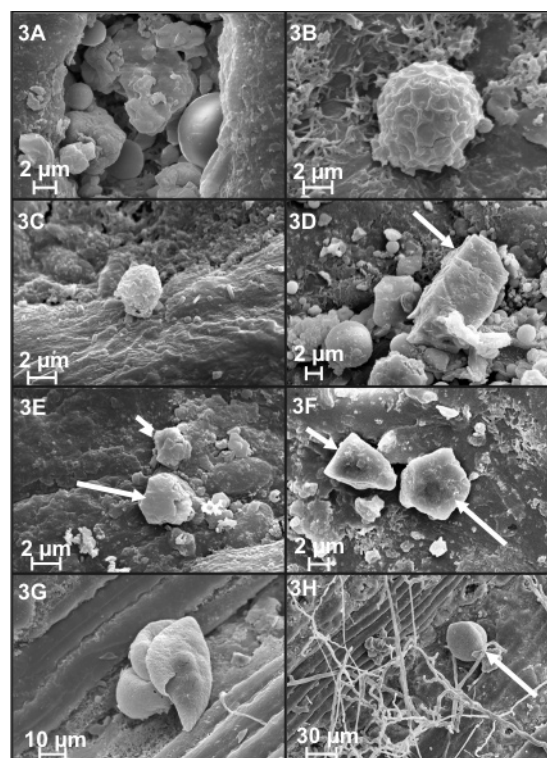


Fig. 3. SEM images of Scott pine needles. (A) Numerous spherical technogenic particulates (Ca, Fe, K, Mg, Na aluminosilicates) filling in stomata; MNP – site II. (B) Technogenic (Ca, K, Mg aluminosilicate) particulate; MNP – site V. (C) Spalerite (α -ZnS) particulate; MNP – site XIII. (D) Geogenic (plagioclase) grain (arrow) among technogenic particulates; MNP – site II. (E) Technogenic particulates composed of ferric oxides with an admixture of Al and Si (arrows); MNP – site XIII. (F) Geogenic quartz grains (arrows) with scarce tiny technogenic particulates; WNP – site X. (G) Pine pollen; MNP – site V. (H) Fungus forming mycelium with associated pollen; WNP – site V. Abbreviations: MNP – Magurski National Park, WNP – Wigierski National Park. For chemical analyses, see Table 1.

samples examined by the SEM/EDS method are presented in Table 1. The summary statistics for the element concentrations in 1-year (2001) and 2-year (*i.e.* 2000) Scots pine needles of Magurski and Wigierski National Parks encompass geometric mean (GM), geometric deviation (GD), as well as observed and expected 95% range (baseline). The latter range was calculated on the basis of the formula: GM/GD^2 to $GM \times GD^2$ [21]. In addition to these statistics, the detection ratio, *i.e.* the number of samples above detectable concentration level (*d*) relative to the total number of samples (*t*), is given (Table 2).

Discussion

Of the bioindicators examined, the pine needles turned out to be the best natural traps for airborne particulates (Figs. 2 – 4). The needle surfaces are covered with a thick layer of cuticle, *i.e.* a mixture of waxes and fatty acids, which protects the needles from a loss of water. The cuticle facilitates particulates to adhere to the needle surfaces. The latter also contain stomata aligned in rows of epidermis favoring immobilization of particulates (Fig. 2A – D) as opposed to the lichen thalli and moss tissues (Fig. 2E – H). These particulates are not washed away easily by rainwater. Moreover, the pine trees shed their needles every 3–4 years, which creates an opportunity for monitoring air pollution for a long time. The SEM images enabled to record differ-

ent particulates, *i.e.* technogenic (Figs. 2D and F, 3A – F, 4A and B), geogenic (Fig. 3D and F) and biogenic (Figs. 3G and H, 4B), on the needle surfaces and in the stomata. It is interesting to note that the stomata are primarily clogged by technogenic particulates (possibly due to electrostatic charge?). In contrast, most of the non-spherical geogenic particulates occur on the needle surfaces. The SEM studies helped us to interpret the results derived from chemical analyses, and to find the relationship between natural- and anthropogenically-altered concentrations of chemical species in the environment. Lack of industrial imprints in pine needles indicated the influence of geogenic (soils and/or bedrock), and biogenic (physiological and genetic) factors. This information enabled us to more accurately measure geochemical background concentrations of elements in relatively pristine areas [18, 19].

The geogenic particulates, *i.e.* quartz, feldspars, hydrous ferric oxides and hydroxides, clay minerals, and biogenic ones, *e.g.* pollens, are prevalent in northeastern Poland [19]. In contrast, the technogenic particulates (various aluminosilicates) occur in excessive amounts in southeastern and partly south-central Poland near industrial centers [18]. The SEM studies indicated that the closer the study area was located to industrial pollution sources the larger amount and bigger size of technogenic particulates was recorded on the pine needles (Fig. 3A-D vs. Fig. 3F). In Magurski National Park (Fig. 1C) some of these particulates reach even 10 μm across. The smaller

Table 1. Concentrations of selected elements in Scots pine needles of different age classes from selected sites of the Holy Cross Mountains, and Magurski and Wigierski National Parks.

Investigation site	Al	Ba	Ca	Cd	Cu	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	S	Sr	Ti	Zn
	mg·kg ⁻¹																
Wymysłów (Holy Cross Mountains)																	
W/1-year (2000)	182	<1	1936	<0.5	8	60	0.022	6761	850	368	<50	10	<5	1445	1	1	48
W/3-year (/1998)	492	2	6490	<0.5	3	104	0.040	3863	568	1356	72	4	<5	1375	3	2	102
Magurski National Park																	
II/1-year (2001)	203	3	3094	<0.5	3	87	0.028	4907	769	554	57	8	<5	971	7	2	38
II/2-year (2000)	159	4	6860	<0.5	2	94	0.039	4286	1241	412	118	4	<5	863	13	3	60
V/1-year (2001)	187	6	2855	<0.5	3	79	0.022	4194	399	863	25	6	<5	1001	5	2	23
V/2-year (2000)	217	32	7087	0.9	3	93	0.044	4106	501	1990	32	3	<5	1178	13	2	59
XIII/1-year (2001)	225	13	2952	0.5	3	82	0.020	5560	453	1093	21	4	<5	1270	4	2	39
XIII/2-year (2000)	310	16	4024	0.5	3	128	0.044	4775	336	1419	49	2	6	1210	5	2	43
Wigierski National Park																	
V/1-year (2001)	344	10	2931	<0.5	5	47	0.020	3918	408	505	29	2	<5	880	5	2	32
V/2-year (2000)	418	14	4714	<0.5	4	54	0.030	3309	305	848	54	1	<5	852	8	2	35
X/1-year (2001)	319	3	3634	<0.5	5	49	0.022	4034	754	575	54	<1	<5	872	3	3	44
X/2-year (2000)	330	3	6509	<0.5	4	66	0.034	3472	683	652	79	<1	<5	774	4	7	49

Note: As – <5 mg·kg⁻¹, Co, Cr, Mo and V – <1 mg·kg⁻¹. For sampling locations, see Figure 1

Table 2. Summary statistics for the element concentrations in 1-year (*i.e.* 2001) and 2-year (*i.e.* 2000 – in parantheses) Scots pine (*Pinus sylvestris*) needles of Magurski and Wigierski National Parks.

Elements mg·kg ⁻¹	Magurski National Park					Wigierski National Park				
	Ratio (d:t)	Geom. mean	Geom. dev.	Observed range	Expected 0.05 range	Ratio (d:t)	Geom. mean	Geom. dev.	Observed range	Expected 0.05 range
Al	15:15	195	1.63	48–357	74–517	15:15	228	1.72	60–649	78–672
	(15:15)	(226)	(1.42)	(112–449)	(112–458)	(15:15)	(226)	(1.57)	(77–446)	(92–557)
Ba	14:15	3	2.29	<1–13	0.5–14	15:15	3	1.82	1–10	1–10
	(15:15)	(5)	(2.31)	(1–32)	(1–25)	(15:15)	(4)	(1.80)	(1–14)	(1–13)
Ca	15:15	3190	1.20	2439–4477	2218–4588	15:15	3185	1.23	2232–4268	2116–4796
	(15:15)	(5315)	(1.26)	(3420–7087)	(3324–8498)	(15:15)	(4723)	(1.24)	(3620–6689)	(3096–7204)
Cd	2:15	0.4	1.13	<0.5–0.5	0.3–0.5	0:15	<0.5	–	–	–
	(2:15)	(0.4)	(1.29)	(<0.5–0.9)	(0.2–0.6)	0:15	(<0.5)	–	–	–
Cu	15:15	(4)	1.25	3–6	2–6	15:15	4	1.15	3–5	3–5
	(15:15)	(3)	(1.14)	(2–4)	(2–4)	(15:15)	(4)	(1.14)	(3–4)	(3–5)
Fe	15:15	76	1.25	54–112	48–118	15:15	52	1.17	45–72	38–71
	(15:15)	(90)	(1.25)	(67–128)	(58–139)	(15:15)	(57)	(1.24)	(43–91)	(37–87)
Hg	15:15	0.020	1.15	0.019–0.032	0.018–0.031	15:15	0.020	1.25	0.014–0.028	0.013–0.032
	(15:15)	(0.040)	(1.18)	(0.030–0.059)	(0.030–0.058)	(15:15)	(0.030)	(1.20)	(0.021–0.045)	(0.021–0.043)
K	15:15	4648	1.15	3798–6106	3510–6155	15:15	3791	1.14	2931–4793	2925–4914
	(15:15)	(3927)	(1.15)	(3299–5623)	(2947–5231)	(15:15)	(3298)	(1.08)	(2779–3838)	(2831–3842)
Mg	15:15	735	1.36	399–1372	395–1370	15:15	787	1.29	408–1057	470–1318
	(15:15)	(629)	(1.39)	(336–1241)	(324–1219)	(15:15)	(621)	(1.30)	(305–893)	(365–1056)
Mn	15:15	450	1.83	97–1093	134–1506	15:15	466	1.64	90–769	173–1259
	(15:15)	(709)	(1.62)	(342–1990)	(270–1859)	(15:15)	(622)	(1.73)	(99–1028)	(207–1864)
Na	11:15	22	1.50	<20–57	10–50	15:15	34	1.48	22–96	15.4–73.1
	(15:15)	(40)	(1.59)	(22–118)	(16–102)	(15:15)	(55)	(1.49)	(29–143)	(25–124)
Ni	15:15	6	1.92	2–15	2–22	11:15	1	1.88	<1–4	<1–5
	(15:15)	(5)	(2.17)	(2–21)	(1–22)	(5:15)	(1)	(1.19)	(<1–1)	(<1–1)
P	15:15	1548	1.24	1048–2304	1013–2367	15:15	1489	1.18	1093–2041	1074–2066
	(15:15)	(1361)	(1.21)	(948–1889)	(923–2007)	(15:15)	(1256)	(1.11)	(1038–1519)	(1020–1547)
Pb	0:15	<5	–	–	–	0:15	<5	–	–	–
	2:15	(4)	(1.18)	(<5–6)	(3–5)	(0:15)	(<5)	–	–	–
S	15:15	1070	1.16	907–1507	800–1432	15:15	877	1.09	753–1049	734–1049
	(15:15)	(1048)	(1.18)	(821–1473)	(758–1449)	(15:15)	(835)	(1.07)	(726–941)	(735–949)
Sr	15:15	4	1.46	2–8	2–9	15:15	3	1.33	2–5	2–5
	(15:15)	(7)	(1.57)	(4–13)	(3–16)	(15:15)	(4)	(1.32)	(3–8)	(2–7)
Ti	15:15	3	1.57	2–9	1–6	15:15	2	1.30	1–3	1–3
	(15:15)	(2)	(1.43)	(1–4)	(1–4)	(13:15)	(1)	(1.91)	(<1–7)	(<1–5)
Zn	15:15	40	1.34	22–68	22–72	15:15	36	1.23	26–48	24–54
	(15:15)	(46)	(1.37)	(20–73)	(24–85)	(15:15)	(33)	(1.26)	(23–49)	(21–53)

Note: As – <5 mg·kg⁻¹, Co, Cr, Mo and V – <1 mg·kg⁻¹, (d) – number of samples above detectable concentration level, (t) – total number of samples

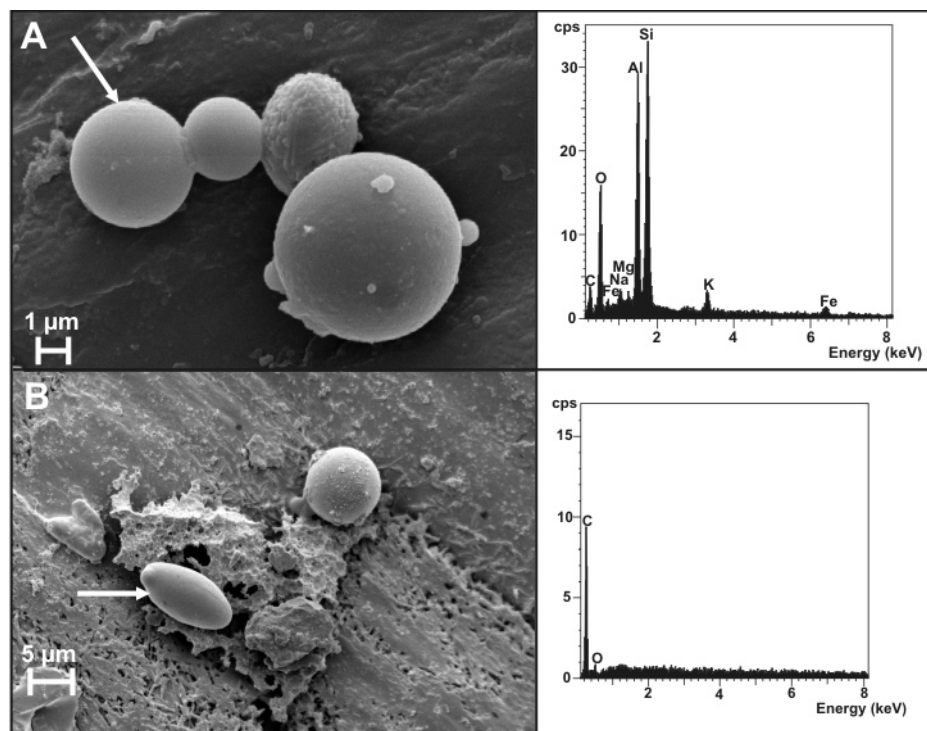


Fig. 4. SEM images and selected X-ray patterns: (A) Four technogenic particulates: three spherical (K, Na Fe, Mg aluminosilicates) and one oval with rough surface (hydrrous ferric oxides and hydroxides). X-ray pattern derived from the left particulate (arrow). (B) Spherical technogenic particulate (K, Na, Fe, Mg aluminosilicate) versus spindle-like pollen (arrow). Pollen spectrum showing two characteristic peaks of C and O. Wymysłów near Daleszyce (central part of the Holy Cross Mountains).

technogenic particulates, not exceeding 3 µm in diameter, predominate in the Holy Cross Mountains (south-central Poland) situated about 100 – 200 km east of the highly industrialized Upper Silesian and Cracovian areas, and the “Konin” power plant. These particulates are scarce in the compact forest complexes of south-central part of the Holy Cross Mountains, *e.g.* near Wymysłów (Fig. 1B).

The X-ray microanalysis (SEM/EDS) of individual particulates enabled us to semi-quantitatively determine major and minor elements (Fig. 4A – B). Most of the pine needles examined show no correlation between the mineralogical and chemical composition of particulates and the trace element concentrations determined with the ICP-OES and AAS methods. However, the relationship between an increased amount of technogenic particulates and raised concentrations of some elements in the pine needles derived from the remote areas has been noted. This is evidenced by the element determinations of the pine needles from Wigierski and Magurski National Parks (Fig. 1A and C), which are the areas highlighted by a various anthropogenic impact. The pine needles of Magurski National Park show higher concentrations of Fe, Ni and S than those from Wigierski National Park (Table 2). Of the areas studied, the highest concentrations of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, Zn as well as technogenic particulates, *i.e.* Ca, Fe, K, Mg and Na aluminosilicates, in places sphalerite (ZnS) and ferric oxides, were recorded in southern part of Magurski National Park near the Polish-Slovakian border, which indicates the possible

location of potential pollution sources in Slovakia [18].

In addition, there is another aspect that should be considered when interpreting the results derived from mineralogical and geochemical studies of plants. Except for the impact of anthropogenic pollution sources, the spatial and temporal distribution of elements in plants depends on many natural factors, *i.e.*, topographic (elevation, extent of mountain ranges), climatic (insolation, wind, temperature, moisture), lithologic and petrographic (rock types, ore mineralization), edaphic (structural and physico-chemical properties of soil), hydrologic, physiological and genetic. Local topographic, climatic, lithologic and petrographic, edaphic, and hydrologic variables are generally linked to the geologic setting of a given area [22, 23]. This is the main reason why the variations in element concentrations in plants cannot be directly linked to the changes in atmospheric pollution level.

Conclusion

Based on our studies, we conclude that:

1. Of the plant bioindicators growing in temperate forest ecosystems, conifer needles seem to be the best natural traps for airborne particulates.
2. The SEM studies combined with X-ray microanalysis enable to interpret the results of element determinations with spectrometric methods performed on pine needle samples.

3. In most cases there is no direct relationship between the amount or types of airborne particulates and the chemistry of pine needles due to the influence of many environmental and biological variables.
4. The SEM/EDS, ICP-OES and AAS analyses indicated that Magurski National Park and partly the Holy Cross Mountains are much more influenced by anthropogenic sources than relatively pristine Wigierski National Park. Moreover, these studies combined with statistical methods enable to determine geochemical background concentrations in relatively pristine areas.

Considering this, identification of mineral phases in dusts should precede detailed element determinations with different spectrometric and speciation techniques. This methodological sequence enables to move from airborne particulate mineralogy to “deep” geochemistry, *i.e.* determining element bioavailability and concentration levels potentially toxic to plants, animals and humans.

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