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Geochemistry of soils and vegetation of the Holy Cross Mts. between 1994 and 1996

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The results of element and sulphur isotope determinations performed on soils from the Holy Cross Mts. region showed that many elements were elevated primarily due to air pollution. The chemical analyses performed on samples collected in 1996 indicated the raised content of many elements, especially Hg, Pb and S, in topsoil. The most contaminated site was Łysica Mt., the tallest mountain of the region, showing the maximum content of many elements. In addition, the lowest pH values and the highest concentrations of PAHs were recorded here. The geometric mean values of a large number of elements, especially As, Cr, Hg, Pb and S, were higher in the Holy Cross Mts. than those in Poland. Scots pine needles from Holy Cross Mountain National Park contained much more Mg than those from the remaining part of the Holy Cross Mts. Compared to the oldest needles, the youngest from the same crop revealed the raised content of Cu, K, Mg, Ni, P and heavy sulphur isotope and the drop of Al, Ba, Ca, Fe, Hg, Mg, Pb, Sr, Ti and Zn. On the other hand, the one-year needles collected in 1994 to 1996 showed the decrease of Cu, K, Mg, Ni, P and S. The needles of all age classes yielded elevated concentrations of B, Mn, P, S, Zn and heavy sulphur isotope; the bark revealed more Al, Ba, Cd, Cr, Fe, Hg, La, Pb, Ti, V, Y and Yb. In turn, the lichen species *Hypogymnia physodes* (L.) Nyl. was enriched in Fe, Hg, K, Mg, P, S, Ti, Zn and heavy sulphur isotope relative to pine bark. The content of sulphur in pine needles and lichens was generally close to that from Finnish Lapland or rural parts of Scandinavia. Moreover, concentrations of heavy metals in pine needles were similar, whereas those in lichens were higher compared to those in northern and eastern Finland.

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INTRODUCTION

This report summarizes the results of three phases of investigation performed in 1994 through 1996 on topsoil (horizon A), lower soil or subsoil (horizons B, E, AB and AC), rocks (quartzitic sandstones, limestones and dolomites), Scots pine (*Pinus sylvestris* L.) needles of 1993-, 1994-, 1995-, 1996-age classes, lichens *Hypogymnia physodes* (L.) Nyl. (1994–1996), Scots pine bark (1995, 1996) and spring waters (1994–1996) from the Holy Cross Mts. (Z. M. Migaszewski *et al.*, 1995; Z. M. Migaszewski, 1996*a–d*, 1997*a*, *b*, in press; Z. M. Migaszewski, A. Gałuszka, 1997). To assess a possible impact of major local industrial facilities, chemical and sulphur isotope analyses were done on stack dust and feedstock.

The scope of analyses included major and trace elements, pH, TIC, TOC and sulphur isotopes. In addition, topsoil, and some pine needle, and lichen samples were tested for four groups of organics, i.e., polynuclear aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), organochlorine pesticides and phenols. The chemical analyses were done in Central Chemical Laboratory of the Polish Geological Institute (P. Pasławski), whereas the stable sulphur determinations in Mass Spectrometry Laboratory of the Maria Curie-Skłodowska University in Lublin (S. Hałas and J. Szaran).

All the investigation sites were covered with a phytosociological survey using Braun-Blanquet's scale (E. Bróż and A. Gałuszka *fide* Z. M. Migaszewski, 1997*b*). The taxonomic study was associated with observations of any detrimental changes in vegetation (S. Cieśliński *fide* Z. M. Migaszewski, 1997*b*). The results of the first phase of investigation (1994), which also included mosses, were presented in the previous report (Z. M. Migaszewski, P. Pasławski, 1996). The preliminary study of organics was initiated, too (Z. M. Migaszewski *et al.*, 1996).

The study was carried out in two areas: (1) Holy Cross Mountain National Park (HCMNP) situated in the north-central part of the region, and (2) southern, central and north-eastern parts of the Holy Cross Mts. (HCM) (Fig. 1).

Holy Cross Mountain National Park was established in 1950. Until 1996, it had taken up an area 5909 ha (at present 7626 ha) including the Łysogóry Range built of Middle and Upper Cambrian quartzitic sandstones with interbedded siltstones and claystones, and some area north, north-west and north-east of it.

Most of HCMNP ecompasses the densely forested Łysogóry Range; European silver fir *Abies alba* Mill. and European beech *Fagus sylvatica* L. are prevalent here. The pine is represented only by the species *Pinus sylvestris*. It is rather scarce and its major stands occur primarily in the northern lower parts of HCMNP. In the park as much as 197 lichen species were originally recorded; this number has dropped to 129 or probably even less (S. Cieśliński, 1985, 1991). Some taxonomic groups have become completely extinct. They include lichens primarily with leafy (foliose) and shrubby (fruticose) thalii, i.e., genera *Usnea, Bryoria, Ramalina, Evernia, Lobaria*, etc.

The second study area (HCM) is geologically and morphologically more diversified. It includes most of the Palaeozoic (except for the Upper Carboniferous through lower Upper Permian) formations spanning Lower Cambrian clayey shales and siltstones to Upper Zechstein carbonate conglomerates. Aside from forest-clad gently sloped ranges, vast harvested valleys occur here. The species *Pinus sylvestris* is much more common in HCM than in HCMNP. Lichen flora is diverse; nonetheless, only crustose and foliose varieties are generally prevalent here (Pl. I, Figs. 3 and 4).

Sampling design with site locations, as well as field sampling, sample preparation and analysis procedure were described in the previous reports (Z. M. Migaszewski, P. Pasławski, 1996; Z. M. Migaszewski *et al.*, 1996). The element and sulphur isotope spatial variation in soils and vegetation was estimated for specific geographic intervals using an unbalanced, nested analysis-of-variance (ANOVA) design (R. L. Anderson, T. A. Bancroft, 1952; L. P. Gough *et al.*, 1988*a*, *b*; J. G. Crock *et al.*, 1992). The results of summary statistics for and variation in the component content in soils and plant bioindicators were presented in the unpublished report (Z. M. Migaszewski, 1997*b*).

SOILS

MAJOR AND TRACE ELEMENTS, PH, TIC AND TOC

The results of soil investigation performed in 1996 generally confirmed those previously done (Z. M. Migaszewski *et al.*, 1995; Z. M. Migaszewski, 1996*d*; Z. M. Migaszewski, P. Pasławski, 1996), i.e., the elevated content of many major and trace elements in the uppermost horizon (topsoil); nonetheless, some local geochemical anomalies linked to different factors (chemical composition of bedrock, soil type, etc.) were recorded. The distribution pattern of chemical elements was as follows:

Aluminum was generally depleted in topsoil showing an elevated content (up to 3.654%) in underlying soil horizons, especially in the area of HCMNP (Las Serwis). This fact was connected with leaching of this element from more acidic topsoil and depositing it at the soil/hostrock boundary. The very hostrock (quartzitic sandstones or limestones and dolomites) did not contain much aluminum. The lowest pH values (down to 3.3 in Łysica Mt.) were noted in the park area. Nearly all sites revealed a close relationship between the pH and the concentration of aluminum; the largest differences in the content of aluminum between topsoil and lower soil horizons corresponded to the greatest excursions in pH. The highest level of this element in hostrock (quartzitic sandstones) did not exceed 0.797% (west of Saint Nicholas chapel).

Arsen appeared in excess within topsoil, particularly at the top of the tallest mountains. Its content reached 19 ppm (Zembrowica Mt.). The only exception was Las Serwis where concentration of arsen was nearly the same in all soil layers. In the southeastern part of the study area, arsen occurred in traces (below 5 ppm), which was reflected both by the location of sites (far from potential industrial sources) and the presence of sandy soils that favoured easy removal of many elements from topsoil. The content of this element was largely linked to air pollution, even though at some sites (Zembrowica Mt. and Święty Krzyż Mt.) another source, i.e., Cu-arsenosulphides or As- and Cu-rich pyrite scattered within hostrock, seems to have played an important role, too. The concentration of arsenic in quartzitic sandstones reached as much as 17 ppm (Święty Krzyż Mt.).

Barium was generally elevated in topsoil reaching 124 ppm (Las Serwis); however, at many sites located in the examined part of the Main Range (Łysogóry and Klonówka Mt.), underlying soil horizons contained even more barium. This fact seems to have been connected with the presence of barite veinlets piercing quartzitic sandstones. The highest level of this element in quartzitic sandstones did not exceed 68 ppm (west of Saint Nicholas chapel). Considering this, two factors, i.e., the geologic and the anthropogenic, played an important role in the spatial distribution of barium.

Beryllium occurred below detection limit (0.5 ppm) nearly everywhere, especially in hostrock. The only exception was the southwestern part of the Holy Cross Mts. and Las Serwis where the concentration of beryllium in topsoil was as much as 1.3 ppm.

Cadmium prevailed in topsoil everywhere reaching 1.9 ppm (Zembrowica Mt.). All rocks contained cadmium below detection limit (0.5 ppm). The analysis of the spatial distribution pattern indicated that this element was connected with westerly winds coming from the Upper Silesian-Cracovian and the Moravian industrial district.

Caesium was commonly elevated in underlying soil horizons reaching 48 ppm (Święty Krzyż Mt.). It is hard to assess the impact of air pollution on the spatial distribution of this

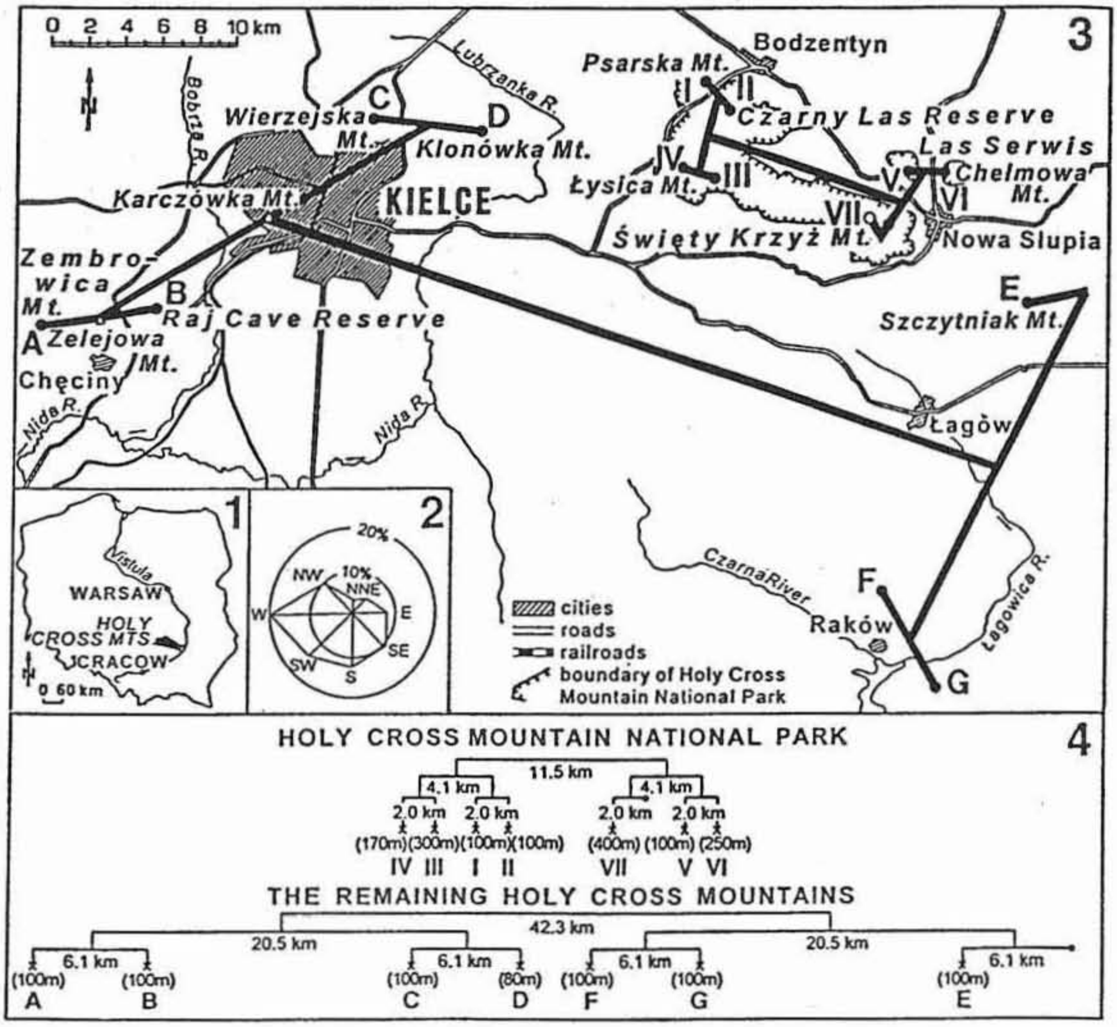

Fig. 1. Location of the study area (1), wind rose (2), the Holy Cross Mts. and Holy Cross Mountain National Park with barbell cluster (3) and nested design (4)
I–VII — investigation sites in Holy Cross Mountain National Park; A–G — investigation sites in the remaining area of the Holy Cross Mts.

Lokalizacja terenu badań (1), róża wiatrów (2), Góry Świętokrzyskie i Świętokrzyski Park Narodowy ze stanowiskami badawczymi wyznaczonymi metodą „sztangi" (3) oraz rozkład gniazdowy (4)
I–VII — stanowiska badawcze w Świętokrzyskim Parku Narodowym; A–G — stanowiska badawcze na pozostałym obszarze Gór Świętokrzyskich

element. In some places of HCMNP, it appears to have been linked to hostrock (29 ppm).

Calcium was only somewhat elevated in topsoil except for sites where hostrock consisted of limestones or dolomites, i.e., in the southwestern part of the Holy Cross Mts.

Chromium varied from 2 to 40 ppm showing no connection with soil type or hostrock. In different places its maximum concentration shifted from topsoil (25 ppm — Las Serwis) through lower soil (40 ppm — same site) to hostrock (37 ppm — Święty Krzyż Mt.).

Cobalt was generally abundant in topsoil (as much as 18 ppm), but within HCMNP primarily in lower soil horizons (up to 20 ppm) at a close contact with impermeable quartzitic sandstones. Most of the content of cobalt was linked to air pollution. Although the concentration of this element in quartzitic sandstones reached 5 ppm, these rocks do not seem to be the potential source of contamination of soil due to their resistance to chemical weathering.

Copper was generally raised in topsoil (up to 259 ppm), but at some sites, especially at those located in the southwestern part of the region, underlying soil horizons or even hostrock (limestones and dolomites) were highly enriched in copper reaching 335 ppm. As a result of weathering, this element was released from scattered and veined Cu-sulphides contained in carbonate hostrock. Thus, in some parts of the Holy Cross Mts. two sources of pollution overlapped, i.e., the geologic and the follout-derived.

Ferrum was generally raised in topsoil (up to 2.79%), but at some sites located in the Main Range higher concentration of iron was noted in lower soil horizons (up to 3.67%) or even in hostrock (up to 1.09% — in quartzitic sandstones of Psarska Mt.). The content of iron at these sites reflected, at least partly, a geologic imprint.

Lanthanum did not show any connection with a given soil horizon, except for the Main Range where it was elevated primarily in lower soil horizons reaching as much as 22 ppm (Święty Krzyż Mt.). Quartzitic sandstones contained as much as 12 ppm of lanthanum (west of Saint Nicholas chapel).

Lead is a typical element connected with air pollution; it was distinctly abundant in topsoil reaching 398 ppm (Łysica Mt.). Except for Zembrowica Mt. (88 ppm), the content of lead in hostrock was relatively low generally averaging around several ppm.

Lithium showed a bimodal distribution. In general, it was raised in topsoil (up to 29 ppm — Las Serwis), but within the Main Range and some area north of it, this element was elevated in lower soil horizons (up to 41 ppm — same site), primarily at a close contact with quartzitic sandstones. These rocks contained up to 5 ppm of lithium (west of Saint Nicholas chapel).

Magnesium was primarily linked to the presence of Mg-bearing carbonate rocks (dolomites) or veinlets (dolomites or ankerites). The highest content of magnesium (12.20%) was recorded in hostrock of Zembrowica Mt.

Manganese was generally elevated in topsoil, but at some places of the Main Range it was raised in lower soil horizons close to a boundary with quartzitic sandstones. The highest content of manganese (up to 4870 ppm) was noted in Las Serwis. Its source was primarily of anthropogenic origin. Some rocks (limestones and dolomites) are fairly enriched in this element reaching as much as 581 ppm (Zembrowica Mt.).

Mercury was greatly elevated in topsoil, especially within HCMNP, reaching as much as 0.628 ppm (Łysica Mt.). It was connected primarily with industrial airborne emissions, even though some quartzitic sandstones contained as much as 0.262 ppm of mercury (Święty Krzyż Mt.). At discussed site, topsoil yielded 0.370 ppm whereas subsoil 0.039 ppm of this element. The lowest content of mercury, as well as other elements, was recorded in the southeastern part of the region reflecting both the minor air pollution and the presence of sandy soils.

Molybdenum occurred nearly in all places below detection limit, i.e., 2 ppm. The only exception was topsoil in Łysica Mt. and Las Serwis where the content of molybdenum reached 3 ppm.

Neodymium was somewhat elevated in topsoil (up to 14 ppm); however, in places where hostrock was made of quartzitic sandstones (Main Range), it tended to concentrate in the lower soil horizon reaching 20 ppm. The content of neodymium in quartzitic sandstones was as much as 12 ppm (west of Saint Nicholas chapel).

Nickel like neodymium occurred primarily in topsoil (up to 28 ppm); nonetheless, in some places of HCMNP, it was distinctly elevated in the lower soil horizon reaching 30 ppm (Czarny Las Reserve). The content of nickel in quartzitic sandstones nowhere exceeded 4 ppm.

pH was closely linked both to the content of sulphur, and the soil and rock type. The lowest values (3.3–3.4) were recorded at Łysica Mt.

Phosphorus was remarkedly raised in topsoil reaching 0.075% (Łysica Mt.). Its concentration was closely linked to organic matter that was highly elevated in the uppermost soil profile.

Potassium was linked to clay minerals, that is why its maximum content was traced in different soil horizons and hostrock.

Scandium occurred in trace amounts; it was generally elevated in topsoil (3.7 ppm — Las Serwis) except for the Main Range where it was highly concentrated in the lower soil horizon (up to 7.0 ppm — Las Serwis). The content of scandium in quartzitic sandstones did not exceed 1.6 ppm (Łysica Mt.).

Silver occurred in all places below detection limit, i.e., 1 ppm.

Sodium did not show any diversity in its distribution pattern; at many sites it occurred below detection limit, i.e., 0.01%. Only topsoil of Zembrowica Mt., Szczytniak Mt. and Las Serwis yielded up to 0.03% of sodium.

Strontium did not show much diversity in distribution pattern. The only exception was the southwestern part of the region made up of limestones and dolomites where an increase of strontium downward the soil profile was observed (40, 64, 78 ppm in topsoil, subsoil and dolomites of Zembrowica Mt.). The limestones contained as much as 252 ppm of strontium (near Raj Cave Reserve).

Sulphur was highly elevated in topsoil. Its content varied from < 0.005 (near Raków) to 0.152% (Łysica Mt.). In hostrock the concentration of sulphur averaged around 0.005%, only in places (Zembrowica Mt.) reaching 0.026%. The latter was linked to Cu- and Pb-sulphides scattered in limestones and dolomites.

Titanium was elevated in topsoil, but within the Main Range primarily in the lower soil at a direct contact with quartzitic sandstones. In such places the content of titanium reached 718 ppm (Klonówka Mt.). Quartzitic sandstones contained as much as 181 ppm of this element (west of Saint Nicholas chapel).

TIC was generally enriched in topsoil, but in places where carbonate hostrock or carbonate veins in quartzitic sandstones occurred, lower soil horizons showed raised concentrations of TIC reaching 11.63% (near Raj Cave Reserve).

TOC was elevated in topsoil of all sites reaching 33.97% (Łysica Mt.). Its content was closely linked to organic matter distinctly prevailing in uppermost soil horizons.

Uranium was determined only in 1994 and 1995. In 1995 its content in topsoil was lower varying from < 0.1 to 1.6 ppm (Łysica Mt.). Quartzitic sandstones yielded up to 1.4 ppm of uranium (Święty Krzyż Mt.).

Vanadium tended to concentrate in topsoil (as much as 35 ppm — Zembrowica Mt. and Las Serwis); however, in many places of the Main Range it showed a raised content in lower soil horizon at a direct contact with quartzitic sandstones. The content of vanadium reached 44 ppm (Las Serwis). Hostrock (limestones and dolomites) contained as much as 22 ppm of vanadium (Zembrowica Mt.).

Yttrium did not show any diversity in soil profiles; the only exception was the site located close to Raj Cave Reserve where topsoil was distinctly enriched in yttrium (up to 12 ppm). Quartzitic sandstones yielded up to 5 ppm of this element (Szczytniak Mt.).

Ytterbium was elevated in topsoil, particularly in Las Serwis (2.7 ppm) and the southwestern part of the Holy Cross Mts. (0.6 to 2.5 ppm). In the remaining area no distinct diversity in the distribution pattern of this element was noted. The highest level of ytterbium (3.8 ppm) was noted in lower soil horizon of Las Serwis. Rocks (limestones) contained as much as 1.6 ppm of this element (near Raj Cave Reserve).

Zinc was elevated in topsoil almost everywhere. The highest content of zinc (166 ppm) was recorded at Zembrowica Mt.; the raised concentration of this element in carbonate hostrock (up to 51 ppm — same site) indicates lithology as a potential source of soil pollution. In the remaining examined area, industrial emissions seem to have played a more important role in distribution of zinc in topsoil, for instance at Łysica Mt., the content of this element in topsoil, subsoil and quartzitic sandstones was 110, 24 and 12 ppm, respectively.

In individual soil profiles, the relationship between the increase of many chemical elements and the increase of TOC or the drop of pH (more acidic) was observed.

In the present author's opinion the best sites recording off-regional pollution from western and northern sectors are Klonówka Mt. (west) and Święty Krzyż Mt. (east). Considering the results of chemical analyses of soil done in 1994 through 1996, the southern slope of Klonówka Mt. was enriched in Ba, Mn and Ti, and somewhat in Cd, Fe, Hg, Pb, S, Sc and Zn, whereas the northern slope of Święty Krzyż Mt. showed an increased level of Ba, Fe, Mn and Ti; in turn, sulphur was nearly uniformly distributed between the northern and southern slopes which indicates the two potential sources of pollution coming generally from the western and northern sectors.

Compared to 1995, topsoil showed a slight increase of Cu, pH (less acidic) and Yb, as well as a decrease of Pb, S and Zn (Z. M. Migaszewski, 1997*a*). The content of the remaining elements was fairly stable which indicated that some sort of equilibrium in element circulation was achieved.

The chemical composition of spring waters from the HCMNP has not changed remarkedly since 1994 (Z. M. Migaszewski, P. Pasławski, 1996). The only exception was higher pH (less acidic) varying in 1996 from 4.22 to 5.54 (from 3.99 to 5.18 in 1994) and the elevated content of HCO_3^- ranging from 0.0 to 14.6 mg/l (from 0.0 to 1.8 mg/l in 1994). In 1996, these waters were somewhat depleted in heavy sulphur isotope (less positive $\delta^{34}S$). These values varied from 3.2 to 4.2‰ compared to 3.7–5.5‰ in 1994, respectively, and were similar to those (4.0–4.5‰) reported for rainfalls from the area of Lublin (S. Hałas, unpubl. data); this fact indicates a rapid circulation of water in the bedrock. In addition, in 1996, the water from spring at Święty Krzyż Mt. contained higher concentrations of Cd (0.004 mg/l), Mn (1.074 mg/l) and Zn (0.263 mg/l), which exceeded several times those from the remaining springs. The high content of these elements was also observed here in topsoil, pine-needles and lichen thalli.

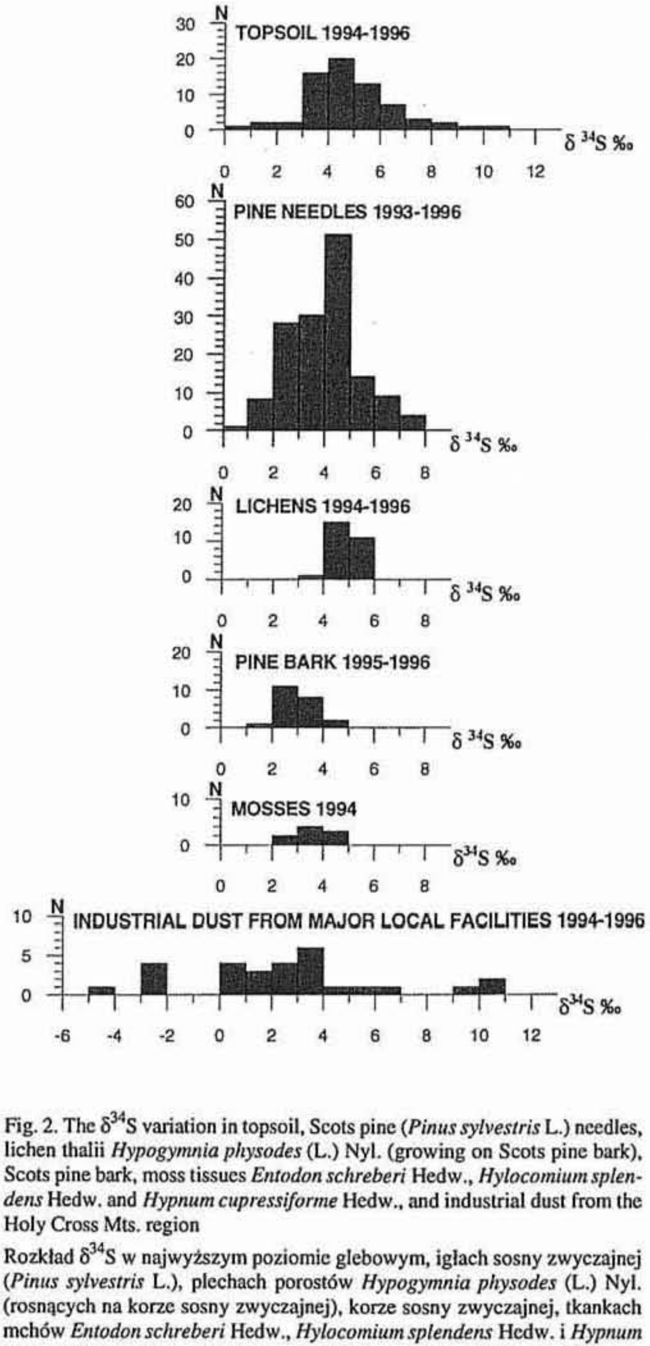

Fig. 2. The $\delta^{34}S$ variation in topsoil, Scots pine (*Pinus sylvestris* L.) needles, lichen thalii *Hypogymnia physodes* (L.) Nyl. (growing on Scots pine bark), Scots pine bark, moss tissues *Entodon schreberi* Hedw., *Hylocomium splendens* Hedw. and *Hypnum cupressiforme* Hedw., and industrial dust from the Holy Cross Mts. region

Rozkład $\delta^{34}S$ w najwyższym poziomie glebowym, igłach sosny zwyczajnej (*Pinus sylvestris* L.), plechach porostów *Hypogymnia physodes* (L.) Nyl. (rosnących na korze sosny zwyczajnej), korze sosny zwyczajnej, tkankach mchów *Entodon schreberi* Hedw., *Hylocomium splendens* Hedw. i *Hypnum cupressiforme* Hedw. oraz pyle przemysłowym z rejonu świętokrzyskiego

SULPHUR ISOTOPES

The sulphur isotope analyses performed on topsoil, lower soil and hostrock samples indicated that air pollution was a decisive factor here. This inferrence was supported by the largest excursion in the $\delta^{34}S$ at these sites where topsoil showed the highest content of sulphur (Table 1) marked by an anthropogenic isotopic "fingerprint" (Fig. 2). In turn, topsoil depleted in sulphur revealed the isotopic composition of its hostrock (see Psarska Mt., Table 1). In general, the $\delta^{34}S$ values in topsoil were different from those in dolomites and

Table 1

The sulphur isotope composition versus the content of sulphur in selected profiles (1995)

Site locations	Profile	S [%]	$\delta^{34}S$ [‰]
A/2 (Zembrowica Mt.)	topsoil	0.100	7.3
	limestone	0.056	–0.8
E/1 (Szczytniak Mt.)	topsoil	0.161	4.0
	quartzite	0.010	10.6
E/2 (Szczytniak Mt.)	topsoil	0.115	5.5
	lower soil	0.020	7.8
	quartzite	0.007	7.5
I/2 (Psarska Mt.)	topsoil	0.015	7.3
	lower soil	0.015	8.3
	quartzite	< 0.005	8.7
IV/2 (Łysica Mt.)	topsoil	0.231	3.8
	lower soil	0.016	7.4
	quartzite	< 0.005	8.2

limestones (–0.8 to –9.7‰) and most quartzitic sandstones (5.3–10.6‰).

The isotopic values from topsoil of Szczytniak Mt. and Łysica Mt. varied from 3.8 to 5.5‰ being close to those in rainwater (4.0 to 4.5‰) and spring water (3.7 to 5.8‰ in 1995). In addition, they differed from those in lower soil (7.4 to 7.8‰) and quartzites (7.5 to 8.2‰). The quartzites and quartzitic sandstones of the Main Range yielded only a small amount of pyrite.

It should be emphasized here that the $\delta^{34}S$ variation pattern in topsoil and bioindicators was nearly identical; it generally coincided with that in industrial dust coming from major local facilities.

The results of $\delta^{34}S$ determinations were also different from those reported for soils collected in Peace River Region, Alberta in Canada (H. R. Krouse, 1978). The obtained $\delta^{34}S$ varied from –19.8 to 4.3‰ and were, in turn, connected with the isotopic composition of bedrock.

ORGANIC COMPOUNDS

Of all the organic groups, polynuclear aromatic hydrocarbons (PAHs) revealed the highest concentrations in topsoil of the Holy Cross Mts. The remaining organic groups, i.e., polychlorobiphenyls (PCBs), organochlorine pesticides, and phenols generally occurred in trace amounts; in addition, they were not recorded at every site.

Of the different PAH compounds, benzo[b]-benzo[k] fluoranthene was the most common reaching 610.72 ppb (southern slope of Łysica Mt.). The highest concentrations of PAHs were recorded within HCMNP and other elevated sites of the Holy Cross Mts. In the southeastern part of the study region (near Raków and Chańcza), the total content of these compounds was the lowest varying from 4.43 to 68.50 ppb.

Regarding the spatial distribution pattern of PAHs, some bimodality was observed between the northern and southern slopes at different sites. In the northwestern part of the Holy Cross Mts. (Klonówka Mt., Psarska Mt. and Czarny Las Reserve) southern slopes were distinctly enriched in PAHs, for instance, at Klonówka Mt. they reached 481.34 ppb (south) versus 115.71 ppb (north). In turn, in the northeastern part of the study region (west of Saint Nicholas chapel, Chełmowa Mt. and Szczytniak Mt.) northern sampling points contained much more PAHs, for instance, at Szczytniak Mt. they were as much as 903.93 ppb (north) versus 218.16 ppb (south). The tallest mountains of the Holy Cross Mts., i.e. Łysica Mt. and Święty Krzyż Mt., did not show much diversity in the content of PAHs between the northern and southern slopes, even though they recorded the highest content of these compounds. At Łysica Mt. they reached 1808.24 ppb (north) versus 1905.83 ppb (south), whereas at Święty Krzyż Mt. 1458.44 and 1241.22 ppb, respectively.

Of the remaining organic compounds, PCB-118 (to 8.53 ppb), PCB-153 (to 10.66 ppb), aldrin (< 0.50 to 33.96 ppb), endosulphan I (< 1.00 to 65.09 ppb) and 4,4'-DDT (< 8.00 to 138.25 ppb) were detected in topsoil of the study region. They were noted primarily in the highest parts of the Holy Cross Mts. The maximum concentrations of these compounds were recorded at Łysica Mt. Phenols were extremely scarce, of which only 4-nitrophenol occurred above detection limits varying in some places from 2.51 to 7.37 ppb.

SCOTS PINE NEEDLES

MAJOR AND TRACE ELEMENTS

In general, individual Scots pine (*Pinus sylvestris*) trees showed an increase of Cu, K, Mg, Ni and P, and a drop in Al, Ba, Ca, Fe, Hg, Mn, Na, Pb, Sr, Ti and Zn going from 1994 through 1996 pine needles of the same crop. The same relationship between the content of elements and the time span was recorded by their geometric mean values (Z. M. Migaszewski, 1997*b*). Of these elements, the most distinct trend was marked by Ca, Hg, Mn and Ni. This secular distribution pattern was similar to that recorded by the previous investigation (Z. M. Migaszewski, A. Gałuszka, 1997).

Compared to their host bark, the pine needles of all age classes were distinctly enriched in B, Mn, P, S, Zn, and depleted in Al, Ba, Cd, Cr, Fe, Hg, La, Pb, Ti, V, Y and Yb.

The results of analyses performed on one-year pine needles (Psarska Mt.) collected in 1994, 1995 and 1996 recorded a drop in the content of Cu, K, Mg, Ni, P and S (Table 2).

SULPHUR ISOTOPES

In 1996, the $\delta^{34}S$ in pine needles of all age classes varied from 1.1 to 7.2‰ with an average value of about 4.0‰. The cumulative $\delta^{34}S$ variation pattern in needles was similar to that in topsoil and generally in other media (Fig. 2).

The pine needles were enriched in heavy isotope (more positive $\delta^{34}S$) relative to their host bark (Z. M. Migaszewski, 1997*b*).

Table 2

The content of sulphur and selected metals in one-year pine needles *Pinus sylvestris* (L.) and topsoil collected in 1994, 1995 and 1996 at Psarska Mt.

Sampling year	Ba [ppm]	Ca [%]	Cd [ppm]	Cu [ppm]	Hg [ppm]	K [%]	Mg [%]	Mn [ppm]	Ni [ppm]	P [%]	S [%]	Zn [ppm]
Needles-1994	5	0.33	1.0	9	0.020	0.96	0.090	577	17	0.260	0.072	59
Needles-1995	3	0.21	0.6	6	0.015	0.92	0.073	468	7	0.214	0.068	50
Needles-1996	<1	0.14	0.5	5	0.014	0.55	0.067	271	4	0.063	0.041	32
Topsoil-1995	56	0.09	< 0.5	12	0.189	0.09	0.050	588	5	0.051	0.053	51
Topsoil-1996	46	0.06	< 0.5	27	0.236	0.10	0.060	388	7	0.041	0.051	46

The raised content of heavy sulphur isotope in the youngest pine needles seems to have been connected with a removal of an excess of sulphur in the form of isotopically lighter H_2S (J. W. Case, H. R. Krouse, 1980). This process was combined with an uptake of SO_2 from the air. The 1996-pine needles showed only small injuries of their stomata, through which moisture and gases pass, favouring more intense gas exchange compared to the older needles.

ORGANIC COMPOUNDS

Of the PAH compounds only phenanthrene occurred in all examined pine needle samples varying from 2.03 to 20.05 ppb. Some relationship between the content of this compound in pine needles and topsoil was recorded, for instance, 1994-pine needles and topsoil from Łysica Mt. (site IV) contained 18.16 and 67.76 $\mu g\ kg^{-1}$ of phenanthrene, whereas those media from Chańcza (site G) yielded 5.30 and 0.75 $\mu g\ kg^{-1}$ of phenanthrene, respectively. The remaining PAHs occurred in trace amounts; only pyrene reached 277.64 ppb in 1994-pine needles from Łysica Mt. Most of these compounds seem to be of anthropogenic origin coming from industrial emissions.

PCBs (only PCB-52) and organochlorine pesticides (α-BHC, γ-BHC, δ-BHC and endosulphan II) generally occurred below detection limits.

Of phenols, only 4-nitrophenol (< 4.50 to 29.77 ppb) and pentachlorophenol (< 0.55 to 3.94 ppb) were detected; other compounds, such as, 4-chloro-3-metylophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol and phenol were scarce. In general, phenols were not recorded in topsoil around pine-trees, from which needles were collected. This fact indicates that these compounds may have been products of metabolism.

LICHENS AND SCOTS PINE BARK

MAJOR AND TRACE ELEMENTS

In 1994 the scope of investigations included lichens *Hypogymnia physodes* growing on a bark of different deciduous (birch, oak, rowan) and coniferous (pine, fir) trees. The obtained results were presented in the previous report (Z. M. Migaszewski, P. Pasławski, 1996). During the next two years (1995, 1996), only lichens from pine and birch trees along with associating host bark were examined.

Aside from the prevalent species *H. physodes*, *Xanthoria parietina* (L.) Th. Fr. from larch bark, occurring in a large amount at Zembrowica Mt., was analysed as well. Compared to *H. physodes*, the latter species contained much more following elements (in parantheses maximum concentrations recorded in 1995 and 1996): Al (0.274%), As (4 ppm), B (5 ppm), Cd (1.3 ppm), Fe (0.349%), La (3 ppm), Li (4 ppm), Mg (0.059%), Ni (4 ppm), P (0.145%), S (0.145%), Sc (0.8 ppm), Sr (11 ppm), Ti (82 ppm), V (12 ppm) and Zr (1.7 ppm).

The same distribution pattern was partly revealed by their host bark; the larch bark yielded far more Al (0.151%), B (9 ppm), Ca (0.90%), Cd (1.4 ppm), Fe (0.235 ppm), La (2 ppm), Mg (0.051%), pH (4.9), S (0.084%), Sc (0.3 ppm), Sr (22 ppm), Ti (88 ppm), V (8 ppm), Y (1.6 ppm) and Zr (0.8 ppm) than the pine or birch bark, respectively.

Lichens *H. physodes* growing on a pine bark were distinctly enriched in Cr, Cu, Fe, Hg and Ti, and depleted in Ba, Ca, K, Mg, Mn, P, Pb, S, Sr and Zn compared to those growing on birch bark.

The chemical analyses showed that lichens *H. physodes* growing on a pine bark were remarkedly enriched in Fe, Hg, K, Mg, P, S, Ti and Zn, and depleted in Ba, and somewhat Pb and Sr relative to their host bark.

A drop in the level of sulphur and somewhat Zn and Mg was observed within a period from 1994 through 1996. The content of sulphur decreased by about twice. Some minor trends observed at individual sites seem to be connected with an influence of local industrial facilities combined with wind rose and topographic features.

SULPHUR ISOTOPES

In 1996, the $\delta^{34}S$ in the examined lichens varied from 3.2 to 5.0‰, whereas in pine bark from 1.9 to 2.3‰. The $\delta^{34}S$ variation pattern in lichens was generally similar to that in pine needles (Fig. 2). Compared to the lichens and pine needles of all age classes, their pine bark was enriched in light sulphur isotope (Fig. 2). This phenomenon seems to have been connected with removing from lichens and pine needles an excess of sulphur in the form of isotopically lighter H_2S (J. W. Case, H. R. Krouse, 1980).

ORGANIC COMPOUNDS

Of all the examined PAH compounds, benzo[a]anthracene (4.66 to 7.07 ppb), benzo[b]+[k]fluoranthene (25.10 to 49.10 ppb), chrysene (13.23 to 26.17 ppb), fluoranthene (16.65 to 29.47 ppb) and pyrene (11.11 to 20.70 ppb) played a major role. Among PCBs, PCB-153 was prevalent varying from 1.33 to 2.21 ppb. This compound was sporadically noted in topsoil, for instance, at Łysica Mt. and Święty Krzyż Mt. No pine needles contained detectable amounts of PCB-153. Organochlorine pesticides were represented by aldrin (3.40 to 10.89 ppb), 4,4'-DDD (2.32 to 3.40 ppb), 4,4'-DDT (15.84 to 22.48 ppb) and endosulphan I (4.64 to 17.18 ppb). Aside from 4,4'-DDD, the remaining compounds also occurred in topsoil. In turn, they all were absent from pine needles of all age classes. No phenols were recorded in the examined lichens.

DISCUSSION

The results of detailed investigations performed in 1994 through 1996 indicated that the content of Hg, P, Pb, S and TOC was highly elevated in topsoil; the remaining analysed elements, such as As, Ba, Cd, Co, Cu, Fe, Mn, Nd, Ni, Sc, Ti, V, U, Yb and Zn, also occurred in excess within the aforementioned soil horizon. Moreover, in 1996 the topsoil/lower soil concentration ratio of lead reached 32 (259 ppm/8 ppm — west of Saint Nicholas chapel), 9 (398 ppm/46 ppm — Łysica Mt.) or 6 (244 ppm/38 ppm — Wierzejska Mt.), whereas that of sulphur was as much as 15 (0.134 ppm/0.009 ppm — Wierzejska Mt.) or 10 (0.152 ppm/0.016 ppm — Łysica Mt.).

The pH value, linked mainly to a concentration of sulphur, was much lower in topsoil (more acidic) than in underlying soil horizons. Its concentration ratio ranged from 0.6 (3.5/6.3 — west of Saint Nicholas chapel) to 0.9 (7.9/9.0 — Zembrowica Mt.).

It should be mentioned here that higher concentrations of different elements in topsoil were associated not only with the degree of air pollution, but also with the soil types featured by the different content of natural sorbents, i.e., clay minerals, organic matter (TOC) and Fe- and Mn-oxides and hydrooxides; thus, chernozems or some rankers and rendzinas tended to accumulate more heavy metals than arenosols. This relationship was sharply marked while comparing the southeastern part of the study area (Raków–Chańcza area) with the remaining part of the Holy Cross Mts. Arenosols, including rusty sandy soils, are prevalent in the Raków–Chańcza area. Chemical elements are only partly bound by humus-depleted topsoil; they are easily leached downward through permeable soil horizons. That is why the lowest concentrations of heavy metals and sulphur in topsoil here resulted not only from minor pollution (area is located far from industrial centers), but also from soil type.

The content of uranium in topsoil was similar to that in hostrock (quartzitic sandstones and carbonate rocks) where it varied from < 0.1 ppm (near Raj Cave Reserve) to 1.4 ppm (Święty Krzyż Mt.). The regional background of this element in rocks averaging around 0.5 ppm was relatively higher than that (< 0.005 ppm) in the Colorado Rocky Mts. (L. P. Gough, 1993).

Only a few elements, i.e., Al, Ce and somewhat La, were raised in lower soil horizon. Nonetheless, it should be stressed here that in the Main Range which is composed of poorly permeable quartzitic sandstones, the content of many elements (Ba, Co, Fe, Nd, Ni, Sc and Ti) was elevated at the boundary between the lower soil horizon and poorly permeable hostrock.

The tallest mountains of the region partly making up Holy Cross Mountain National Park also showed an elevated concentration of most elements. Thus, Łysica Mt., the tallest mountain of the Holy Cross Mts., was greatly abundant in many chemical elements and organic compounds. The highest content of Pb (398 ppm), S (0.152%) and PAHs (1905.83 ppb), and simultaneously the lowest pH value (3.3) was recorded here. Elevated levels of many elements were also observed at Wierzejska Mt. near Kielce and at Święty Krzyż Mt.

Considering this, the geologic (especially lithologic) and topographic features are the main reason why the geometric mean values of many elements (As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, S, Ti, V and Y) were raised in HCM, especially in HCMNP compared to those in Poland, even the Upper Silesia (Z. M. Migaszewski, 1996*c*, *d*, 1997*a*, *b*; Z. M. Migaszewski, P. Pasławski, 1996). The high mean content of As, Cr, Hg, Pb and S in the Holy Cross Mts. is a concern; some of these elements, particularly nonessential heavy and toxic metals have a detrimental impact on flora and fauna (A. Kabata-Pendias, H. Pendias, 1992). In addition, soils in the study region were more acidic (lower pH).

The content of many components has not changed in topsoil since 1995. Only the level of Cu somewhat increased, whereas that of Pb, S and Zn dropped at numerous individual sites, as well as for the whole region. An increase of pH (less acidic) of topsoil was observed, too (Z. M. Migaszewski, 1997*a*, *b*).

Nonetheless, the best secular trend in concentrations of different major and trace elements was revealed by *Pinus sylvestris* pine needles of three age classes (1994, 1995, 1996) collected from the same crop. Going from the oldest to the youngest needles an increase in the content of Cu, K, Mg, Ni, P and heavy sulphur isotope (more positive $\delta^{34}S$), and a drop of Al, Ba, Ca, Fe, Hg, Mn, Pb, Sr, Ti and Zn was recorded. Sulphur showed rather steady level in pine needles of all age classes, which can be explained by some sort of equilibrium reached in the process of absorption-removal of this element; besides, older pine needles do not take up lots of sulphur due to injuries of stomata (chlorosis and/or necrosis). The highest content of many elements in the oldest pine needles may be explained by a longer period of uptake. The second case, i.e., an elevated level of Cu, K, Mg, Ni and P in the youngest needles, seems to have been linked to an increased uptake of these essential elements during the rapid growth and metabolism of needles. On the other hand, the one-year needles collected in 1994, 1995 and 1996 showed a decrease of Cu, K, Mg, Ni, P and S (Table 2).

An increase in the content of some elements, for instance copper, in the youngest needles of the 1996 crop may be paradoxically connected with a decrease of air pollution from 1994 to 1996. Copper is an important essential element required for metabolism (metal-binding enzymes). However, an excess of copper leads to the damage of tree roots (and probably stomata) retarding metal uptake. This case was observed while examing tree rings from cottonwood (*Populus angustifolia* James) and aspen (*Populus tremuloides* Michx.) near Summitville, Colorado (T. V. V. King, 1995).

The pH of pine bark dropped from 3.3–4.5 in 1995 to 3.0–3.4 in 1996. It reached higher acidity similar to that (2.8–3.4) in the Białowieża Forest (K. Grodzińska, 1971). According to M. Świeboda and A. Kalemba (1979), bark acidity of 2.9 indicates nearly unpolluted environment.

As mentioned before, a considerable drop of sulphur (twice as much) in lichens *H. physodes* was observed in a period of three years; however, it did not influence a fast recolonization of lichen flora, which is still scarce in previously more polluted areas. The best example of it is Łysica Mt. and Święty Krzyż Mt. versus the Raków area. The species *H. physodes* was scarce on slopes of these mountains, but common in the second area even though the content of sulphur in lichen thalii was lower in Łysica Mt. and Święty Krzyż Mt. (0.036–0.034%) than in the Raków area (0.037–0.044%). In turn, the level of sulphur in *Pinus sylvestris* pine needles was distinctly higher in the former area (0.050–0.090%) compared to the Raków area (0.037–0.44%). The highest concentration of sulphur (0.107%) was recorded in a lichen "oasis" (about 1 km north of Zembrowica Mt.) located within a lichen "desert". This microenvironment was featured by wet conditions that favoured the growth of *H. physodes*. The microclimatic factors seem to play an important role in a spatial distribution of lichens.

The examined media responded differently to chemical changes in atmospheric emissions. As opposed to vegetation, topsoil marks nearly uninterruptive deposition of pollutants; the overall content of elements and sulphur isotopes and their spatial distribution pattern resulted largely from geomorphologic features, wind rose, soil and hostrock type, as well as intensity of biogeochemical circulation of chemical elements triggered by micro- and mesofauna activity. The behaviour of many heavy and toxic metals as well as organics in soil depends not only on their origin, form and concentration, but also on the properties of the very substrate, i.e., structure, pH, ion exchange capacity, an amount of natural sorbents, etc.

The reaction of vegetation to air pollution is much more complex and results not only from concentrations and specific properties of pollutants, but also from many environmental factors, i.e., topographic, climatic (insolation, wind, temperature, moisture), edaphic (structure and chemistry of soil), physiologic and genetic. This fact gives a potential challenge to data interpretation. An example of it is production of metal chelating acids (especially usnic acid and atranorin) in larger amounts by lichens as elevation increases — causing metal concentrations in lichens at higher elevations to be higher (D. M. Greene, 1993). An impact of different geomorphologic, climatic and soil-bedrock factors on the uptake of SO_2 by Scots pine needles was discussed in many papers (Z. M. Migaszewski, A. Gałuszka, 1997 with references cited). Nonetheless, the most important here seems to be the time relationship between metabolism and atmospheric emissions, as well as the type and form (soluble or insoluble) of pollutants. It should be emphasized here that the periods of maximum concentrations of SO_2 and other pollutants in the air do not always coincide with the increased metabolic activity and resultant uptake of flora species. Needles to say that even short periods of high concentrations of SO_2 can be detrimental to vegetation, for instance, an hour exposition of white pine (*Pinus strobus* L.) needles to air containing 130 $\mu g\ m^{-3}$ SO_2 led to their partial chlorosis and necrosis (A. C. Costonis, 1970). Lichens, in turn, do not absorb much SO_2 and other gases during drought periods (D. H. S. Richardson, 1981; *USDA Forest Service...*, 1993). The best example of this variability in the content of SO_2 was recorded at Święty Krzyż Mt. Although the mean yearly (1994) content of SO_2 was only 32 $\mu g\ m^{-3}$, its daily excursions varied from 0 (in April) to 532 $\mu g\ m^{-3}$ (in December); in the season of intense metabolism (May), they occasionally reached 277 $\mu g\ m^{-3}$ (*Raport o stanie środowiska...*, 1995).

The biogeochemical study of vegetation indicated that the concentrations of sulphur as well as many heavy and toxic metals in *Pinus sylvestris* needles and sulphur in *Hypogymnia physodes* from the Holy Cross Mts. were similar to those in the same species of Norway and northern and eastern Finland. The level of metals was a bit higher in *H. physodes* of the study area than that of northern Finland (S. Manninen, 1988; S. Manninen *et al.*, 1991, 1995; S. Manninen, S. Huttunen, 1995; A. Kytömaa *et al.*, 1995). In 1996, the content of sulphur in pine needles of the Holy Cross Mts. varied from 0.038 to 0.090%. W. Dmuchowski and A. Bytnerowicz (1995) recognized the value of 0.06% as a "normal" level for the species *P. sylvestris*.

The source of a considerable amount of sulphur as well as heavy and toxic metals for both topsoil and vegetation was generally common, which was evidenced by the same distribution pattern of $\delta^{34}S$ in the examined media (Fig. 2); it was close to the $\delta^{34}S$ in rainfall and spring waters. Its industrial "fingerprint" was also highlighted by the raised concentrations of sulphur and other elements in topsoil relative to underlying soil horizons and hostrock (Table 1).

The detailed study of soils also showed that topsoil from southern mountain slopes in the western part of the Holy Cross Mts. contained raised concentrations of Ba, Cd, Hg, Pb, S, Zn and PAHs. Both this fact and the prevalent wind rose indicated that a considerable amount of different pollutants had come from the western and southwestern sectors, i.e., from the highly industrialized Silesian-Cracovian, and the Moravian district (G. Żarnowiecki, 1993). This pattern was somewhat distorted by industrial facilities (heat generating plants, cement and lime plants, etc.) located in the southwest-central part of the study region. The results of chemical analyses (Z. M. Migaszewski, 1997*a*, *b*) showed that local stack dust contained excessive amounts of sulphur (up to 1.690% — Nowiny Cement Plant) and many heavy and toxic metals including As (up to 44 ppm), Co (28 ppm), Ni (60 ppm), Sr (729 ppm) — "Chemar" in Kielce; Ba (125 ppm), Cd (161 ppm), Cu (114 ppm), Cr (182 ppm), Pb (1720 ppm), Zn (2970 ppm) — Nowiny Cement Plant; Hg (0.174 ppm), Fe (7.58%), Mn (884 ppm), Ti (894 ppm), V (215 ppm) — Kielce Heat Generating Plant.

In addition, the obtained results highlight another potential nonpoint source of pollution. It encompasses many industrial facilities situated along the Kamienna River close to the northern margin of the Holy Cross Mts. They include Ostrowiec steelworks in Ostrowiec Świętokrzyski and Mesko metal facility in Skarżysko-Kamienna. The aforementioned industrial facilities are the greatest sources of hazardous element contamination. Even though their gas and particulate emissions are largely reduced by using various types of extraction equipment, they still spew a lot of pollutants including many hazardous or even toxic elements, such as, As, Ba, Cd, Cr, Cu, Hg, Mn, Ni, Pb, S, Sr, Ti, V and Zn. Their overall concentrations in stack dust commonly exceeds many times those coming from the industrial facilities located southwest of Kielce. The Ostrowiec steelworks affects the northeastern part of the Holy Cross Mts. which was evidenced by raised levels of many elements, especially Ba and Mn, as well as PAHs in topsoil of northern slopes.

CONCLUSIONS

The results of geochemical studies performed on different media of the Holy Cross Mts. showed raised concentrations of many hazardous and toxic elements primarily due to air pollution. As opposed to the pedosphere, the atmosphere is featured by rapid changes of its chemical composition. It also reacts much faster to changing levels of pollution. By contrast, the soil (especially topsoil) tend to accumulate heavy and toxic metals; its "self-purification" is a far slower process compared to vegetation.

Based on the results of investigation carried out on the moss species *Hylocomium splendens* Hedw. and *Entodon schreberi* Hedw. (K. Grodzińska, 1980), Holy Cross Mountain National Park was assigned to the most contaminated national parks in Poland. According to the present author, taking into account topsoil and its specific relationship with the geologic structure and topography, it seems to be number one on this list.

The next monitoring of soils, vegetation and spring waters should be done in 2002 to better record any changes in the content and spatial distribution pattern of elements and sulphur isotopes. Needles to say that samples ought to be taken from the same sites and, if possible, prepared and analysed by the same laboratories. Attention should also be shifted from sulphur and heavy metals to nitrogen oxides, ozone and volatile aromatic hydrocarbons.

In the present state of the art it is impossible to assess the potential impact of specific local facilities on the total regional balance of air pollution. To meet this objective an additional investigation is needed. It should include chemical and sulphur isotope determinations both on soils and vegetation (along transects from a given potential source of pollution), as well as on stack dust and feedstock.

As the results have shown, there are some signs of improvement of air quality in the study region. Whether it be a steady trend or a temporary shift depends on reducing a number of local point and nonpoint pollution sources and an amount of off-regional emissions. Because the human beings are an integral part of the nature, so it is vital for them that the natural environment be protected and restored.

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BADANIA GEOCHEMICZNE GLEB I ROŚLINNOŚCI W GÓRACH ŚWIĘTOKRZYSKICH W LATACH 1994–1996

Streszczenie

Głównym celem trzyletnich badań gleb i roślinności w regionie świętokrzyskim (fig. 1) było ustalenie bazowej koncentracji pierwiastków chemicznych i izotopów siarki oraz określenie ich rozkładu przestrzennego. Cel ten osiągnięto stosując pięcio- oraz czteropoziomową, niewyważoną, gniazdową analizę wariancji (ANOVA). Badaniami objęto: gleby, igły sosny *Pinus sylvestris* L., plechy porostów *Hypogymnia physodes* (L.) Nyl. i częściowo *Xanthoria parietina* (L.) Th. Fr., tkanki mchów *Entodon schreberi* Hedw., *Hylocomium splendens* Hedw. i *Hypnum cupressiforme* Hedw. (tylko w 1994 r. — Z. M. Migaszewski, P. Pasławski, 1996; Z. M. Migaszewski, 1997*b*), wody ze źródeł oraz pyły przemysłowe i węgiel z największych zakładów przemysłowych regionu. Zainicjowano również oznaczenia wielopierścieniowych węglowodorów aromatycznych (WWA), polichlorobifenyli (PCB), pestycydów chloroorganicznych i fenoli.

Najwyższy poziom glebowy (A) zawierał podwyższoną koncentrację wielu pierwiastków, szczególnie Hg (do 0,628 ppm), Pb (do 398 ppm) i S (do 0,152%). Najwyższe zawartości wielu pierwiastków, w tym również wyżej wymienionych, stwierdzono na Łysicy. Zarejestrowano tu również najniższą wartość pH (3,3) oraz maksymalną koncentrację WWA (do 1905,83 ppb). Średnie geometryczne wielu pierwiastków, w tym As, Cr, Hg, Pb i S, są wyższe na terenie Świętokrzyskiego Parku Narodowego i Gór Świętokrzyskich niż na pozostałym obszarze Polski, a nawet na Górnym Śląsku (Z. M. Migaszewski, P. Pasławski, 1996; Z. M. Migaszewski, 1997*b*). Wynika to po części ze specyficznej budowy geologicznej Gór Świętokrzyskich. Znaczna ich część zbudowana jest ze zwięzłych i słabo przepuszczalnych piaskowców kwarcytycznych kambru i dewonu dolnego charakteryzujących się słabo rozwiniętym profilem glebowym (rankery). Układ ten sprzyja akumulacji wielu pierwiastków, a szczególnie siarki i metali ciężkich. Igły sosny zwyczajnej z terenu parku zawierały więcej manganu niż ich odpowiedniki z pozostałego obszaru badań. Najmłodsze igły (z 1996 r.) w porównaniu ze starszymi (1994 i 1995 r.) pochodzącymi z tego samego zbioru, zawierały więcej Cu, K, Mg, Ni i P, wykazując jednocześnie większe wzbogacenie w cięższy izotop siarki. Igły jednoroczne pobrane w 1994, 1995 i 1996 r. ujawniały spadek zawartości Cu, K, Mg, Ni, P i S (tab. 2). W porównaniu z korą igły sosny reprezentujące wszystkie badane przedziały wiekowe były wzbogacone w B, Mn, P, S, Zn i cięższy izotop siarki, natomiast kora zawierała więcej Al, Ba, Cd, Fe, Hg, La, Pb, Ti, V, Y i Yb.

Porosty *H. physodes* ujawniały w stosunku do kory wzbogacenie w Fe, Hg, K, Mg, P, S, Ti, Zn i cięższy izotop siarki. Porosty z 1996 r. wykazywały w porównaniu z porostami z 1994 r. znaczny spadek zawartości siarki. Koncentracje siarki oraz niektórych metali ciężkich i toksycznych w igłach sosny oraz siarki w porostach były prawie takie same jak w północnej i wschodniej Finlandii i Norwegii. Z kolei porosty z obszaru Gór Świętokrzyskich ujawniały wyższy poziom skażenia metalami.

Skład izotopowy siarki w różnych elementach środowiska przyrodniczego oraz w pyłach przemysłowych potwierdził jej pochodzenie antropogeniczne (fig. 2, tab. 1).

Analiza rozkładu przestrzennego pierwiastków chemicznych w glebach oraz róży wiatrów wykazała, że zanieczyszczenia pochodzą głównie z sektora południowo-zachodniego. Nie jest zbadany jednak zasięg oddziaływania zakładów przemysłowych i kotłowni zlokalizowanych w południowo-zachodniej części badanego obszaru (Bukowa, Małogoszcz, Nowiny, Trzuskawica, Kielce) oraz w dolinie Kamiennej (Ostrowiec Świętokrzyski, Suchedniów, Skarżysko-Kamienna). Analizy chemiczne pyłów i węgli pobranych z największych zakładów przemysłowych regionu wskazują na istnienie, obok ponadregionalnego tła, szeregu lokalnych potencjalnych źródeł skażeń.

EXPLANATIONS OF PLATE

PLATE I

Fig. 3. The lichen species *Hypogymnia physodes* (L.) Nyl. with greenish gray foliose thalii and *Lecanora conizaeoides* Nyl. in Cromb. with green crustose thalii, growing on Scots pine (*Pinus sylvestris* L.) bark. *H. physodes* belongs to the most common foliose epiphytic lichen flora in Europe used for qualitative and quantitative biomonitoring of air pollution based on different Lichen Scales or chemical composition of thalii. Dąbrowa near Kielce

Porosty z gatunków pustułka pęcherzykowata (*Hypogymnia physodes* (L.) Nyl.) o plechach listkowatych barwy seledynowoszarej i misecznica proszkowata (*Lecanora conizaeoides* Nyl. in Cromb.) o zielonych plechach skorupiastych, rosnące na korze sosny zwyczajnej (*Pinus sylvestris* L.). *H. physodes* należy do najpospolitszych listkowatych porostów nadrzewnych (epifitycznych), wykorzystywanych w Europie do jakościowej i ilościowej oceny bioindykacyjnej skażeń atmosferycznych na podstawie różnych skal porostowych lub odpowiednio składu chemicznego plech. Dąbrowa k. Kielc

Fig. 4. The foliose lichen species *Parmelia sulcata* Taylor growing on a wall made of Lower Triassic joint sandstones. This bioindicator is widely applied in Europe, U.S.A. and Canada. Tumlin near Kielce

Porosty listkowate z gatunku tarczownica bruzdkowana (*Parmelia sulcata* Taylor), rosnące na murze zbudowanym z dolnotriasowych piaskowców ciosowych. Wymieniony biowskaźnik jest szeroko rozpowszechniony w Europie, USA i Kanadzie. Tumlin k. Kielc

Fig. 3

Fig. 4

Zdzisław M. MIGASZEWSKI — Geochemistry of soils and vegetation of the Holy Cross Mts. between 1994 and 1996