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Baseline element concentrations in soils and plant bioindicators of selected national parks of Poland

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This report presents an assessment of chemical variability in forest ecosystems of three selected national parks in Poland, i.e. Magurski National Park, Świętokrzyski National Park (Holy Cross Mts.) and Wigierski National Park derived from the calculation of geochemical baselines using a "barbell" cluster and ANOVA design. In addition, results of summary statistics for elemental concentrations and pH in the soil horizons-O (Ol + Ofh), -A and -B (or -E), 1 and 2 year old *Pinus sylvestris* needles, pine bark and *Hypogymnia physodes* thalli are given. The variability of elements in soils and plant bioindicators of Wigierski National Park is primarily governed by underlying glacial sediments and to a lesser extent by anthropogenic factors; the two remaining parks reveal a more distinct anthropogenic imprint. The most interesting of all the parks examined is Wigierski National Park because this area has experienced low levels of air pollution compared to other parts of Poland.

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Key words: Poland, Magurski, Świętokrzyski and Wigierski national parks, elements, soils, rocks, plant bioindicators.

INTRODUCTION

A range of soils, including those in forest ecosystems, over a widespread area of Poland have been analyzed for elements and pH in previous studies (e.g. Lis, 1992; Lenartowicz, 1994; Lis and Pasieczna, 1995; Pasieczna and Lis, 1995; Uścinowicz and Zachowicz, 1996; Lis *et al*., 1999). In addition, selected chemical elements were determined in pine trees (e.g. Świeboda and Kalemba, 1979; Dmuchowski and Bytnerowicz, 1995), lichens (e.g. Fabiszewski *et al*., 1983), mosses (e.g. Grodzińska, 1971, 1980, 1983; Klich and Szarek-Łukaszewska, 2001), and aquatic bryophytes (e.g. Samecka-Cymerman and Kempers, 1994). However, none of these studies were conducted simultaneously on soils and different plant bioindicators.

This report presents the results of element determinations in soils and vegetation (pine needles and bark, lichens) from three selected national parks in Poland, i.e. Magurski National Park (south-east), Świętokrzyski National Park (Holy Cross Mts.) (mid-south) and Wigierski National Park (north-east) (Fig. 1). The overall objective of this investigation, which was performed during the spring of 2002, was to determine the baseline concentrations of elements in the aforementioned media, as well as to outline the impact of potential industrial sources located near and far from the areas examined. The baseline results reported in this study will serve as a benchmark for the future monitoring. The use of the same field and laboratory methods and techniques developed by the authors in cooperation with the U.S. Geological Survey has enabled us to compare the present results with those derived from previous studies conducted in the Holy Cross Mts. region (Migaszewski and Pasławski, 1996; Migaszewski, 1998; Migaszewski *et al*., 2001*b*, 2002; Gałuszka, 2003).

STUDY AREAS

MAGURSKI NATIONAL PARK

Magurski National Park (MNP) is the second youngest national park in Poland. Established in 1995, MNP has an area of 199.6 km^2, extending along the Polish-Slovakian border (Fig. 1). MNP lies within the Lower Beskid Mountains which

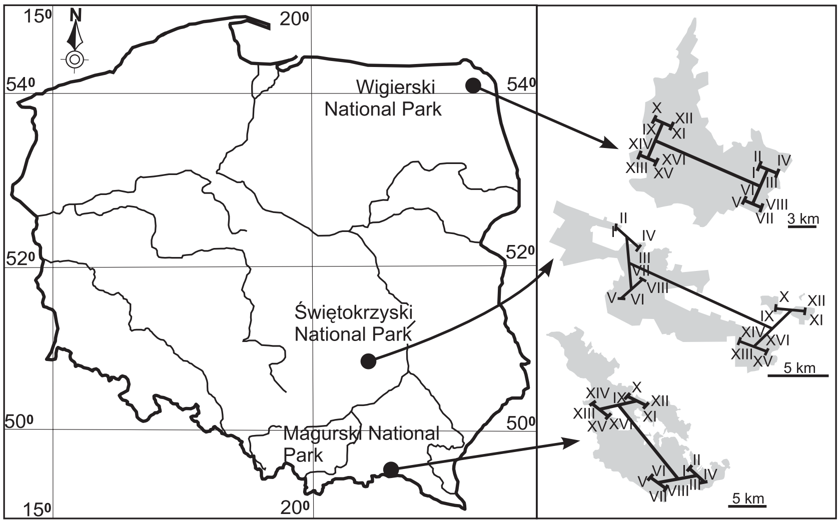

Fig. 1. Location of Magurski, Świętokrzyski and Wigierski national parks with "barbell" cluster design

are part of the Carpathians. The park extends along the Magura Wątkowska Massif, including Wątkowa Mt. (847 m a.s.l.), Magura Mt. (842 m a.s.l.) and Kornuty Mt. (830 m a.s.l.). The landscape is characteristic of medium and low mountains with a relative elevation in places exceeding 400 m.

Both, the topography and the spatial distribution of soils and plant communities are closely connected to the geologic setting of the region. In general, the investigation sites were located within the Magura Nappe, composed of flysch sediments (sandstones with clayey shale interbeds). The spectrum of soil types includes rankers, and gray and brown soils. Plants are represented by typical submontane, thermophilous and xerothermic species. The largest area is occupied by beech (*Fagus sylvatica*), stands with scattered Scots pine (*Pinus sylvestris*) and European silver fir (*Abies alba*). In general, trees of young and medium age classes are prevalent; old-growth trees, reaching the age of 110–140 years occur only in selected locations (Borejszo, 2000).

ŚWIĘTOKRZYSKI NATIONAL PARK

Established in 1950, Świętokrzyski National Park (ŚNP) is one of the oldest national parks in Poland. ŚNP is located in the northern part of the Holy Cross Mts. and occupies an area of 7 6.26 km^2 (Fig. 1). The core part of the park encompasses the highest range of the mountains — the Łysogóry with Łysica Mt. (612 m) in western part and Holy Cross Mt. (595 m) in eastern part. This range is made of Middle and Upper Cambrian quartzitic sandstones and siltstones with clayey shale interbeds. The central and northern area of the park consists of eastern part of the Wilków Valley abutted to the north by the Klonów Range. ŚNP also includes three northeastern enclaves: Chełmowa Mt., Las Serwis (Serwis Forest) and Zapusty Mt. The basement of the Wilków Valley consists of Silurian clayey shales and graywackes covered by Pleistocene sands and tills, whereas the Klonów Range is composed of Early Devonian quartzitic sandstones, siltstones and clayey shales (Migaszewski *et al.*, 2001*b*, 2002). The Łysogóry Range belongs to medium and low mountains, with relative elevations in places exceeding 300 m. The soil taxonomy corresponds to the geologic structure of the park. Rankers and acidic brown soils are developed on sandstones, whereas gleyed acid brown soils, chernozems and pseudogley lessives exist on tills. The park tree stands include European silver fir (*Abies alba*) and common beech (*Fagus sylvatica*); Scots pine (*Pinus sylvestris*) is scarce occurring primarily in northern parts of ŚNP. The number of lichen species has dropped to about 130; the foliose species *Hypogymnia physodes* occurs only in a few places (Cieśliński and Kowalkowski, 2000).

WIGIERSKI NATIONAL PARK

Established in 1989, Wigierski National Park (WNP) is situated in north-easternmost Poland close to the Polish-Lithuanian border (Fig. 1). The northern part of the park belongs to the Eastern Suwałki Lake District (Lithuanian Lake District), whereas the southern part — to the Augustów Plain. The area of this park is 151.13 km^2. There are 42 lakes in WNP, among which Lake Wigry is the largest taking up an area of 21.18 km^2 and reaching 73 m of deep. The Czarna Hańcza is the main river of the park. The whole area is hilly, with relative elevations range of tens of metres; the highest elevation reaches 171.5 m.

The area of WNP is covered by up to 150 m thick glacial sediments of Würm Glaciation (tills and fluvioglacial sands with cobbles and boulders) reaching 150 m deep. The spectrum of soils developed on this allochtonous material includes rusty (arenosols) and podzolic soils. Tree stands encompass Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). About 800 vascular plant species have been recorded here. In addition, 200 bryophyte species and 300 lichen species (including the foliose species *Hypogymnia physodes*) occur in WNP (Hanas, 2001).

METHODS

SAMPLING DESIGN AND FIVE-LEVEL ANOVA

An assessment of chemical variability in different ecosystems can be obtained through the calculation of geochemical baselines using "barbell" cluster and ANOVA designs (see Gough *et al.*, 1988*a*, *b*; Severson *et al.*, 1992; Migaszewski and Pasławski, 1996; Migaszewski, 1998, 1999). This approach enables to obtain statistically valid information using a minimum number of samples.

Element spatial variation in soils and plant bioindicators was estimated for specific geographic intervals using a five-level, unbalanced, nested analysis-of-variance (ANOVA) design. Sampling sites in MNP, ŚNP and WNP (Fig. 1) were randomly selected by a "barbell" sampling plan with a longer axis (level 1), two medium axes (level 2) and four short axes

Table 1

Concentration geometric means and observed ranges of selected elements in the soil horizons-O (Ol + Ofh), -A and -B (-E) in Magurski, Świętokrzyski and Wigierski national parks

Element [mg kg^{-1}]	Soil horizon	Magurski National Park* N from Ol to E = 15, 15, 15, 8	Świętokrzyski National Park N from Ol to B = 16, 16, 16, 10	Wigierski National Park N from Ol to B = 15, 9, 15, 15			
		Geom. mean	Observed range	Geom. mean	Observed range	Geom. mean	Observed range
As	Ol	< 5	–	< 5	–	< 5	–
	Ofh	7	< 5–16	5	< 5–13	< 5	–
	A	12	8–32	10	6–16	< 5	–
	B (E)	6	< 5–9	6	< 5–20	< 5	–
Cd	Ol	1.1	0.6–6.5	1.0	0.5–2.5	0.4	< 0.5–0.7
	Ofh	1.1	0.5–5.2	1.3	0.7–2.2	< 0.5	–
	A	< 0.5	–	< 0.5	–	< 0.5	–
	B (E)	< 0.5	–	< 0.5	–	< 0.5	–
Cr	Ol	1	< 1–7	1	< 1–2	3	< 1–15
	Ofh	12	7–23	6	3–13	7	3–23
	A	22	10–52	10	8–17	5	2–10
	B (E)	27	16–64	10	6–19	6	3–13
Cu	Ol	11	7–27	8	4–13	7	4–16
	Ofh	17	9–28	13	7–24	7	4–14
	A	18	7–192	10	4–32	3	1–13
	B (E)	13	5–28	4	2–22	2	2–8
Fe	Ol	627	259–6588	343	99–13659	654	162–2589
	Ofh	7788	4051–13460	3874	1466–19000	2236	1257–3624
	A	17706	11500–32500	8962	5300–27300	5803	3900–12600
	B (E)	20081	13300–33800	10071	6100–31000	6521	3900–16900
Hg	Ol	0.120	0.064–0.197	0.090	0.053–0.160	0.080	0.022–0.169
	Ofh	0.230	0.120–0.500	0.220	0.086–0.436	0.130	0.090–0.172
	A	0.160	0.087–0.468	0.180	0.072–0.603	0.049	0.018–0.128
	B (E)	0.070	0.053–0.097	0.060	0.029–0.121	0.020	0.007–0.041
Mn	Ol	1932	626–5730	2427	775–5389	729	245–2663
	Ofh	988	295–5265	1770	515–5026	643	232–1980
	A	691	152–1801	407	89–3693	374	58–1490
	B (E)	962	307–2052	719	70–3186	226	52–783
Ni	Ol	5	3–10	2	1–7	2	< 1–3
	Ofh	14	8–40	6	4–23	3	2–3
	A	21	7–82	6	4–27	3	2–7
	B (E)	27	10–85	5	2–29	4	2–10
Pb	Ol	23	11–56	13	< 5–46	9	< 5–23
	Ofh	77	40–243	85	35–239	25	21–34
	A	76	32–499	89	29–478	19	8–28
	B (E*)	20	14–25	26	11–67	6	< 5–18
S	Ol	1231	941–1747	1016	611–1554	1022	723–1402
	Ofh	1166	618–1728	1147	510–2140	876	485–1302
	A	441	250–960	468	230–1580	199	100–2100
	B (E)	159	100–210	130	80–270	60	< 50–120
Ti	Ol	6	3–16	4	2–13	10	2–35
	Ofh	7	3–21	21	4–57	21	17–34
	A	59	37–74	105	46–174	115	39–12
	B (E)	39	11–71	113	29–223	130	86–239
V	Ol	4	3–14	2	< 1–7	2	<1–6
	Ofh	15	11–22	11	6–17	6	5–7
	A	26	13–42	15	10–21	9	3–18
	B (E)	29	22–47	15	11–24	10	6–24
Zn	Ol	72	46–440	88	40–214	49	32–106
	Ofh	78	43–257	94	61–159	37	23–96
	A	67	36–268	58	32–119	21	12–121
	B (E)	55	28–86	35	19–98	16	9–36

soil horizon/subhorizon symbols: Ol — organic (litter), Ofh – organic (fermentative-humic or detritic-epihumic), A — humic, B — illuvial, E — eluvial; * — horizon-E in Magurski National Park; N — total number of samples for each soil horizon

Table 2

Concentration geometric means and observed ranges of selected elements in the sandstones of Magurski National Park

Element [mg kg^{-1}]	Geometric mean	Observed range
	N = 6	
As	< 5	–
Cd	< 0.5	–
Cr	13	10–23
Cu	7	4–33
Fe	15496	9379–27504
Hg	0.020	0.008–0.032
Mn	599	265–1276
Ni	15	7–22
Pb	13	7–20
S	74	59–93
Ti	5	4–7
V	9	6–25
Zn	31	23–55

N — total number of samples

(level 3) resembling the strongly flattened letter "H". Each end of this figure provided two investigation sites (level 4). The level 5 referred to duplicated analyses of an individual sample. The axial pattern was similar for the three parks, but the axes were of different length, depending on the shape, size and topography of a given area:

— Magurski National Park — 13.3 km — 5.6 km —3.0 km — 1.0 km,

— Świętokrzyski National Park — 12.6 km — 4.4 km — 2.5 km — 0.5 km,

— Wigierski National Park — 12.0 km — 4.0 km — 2.0 km — 1.0 km.

In all, 48 sampling sites were chosen for investigation. ŚNP and MNP include various habitats controlling presence of lichens and pine trees at each site. In addition, particular habitats contain diverse lichen and tree species. The lichen taxon *Hypogymnia physodes*, chosen for this study, grows on bark of different tree species and reflects, at least partly, the chemistry of their host barks (Migaszewski and Pasławski, 1996). Considering this, the severe unbalancing of the sampling design, because of missing (or the lack of uniform) sites, has potentially made all ANOVA results invalid for lichens in ŚNP and MNP, as well as for pine needles in ŚNP. For *H.*

Table 3

Concentration geometric means and observed ranges of selected elements in 1 and 2 year old, i.e. 2001 and 2000, Scots pine needles (in parentheses) in Magurski, Świętokrzyski and Wigierski national parks

Element [mg kg^{-1}]	Magurski National Park		Świętokrzyski National Park		Wigierski National Park	
	Geom. mean N = 15 (15)	Observed range	Geom. mean N = 8 (8)	Observed range	Geom. mean N = 15 (15)	Observed range
Ba	3 (5)	< 1–13 (1–32)	1.5 (2)	< 1–3 (< 1–4)	3 (4)	1–10 (1–14)
Cd	0.4 (0.4)	< 0.5–0.5 (< 0.5–0.9)	1.9 (0.4)	< 0.5–3.5 (< 0.5–0.7)	< 0.5 (< 0.5)	– (–)
Cu	4 (3)	3–6 (2–4)	4 (3)	3–6 (3–4)	4 (4)	3–5 (3–4)
Fe	76 (90)	54–112 (67–128)	61 (68)	42–107 (55–88)	52 (57)	45–72 (43–91)
Hg	0.020 (0.040)	0.019–0.032 (0.030–0.059)	0.020 (0.034)	0.016–0.027 (0.025–0.043)	0.020 (0.030)	0.014–0.028 (0.021–0.045)
Mn	450 (709)	97–1093 (342–1990)	831 (1254)	584–1152 (842–1745)	466 (622)	90–769 (99–1028)
Ni	6 (5)	2–15 (2–21)	2 (2)	1 – 8 (< 1–5)	1 (1)	< 1–4 (< 1–1)
Pb	< 5 (4)	– (< 5–6)	4 (< 5)	< 5–7 (–)	< 5 (< 5)	– (–)
S	1070 (1048)	907–1507 (821–1473)	1105 (1087)	914–1255 (1024–1163)	877 (835)	753–1049 (726–941)
Ti	3 (2)	2–9 (1–4)	2 (2)	2–3 (1–3)	2 (1)	1–3 (< 1–7)
V	3 (2)	2–9 (1–4)	< 1 (< 1)	– (–)	< 1 (< 1)	– (–)
Zn	40 (46)	22–68 (20–73)	46 (53)	37–57 (43–76)	36 (33)	26–48 (23–49)

As — < 0.5 mg kg^{-1}; Co, Cr and Mo — < 1 mg kg^{-1}; N — total number of samples

Table 4

Concentration geometric means and observed ranges of selected elements in *Hypogymnia physodes* thalli and Scots pine bark (in parentheses) in Magurski, Świętokrzyski and Wigierski national parks

Element [mg kg^{-1}]	Magurski National Park		Świętokrzyski National Park		Wigierski National Park	
	Geom. mean N = 5 (5)	Observed range	Geom. mean N = 2 (2)	Observed range	Geom. mean N = 14 (14)	Observed range
Ba	6	5–9	7	6–9	5	3–9
	(5)	(2–10)	(8)	(4–18)	(4)	(2–7)
Cd	0.6	0.5–1.3	0.6	0.6–0.7	0.4	< 0.5–0.6
	(< 0.5)	(< 0.5–0.5)	(0.6)	(0.5–0.7)	(< 0.5)	(–)
Cu	7	7–8	8	8–8	6	5–7
	(4)	(3–4)	(3)	(3–4)	(4)	(3–5)
Fe	616	550–733	547	544–550	352	252–818
	(84)	(45–161)	(82)	(59–113)	(40)	(27–68)
Hg	0.210	0.143–0.263	0.201	0.189–0.214	0.171	0.131–0.209
	(0.050)	(0.040–0.055)	(0.040)	(0.032–0.051)	(0.040)	(0.027–0.064)
Mn	70	33–143	66	64–67	88	30–160
	(16)	(9–29)	(42)	(31–56)	(32)	(18–48)
Ni	1	< 1–2	1	1–1	1	< 1–1
	(< 1)	(–)	(< 1)	(–)	(< 1)	(–)
Pb	18	9–27	11	11–11	6	< 5–9
	(12)	(4–35)	(6)	(4–9)	(< 5)	(–)
S	1152	1045–1254	1461	1445–1478	1076	836–1321
	(280)	(227–356)	(231)	(207–257)	(214)	(182–265)
Ti	10	9–13	12	11–12	7	6–15
	(6)	(3–12)	(16)	(3–83)	(5)	(1–35)
V	< 1	–	1	1–1	1	1–2
	(< 1)	(–)	(< 1)	(–)	(< 1)	(–)
Zn	71	59–83	83	77–90	67	50–84
	(10)	(7–24)	(12)	(11–14)	(13)	(9–16)

for explanations see Table 3

physodes thalli and *P. sylvestris* bark and needles only geometric means and observed ranges of elemental concentrations are given.

Tables I through III (in the Geological Quarterly Data Depository, free of charge upon request and also available at the website of the Geological Quarterly) also present the results of summary statistics for elemental concentrations and pH in the most representative soil horizons, i.e. humic horizon-A (topsoil) and illuvial horizon-B or eluvial horizon-E (subsoil). Summary statistics for each component include 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 GD^2. 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 W:N, is given. When the number of samples containing a specific element below the detection limit (censored) was more than 20% of the total number of samples, then only summary statistics calculations were performed. For some elements with the detection ratio close to 0% only the lower limits of determination values were presented. The ANOVA was preceded by a common logarithmic transformation of particular concentrations. After that, the frequency distributions of data more closely resembled normal distributions. The ANOVA included calculation of total log$_{10}$ variance and its percentage split into five basic levels (Anderson and Bancroft, 1952).

FIELDWORK AND SAMPLING

Fieldwork, which included establishing investigation sites and sampling, was performed in April and May 2002. Locations of sampling points were determined using a Global Positioning System (GPS 12XL GARMIN Olathe, KS, USA) with a precision of 5–10 m. Forty eight pits were dug to a depth of about 0.5 m. 0.5–1 kg soil samples were collected from every distinguishable horizon.

Thalli of the lichen species *H. physodes* along with their substratum, i.e. Scots pine bark, were sampled (21 samples each). Samples were taken from individual trees at a height of about 1.5 m; each sample weighed about 40 g. The thalli were separated from the tree bark on the day of sampling. Pine needles of two age classes (2000, 2001), weighing 50 g each, were collected from tree tops; 76 samples were collected from 3 to 6 trees.

During sample collection and preparation, measures were taken to reduce the possibility of contamination. Stainless steel scrapers, shovels, scissors, and clean surgical gloves were used, and cigarette smoking was prohibited. Adhering materials were removed with forceps, and the sampled materials were dried at ambient temperature to avoid decay and developing fungi. The samples were placed in paper bags and sent for chemical analysis to the Central Chemical Laboratory of the Polish Geological Institute in Warsaw.

SAMPLE PREPARATION AND ANALYSIS

After drying at ambient temperature (16°C), the soil samples were disaggregated to pass a < 0.068 mm sieve using a Fritsch's blender. Each sample (2 g) was digested with aqua regia (15 ml concentrated HCl + 5 ml concentrated HNO_3), evaporated (160°C), dissolved with concentrated hydrochloric acid (10 ml), and the insoluble residue was filtered. Except for the subhorizon-Ol and -Ofh sample materials, the pine needles and bark, and lichen thalli were placed in teflon beakers, rinsed 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 plant samples were pulverized using the Retsch's blender. The fraction that passed a 0.5 mm sieve was digested with a mixture of concentrated nitric acid and deionized water (1:1) in a closed microwave system (MDS 81, CEM Corp.).

Chemical analyses were performed according to methods and techniques used for environmental samples (soils and vegetation) in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw. Determinations were made for 198 soil and rock samples and for 118 plant samples. Of this number, 10% were randomly selected for routine replicate analyses, and international standards were inserted at a frequency of 5%. The samples were analyzed for 29 elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, La, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, S, Sc, Sr, Ti, V, Y, Yb, Zn) using inductively coupled plasma-atomic emission spectrometry (*ICP-AES*; spectrometer *Jobin-Yvon* model *JY 70 PLUS* with vertical plasma), and by flame atomic absorption spectrometry (*FAAS*; spectrometer *PU 9100 X UNICAM*). Total sulfur was determined using a coulometric technique. Arsenic was determined both by *ICP-AES* and by hydride generation atomic absorption spectroscopy (*HGAAS*). Mercury was determined using an atomic absorption spectroscopic method (*AAS*; *Altec amalgam analyzer AMA 254*). The pH of soils and bark was determined in a 1:1 water extract using a pH-meter *PH 204 Slandi*, Poland.

In addition, the study of injuries of pine needle epicuticular waxes and distribution of air-borne particle types was carried out with a *Surface Scanning Electron Microscopy* (*SSEM*) *LEO 1430* (signal A = SE1, magn. = 50–15380 , EHT = 5.00–20.00 kV, WD = 8–36 mm) at the Polish Geological Institute in Warsaw.

RESULTS

The results of summary statistics and ANOVA calculations for selected element concentrations and pH in the soil horizons-A, -B and -E were presented in Tables I–III (The Geological Quarterly Data Depository and Website). Tables 1–4 in this manuscript present only concentration geometric means and observed ranges of selected elements in the soil horizons-O (Ol + Ofh), -A and -B (-E), sandstones (Magurski National Park), 1 and 2 year old, i.e. 2001 and 2000, Scots pine needles, and *Hypogymnia physodes* thalli and Scots pine bark, respectively.

Magurski National Park (MNP). The largest proportion of variability in topsoil (horizon-A) and subsoil (horizon-E) of MNP is associated with the smallest distance, i.e. the 1.0 km (level 4). Both in topsoil and subsoil Al, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr and Zn record 50–96% of their variability. In addition, 52–86% of the total variability of As, Ba, Hg, Na, pH and partly K (47%) is linked to the 1.0 km distance of the horizon-A. The largest proportion of variability (56–68%) of Ca and Ti is associated with the 1.0 km distance of the horizon-E. In addition, the values of Ca (horizon-A), and to some degree also pH (horizon-E) vary much over the 3.0 km (level 3) and 1.0 km distance increments. Of the remaining elements, the variability of V (both horizons) and Na (horizon-E) changes over several levels. It should be pointed that 43–89% of the total variability of Ti (horizon-A) and Hg, K, V, and partly Ba (horizon-E) is associated with analytical uncertainty (level 5) linked to the sample type and the applied analytical method (sample preparation and measurement errors).

The largest proportion of variability in 1 and 2 year old Scots pine needles of MNP is linked to the 1.0 km (Ba, Ca, Cu, Mg, Na, Zn) and the 3.0 km (Al, Fe). In addition, the largest proportion of variability in 1 year old pine needles is associated with the 3.0 km (Mn, P) and 1.0 km (Ti), whereas in 2 year old pine needles to the 1.0 km (Mn, Ni, S). By contrast, P (2 year old pine needles) and S (1 year old pine needles) record their variability over the 3.0 and 1.0 km distances. Sr (1 and 2 year old pine needles) and Ti (2 year old pine needles) show no specific variability. 100% of the total variability for Hg and K is linked to analytical uncertainty.

Świętokrzyski National Park (ŚNP). The largest proportion of variability in the horizon-A of ŚNP is associated with smaller distances, i.e. the 2.5 km (level 3) (Al, Co, Cu, Fe, Hg, Mn, Ni, P, Pb, S, pH and partly Cr, K, Mg) and the 0.5 km (level 4) (Ca, Na, Sr, Zn). Only Ti records 45% of its variability over the 4.4 km distance (level 2). 49 and 81% of the total variability for As and V is linked to analytical uncertainty (level 5). The chemistry of the underlying horizon-B differs from the horizon-A. The variability of Co, Cu, Fe, Mn, Ni, S, Ti and Zn is associated with the 2.5 km distance, Ca and Pb with the 0.5 km distance (level 4), Al, Cr, Mg and partly Sr with the 12.6 km distance (level 1), Hg and pH with the 4.4 km distance. The variability of Ba, Ce, K, Na, Nd, P, Sr and V is almost evenly split over the remaining distance increments.

Wigierski National Park (WNP). The largest proportion of variability in the horizon-A in the WNP is associated with the smallest distance, i.e. the 1.0 km (level 4) (Al, Ba, Co, Cr, Fe, Hg, Mn, Pb, Sr, Ti, V, Zn, pH). The variability of Ca, Cu, Mg, Ni, P and S concentrations is almost evenly split over the 12 km, 2 km and 1 km distance increments. 84 and 100% of the total variability for K and Na is linked to analytical uncertainty (level 5). The chemistry of subsoil yields even greater diversity than that of topsoil. The largest proportion of variability in the horizon-B is associated with smaller distances, i.e. the 2.0 km (level 3) (Ca, Cu, Fe, Mn, Sr and partly V) and the 1.0 km (Al, Hg, P, Pb, S, Zn). The variability of Cr and pH is almost evenly split over the 2.0 km and 1.0 km distance increments. The exceptions are Ba, Co, Mg and Ni; their values vary sharply over different levels. 78 samples and 100% of the total variability for K and Na is linked to analytical uncertainty.

The largest proportion of variability in 1 year old Scots pine needles of WNP is associated with the smallest distance, i.e. the 1.0 km (Al, Ba, Ca, Fe, Mg, Mn, P, Zn and partly Cu and S). The variability of Sr and Ni concentrations (56–68%) is linked to the 2.0 km and the 4.0 km (level 2), respectively. The value of Na varies much over different levels. 65, 68 and 100% of the total variability for Hg, Ti and K is linked to analytical uncertainty. By contrast, in 2 year old pine needles Ba, Ca, Fe, Mg, Mn, Na, S, Sr, Ti, Zn and partly Al record 50–88% of their variability over the smallest distance, i.e. the 1.0 km. Cu and P show no specific variability. 100% of the total variability for Hg and K is associated with analytical uncertainty.

The largest proportion of variability in *H. physodes* thalli of WNP is associated with the longest distance, i.e. the 12.0 km (Al, Ba, Ca, Mn, Pb and Sr), and the smallest one, i.e. 1.0 km (P, S and Zn). Fe, Mg and V show no distinct variability. The total variability for Cu, Hg, K, Na and Ti, associated with analytical uncertainty, varies from 68 to 100%. As for the pine bark, the largest proportion of variability is linked to the shortest distance, i.e. the 1.0 km (Al, Ba, Ca, Cu, Fe, K, Mn, P, S, Sr, Zn and pH). The value of Ti and partly Mg varies much over the 12.0 km. Hg shows no distinct variability. 84% of the total variability for Na is associated with analytical uncertainty.

DISCUSSION

The distribution pattern of total variability in the soils (horizons-A, -B and -E) of the parks examined reflects generally different parent material lithology, i.e. sandstones and clayey shales (Magurski National Park), quartzites, quartzitic sandstones, sands and tills (Świętokrzyski National Park) and allochtonous glacial deposits (Wigierski National Park). This is evidenced by the association of the largest proportion of chemical variability with the smallest distances (levels 3 and 4) and an increase of many elements (except for Cd, Hg, Pb and in places Cu, Mn and Zn) with a depth of soil profiles (Tables 1 and 2; Migaszewski and Gałuszka, 2003).

Like the soils, the pine needles of Magurski and Wigierski national parks and the bark of Wigierski National Park reveal similar variability, i.e. associated with the shortest distance (level 4). Even though the lichen thalli take up most of the elements from the air, the largest proportion of variability for some elements (P, S, Zn) of Wigierski National Park is associated with the smallest distance (level 1). Rainwater removes these and partly other elements from pine bark and deposits them especially on crustose and foliose lichen thalli, reflecting the chemistry of soils and parent material (Migaszewski and Pasławski, 1996). The only distinct positive correlation (r^2 = 0.20) reveals Mn concentrations in the horizon-Ol and 2 year old Scots pine needles of Magurski National Park.

A considerable drop in concentrations of most elements in soils is noted proceeding from south to north, i.e. from Magurski through Świętokrzyski and Wigierski national parks (Table 1). This corresponds to the reduction of air pollution northward. Element concentrations in Wigierski National Park are low and approach background levels. The only exception is Ti, which is slightly raised in the soil profiles of Wigierski National Park. This and other elements (Cr, Fe, Ni, V) are of geologic origin and are closely linked to the parent material, i.e. glacial tills and sands. In turn, the geologic "signature" of Mn is partly obliterated by biogeochemical processes. Compared to Magurski National Park, the soils of Świętokrzyski National Park reveal distinctly elevated concentrations of Mn (with mean values of 407–2427 mg kg^{-1}) and to a lesser extent Pb (13–89 mg kg^{-1}), Ti (4–113 mg kg^{-1}) and Zn (35–94 mg kg^{-1}).

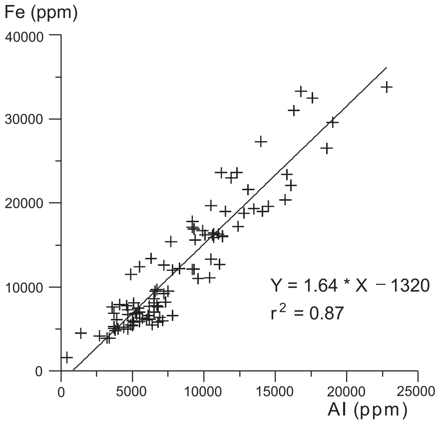

Fig. 2. Correlation between Fe and Al in soils of Magurski, Świętokrzyski and Wigierski national parks

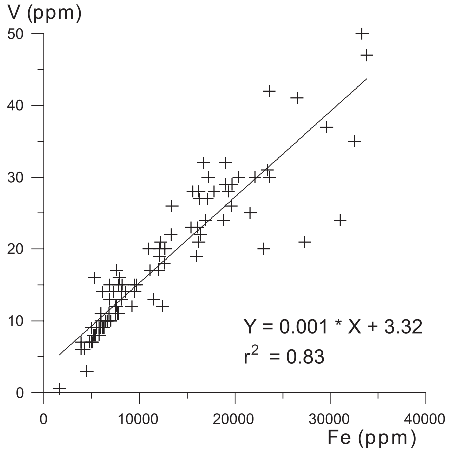

Fig. 3. Correlation between V and Fe in soils of Magurski, Świętokrzyski and Wigierski national parks

Also, soil mineralogy generally reflects bedrock lithology. Potential geoavailability of some elements is well depicted in the soil-sandstone sequences (compare Tables 1 and 2). Of the elements discussed, the strongest positive correlation was recorded between Fe and Al (clay minerals) as well as V and Fe (oxides and hydrooxides) (Figs. 2 and 3).

By contrast, the pine needles do not exhibit such distinct diversity (Table 3). Higher concentrations of Cd (with mean values of 0.4–1.9 mg kg^{-1}) and Mn (831–1254 mg kg^{-1}) and somewhat Zn (46–53 mg kg^{-1}) are noted only in the pine needles of Świętokrzyski National Park, and similarly Fe (76–90 mg kg^{-1}), Ni (5–6 mg kg^{-1}) and V (2–3 mg kg^{-1}) in Magurski National Park. Similar contents of Hg and Cu are observed in the needles of all the parks.

It is interesting to compare element concentrations in *H. physodes* thalli and *P. sylvestris* bark of the parks examined (Table 4). The lichen thalli of Świętokrzyski National Park are substantially enriched in S (mean of 1461 mg kg^{-1}) and somewhat in Zn (83 mg kg^{-1}), whereas those of Magurski are enriched in Fe (616 mg kg^{-1}) and Pb (18 mg kg^{-1}). By contrast, *H. physodes* thalli of Wigierski National Park exhibit the highest mean concentrations of Mn (88 mg kg^{-1}), whereas those from Świętokrzyski National Park the lowest (66 mg kg^{-1}). The pine bark of Świętokrzyski National Park reveals distinctly higher concentrations of Ba (mean of 8 mg kg^{-1}), Cd (0.6 mg kg^{-1}) and Mn (42 mg kg^{-1}), and it contains about the same concentration of Fe as the bark of Magurski National Park (82 versus 84 mg kg^{-1}).

The present biogeochemical study of three remote national parks, which are affected by different anthropogenic stress factors, provides an opportunity to compare element concentrations between 1 and 2 year old pine needles or *H. physodes* thalli and their substratum — *P. sylvestris* bark. Our study shows that K, Mg, Ni, P and locally Cu tend to concentrate in 1 year old pine needles, whereas Ca, Hg, Na and in places Fe, Mn and Zn — in 2 year old pine needles. The high content of K, Mg, Ni, P and Cu in the youngest needles can be explained by an increased assimilation of these elements during rapid needle growth; in addition, Cu seems to play an important role in the metabolism of young needles (e.g. Price *et al.*, 1972). The elements of the second group are not as active in biogeochemical processes and tend to accumulate in pine needles with age. However, in Magurski National Park this picture may be distorted by the occurrence of metal-bearing outer contamination (industrial and soil particles).

H. physodes thalli are bioaccumulators of many elements and are distinctly enriched in Ca, Fe, Hg, K, Mg, Mn, Ni, P, Pb, S, Zn relative to the *P. sylvestris* bark. Ca is the only element that is enriched in the bark relative to the thalli. The same trend is recorded when comparing lichen thalli and pine needles of individual trees. The *H. physodes* thalli are always enriched in Fe, Hg, Pb and in most places in S.

Considering this, the degree of elemental uptake by plants is affected by combined interactive environmental factors: (i) bedrock lithology, (ii) edaphic properties of soils, (iii) complex local topography (elevation, range and valley pattern), and (iv) local climate (wind rose, temperatures, barometric highs and lows, precipitation) (e.g. Brooks, 1983; Huttunen *et al.*, 1985; Kovalevskii, 1987; Dunn, 1989; Dunn *et al.*, 1992, unpubl.; Migaszewski and Gałuszka, 1998; Migaszewski *et al.*, 2001*b*). Some fluctuations of elemental variability within 1 and 2 year old needles seem to be also connected with physiologic and genetic factors.

It is interesting to compare an element spatial distribution pattern in the soils of the parks examined. The highest concentrations of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, Zn and industrial particles (Ca, Fe, K, Mg and Na aluminosilicates and in places Zn sulfide, plagioclase and Fe oxides and hydrooxides) are noted in the southern sector of Magurski National Park close to the Polish-Slovakian border, which indicates that the location of potential pollution sources might be in Slovakia. Moreover, the size of industrial particles recorded on pine needle surfaces is larger (1–5 m) in Magurski National Park relative to that from Świętokrzyski National Park (less than 1 µm) which implies that pollution sources are closer to MNP than they are to ŚNP (Figs. 4 and 5). By contrast, the soils of the northern sector of Magurski National Park are highlighted by the presence of somewhat increased levels of As, Cd, Hg, Pb, S, Zn but relatively low levels of Co-Cr-Cu-Fe-Mn-Ni, which

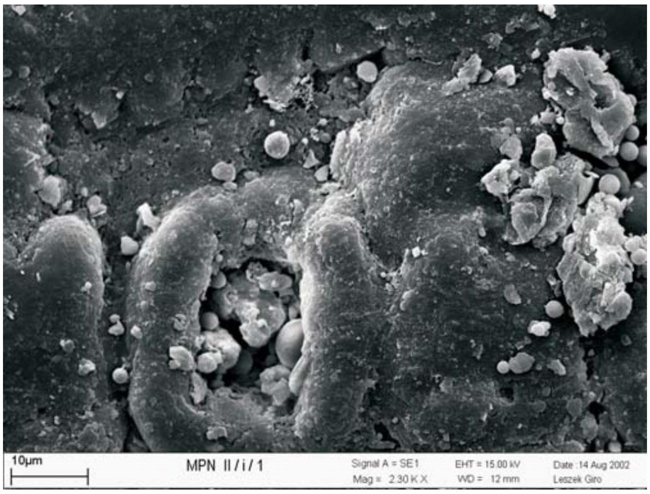

Fig. 4. Scots pine needle stomata filled in with spherical industrial particles (Ca, Fe, K, Mg and Na aluminosilicates) varying from 1 to 5 m in diameter (S sector of Magurski National Park)

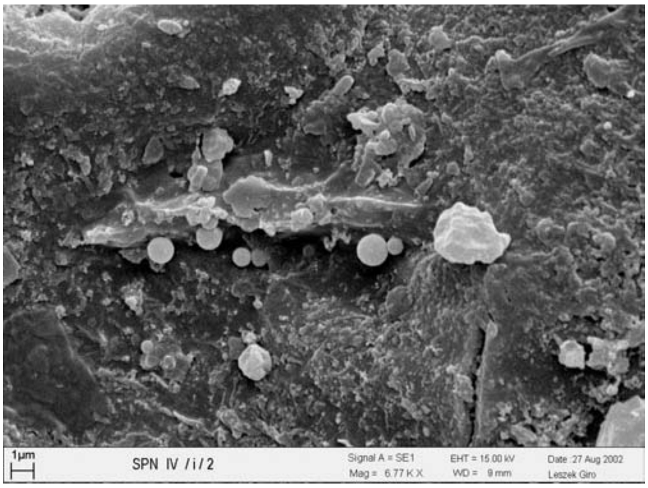

Fig. 5. Spherical industrial particles up to 1 m in diameter on Scots pine needle of Świętokrzyski National Park

is characteristic of the southern sector of this park. The As-Cd-Hg-Pb-S-Zn association seems to be a “fingerprint” of the Moravian-Silesian-Cracovian industrial area. The plant bioindicators show a different distribution pattern of maximum elemental concentrations. The pine needles of Magurski National Park reveal the highest concentrations of Fe, Hg, Mn, Pb and S in the northern sector, and Ba, Cd, Cu and Ni in the southern one. By contrast, *H. physodes* thalli contain the highest levels of Ba, Cu, Fe, Hg, Pb, S and Zn in the northern sector and Mn in the southern one. This diversity may result from poor coverage of Scots pine trees and *H. physodes* thalli in our investigation sites, and/or shorter exposure of these bioindicators to pollutants compared to soils (which show cumulative multi-annual elemental concentrations).

Minimal diversity of element concentrations is noted in the soils of Świętokrzyski National Park. The elevated levels of Cd, Cu, Hg, Mn, Pb, S and Zn are recorded in the western sector, especially at Łysica summit — the highest mountain of the region. These raised concentrations are connected with air-borne pollution coming primarily from the Moravian-Silesian-Cracovian and the Konin areas. Only a small local As, Co, Cr, Fe and Ni anomaly of geologic origin is noted in Las Serwis (eastern sector). The pine needles reveal only elevated levels of S in the western sector, and Mn and Ni in the local anomaly mentioned above. Compared to Magurski National Park, pine needles contain less industrial particles and are smaller in size (compare Figs. 4 and 5).

The soils of Wigierski National Park do not reveal a distinct diversity in concentrations of elements. Only small local anomalies, which may be linked to parent material lithology, domestic coal-fired furnaces, heat generating plants or transportation were detected. The pine needle surfaces and stomata show no injuries and they lack any industrial particles. The maximum concentrations of sulfur in pine needles and lichen thalli occur close to the town of Suwałki, and overlap those in the soils.

The Holy Cross Mountains are the only region of Poland where systematic environmental geochemical and biogeochemical studies have been performed since 1994 (Migaszewski and Pasławski, 1996; Migaszewski, 1998; Migaszewski *et al*., 2001*a*, 2002; Gałuszka, 2003). This fact, combined with similar methodology gives us an opportunity to compare the results obtained from this study with the previous ones. Concentration geometric means and observed ranges in the soil horizon-A and 2 year old, i.e. 1993 and 2000, Scots pine needles of Świętokrzyski National Park are very similar despite a minor modification to the sampling “barbell” scheme. This similarity includes such elements as As, Cd, Co, Cr, Fe, Mn, Ni, Pb, S, Ti, V and Zn, as well as Ba and pH in soils and Hg in pine needles. The differences in elemental concentrations recorded in the 1994 and 2002 studies vary from 10 to 20%, falling within sample preparation and measurement errors.

In the soils examined the geometric mean concentrations of As, Cd, Cr, Hg and Pb occur below maximum allowable values (Gough *et al.*, 1979; Kabata-Pendias and Pendias, 1992, 1999). The topsoil of Magurski National Park exhibits, in places, an increase in the levels of As (> 20 mg kg^{-1}), Cd ($>$ 5 mg kg^{-1}) and Pb (> 100 mg kg^{-1}). Of the two remaining parks, only the soil horizons-A and subhorizon-Ofh of Świętokrzyski National Park reveal, locally, elevated concentrations of Pb (Table 1). The plant bioindicators show elemental concentrations below maximum allowable levels (Tables 3 and 4). Only Cd (> 0.5 mg kg^{-1}) in *H. physodes* thalli and *P. sylvestris* needles of Magurski and Świętokrzyski national parks is of concern and should be studied further. It should be stressed that Hg occurs in excessive amounts (> 50 μg kg^{-1}) in *H. physodes* thalli of each of the individual park, which may be related to bioaccumulative capabilities of this species (Richardson, 1981; USDA..., 1993). Of the other elements (Cu, Mn, Zn) potentially toxic to plants, only Mn occurs in excessive amounts (> 1000 mg kg^{-1}) at most of the sites of Świętokrzyski and Magurski national parks, and in some places of Wigierski National Park. Concentrations of Mn in pine needles exceed commonly a factor of ten compared to other parts of a given pine tree and *H. physodes* thalli. This relationship indicates that *P. sylvestris* needles have strong bioaccumulative capabilities (Gałuszka, 2003). It is interesting to note that the soil subhorizons-Ol and -Ofh of Świętokrzyski and Magurski national parks also reveal an increase in the levels of Mn.

Of the elements discussed, S is particularly vital to plant metabolic processes as a component of different organic compounds, for example, glutathione, methionine, cysteine, cystine, biotin, lipoic acids, thiols, sulphoquinovose. On the other hand, an excessive concentration of SO_2 and SO_4^{2-} in the air leads to degradation of pine needle stomata and to the development of chlorosis and/or necrosis. Pine needles show exceptionally low concentrations of inorganic sulfur varying from 0.01 (MNP) to 2.44 mg kg^{-1} (MNP), with a mean value of 0.68 mg kg^{-1}. An enormous dominance of organic sulfur, exceeding at least an average factor of 900 (MNP) indicates a lack of stress induced by atmospheric SO_2 and SO_4^{2-} (Legge *et al.*, 1988; Manninen *et al.*, 1997). This fact is further supported by the lack of stomata injuries in the parks examined.

Because of different soil and plant taxonomy, extrapolation of maximum allowable concentrations for cultivated soils and plants to forest ecosystems should be treated with caution. Considering the maximum concentration levels of some potentially toxic elements and their spatial distribution patterns, the elements examined in this study do not seem to jeopardize the health of plants and animals inhabiting the forest ecosystems examined.

CONCLUSIONS

From these geochemical and biogeochemical studies we conclude:

The largest proportion of chemical variability in the soils and partly *P. sylvestris* needles and bark is linked to smaller distance increments (levels 3 and 4). By contrast, the elemental variability of *H. physodes* thalli is generally associated with the largest and smallest geographic intervals (levels 1 and 4), which seems to be connected with air and soil (through bark) chemistry.

Concentration geometric means as well as the observed and expected ranges of elements and pH provide a reference level for future monitoring in the parks examined. The most interesting of all the parks examined is Wigierski National Park because this area has experienced low levels of air pollution relative to other parts of Poland.

Spatial distribution pattern of elements in soils and plant bioindicators displays generally a bedrock lithology "signature", modified by geochemical and/or biogeochemical processes, with a more distinct anthropogenic imprint in Świętokrzyski and Magurski national parks.

Concentrations of many elements in the plant bioindicators achieve the level necessary for adequate functioning of these biological organisms.

The results obtained in this study are similar to those previously reported for the Holy Cross Mts.

Considering this, the results obtained indicate that the "barbell" cluster and ANOVA study design gives the best "snapshot" of environmental pollution.

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Table I

Summary statistics for and variation in the element concentrations and pH in the soil horizon-A vs the horizon-E (in parentheses) in Magurski National Park (SE Poland)

Element [mg kg^{-1}]	Ratio (W:N)	Summary statistics				Analysis of variance					
		Geom. mean	Geom. deviation	Observed range	Expected 0.05 range	Total $\log_{10}$ variance	Levels				
							1	2	3	4	5
Al	15:15 (8:8)	10509 (13947)	1.43 (1.29)	4900–18600 (10500–22800)	5130–21526 (8361–23265)	0.0242 (0.0123)	0 (0)	0 (0)	8 (0)	85 (86)	7 (14)
As	15:15 (6:8)	12 (6)	1.56 (1.46)	8–32 (< 5–9)	5–28 (3–13)	0.0372 (–)	0 (–)	0 (–)	21 (–)	52 (–)	27 (–)
Ba	15:15 (8:8)	56 (63)	1.46 (1.37)	28–109 (33–90)	26–119 (33–119)	0.0273 (0.0190)	0 (9*)	1 (5)	6 (0)	61 (41)	32 (45)
Ca	15:15 (7:8)	625 (305)	2.33 (2.55)	300–3300 (< 100–1000)	115–3397 (47–1993)	0.1351 (0.1659)	1 (0)	0 (32)	49 (0)	49 (68)	<1 (0)
Cd	1:15 (0:8)	< 0.5 (< 0.5)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)
Co	15:15 (8:8)	9 (14)	1.82 (1.43)	3–21 (7–23)	3–30 (7–28)	0.0672 (0.0241)	0 (0)	0 (13*)	0 (0)	92 (66)	8 (21)
Cr	15:15 (8:8)	22 (27)	1.56 (1.52)	10–52 (16–64)	9–53 (12–62)	0.0371 (0.0333)	3 (0)	0 (21)	6 (0)	83 (71)	8 (8)
Cu	15:15 (8:8)	18 (13)	2.09 (1.69)	7–192 (5–28)	4–78 (5–38)	0.1022 (0.0520)	2 (6)	0 (0)	8 (0)	89 (92)	1 (2)
Fe	15:15 (8:8)	17706 (20081)	1.32 (1.32)	11500–32500 (13300–33800)	1096–31050 (11511–35033)	0.0149 (0.0146)	5 (0)	0 (0)	1 (0)	88 (94)	6 (6)
Hg	15:15 (8:8)	0.160 (0.070)	1.69 (1.20)	0.087–0.468 (0.053–0.097)	0.057–0.471 –	0.0523 (0.0061)	0 (0)	0 (0)	12 (35*)	81 (4)	7 (61)
K	15:15 (8:8)	1381 (1504)	1.41 (1.37)	600–2300 (1100–2700)	691–2759 –	0.0226 (0.0188)	11* (0)	0 (21)	0 (0)	47 (29)	42 (50)
Mg	15:15 (8:8)	2153 (3101)	1.84 (1.62)	700–6300 (1600–7900)	633–7322 (1186–8110)	0.0706 (0.0436)	0 (0)	0 (19)	9 (0)	90 (80)	1 (1)
Mn	15:15 (8:8)	691 (962)	2.07 (1.85)	152–1801 (307–2052)	161–2958 (282–3283)	0.0998 (0.0711)	0 (5)	0 (21)	20 (0)	80 (73)	0 (1)
Na	15:15 (8:8)	90 (108)	1.31 (1.37)	60–130 (60–180)	53–153 (58–201)	0.0134 (0.0183)	0 (0)	0 (36)	0 (0)	57 (33)	43 (31)
Ni	15:15 (8:8)	21 (27)	1.92 (1.90)	7–82 (10–85)	6–77 (7–97)	0.0801 (0.0776)	0 (0)	0 (12)	9 (0)	83 (80)	8 (8)
P	15:15 (8:8)	459 (207)	1.46 (1.35)	280–1000 (120–300)	217–974 (115–375)	0.0266 (0.0166)	6 (8)	0 (0)	14 (0)	79 (90)	1 (2)
Pb	15:15 (8:8)	76 (20)	2.19 (1.20)	32–499 (14–25)	16–365 (14–28)	0.1164 (0.0061)	3 (10)	0 (0)	0 (0)	95 (50)	2 (40)
S	15:15 (8:8)	441 (159)	1.48 (1.28)	250–960 (100–210)	200–969 (97–258)	0.0293 (0.0112)	1 (0)	0 (19)	0 (0)	96 (73)	3 (8)
Sr	15:15 (8:8)	6 (5)	2.03 (1.41)	2–23 (4–10)	1–24 (3–11)	0.0941 (0.0223)	9 (24*)	0 (0)	12 (0)	78 (73)	1 (3)
Ti	15:15 (8:8)	59 (39)	1.20 (1.79)	37–74 (11–71)	– (12–125)	0.0064 (0.0645)	0 (5)	0 (0)	7 (30)	4 (56)	89 (9)
V	15:15 (8:8)	26 (29)	1.34 (1.27)	13–42 (22–47)	15–47 –	0.0158 (0.0108)	18 (4)	0 (0)	12 (0)	30 (38)	40 (58)
Zn	15:15 (8:8)	67 (55)	1.58 (1.44)	36–268 (28–86)	27–168 (26–113)	0.0393 (0.0251)	0 (12)	0 (0)	32 (0)	66 (85)	2 (3)
pH	15:15 (8:8)	4.71 (5.23)	1.16 (1.04)	3.79–6.26 (5.00–5.52)	3.51–6.32 (4.86–5.62)	0.0041 (0.0003)	0 (0)	0 (0)	12 (56)	86 (15)	2 (29)

d — number of samples above detectable concentration level, t — total number of samples; the computation of a 95% expected range was not made for elements with most of the chemical variability at the analytical level; * — significant at 0.05 probability level

Table II

Summary statistics for and variation in the element concentrations and pH in the soil horizon-A vs the horizon-B (in parentheses) in Świętokrzyski National Park (S-Central Poland)

Element [mg kg^{-1}]	Ratio (W:N)	Summary statistics				Analysis of variance					
		Geom. mean	Geom. deviation	Observed range	Expected 0.05 range	Total log$_{10}$ variance	Levels				
							1	2	3	4	5
Al	16:16 (10:10)	5957 (7368)	1.51 (1.52)	3600–14000 (3900–16300)	2620–13543 (3173–17107)	0.0318 (0.0335)	19 (54*)	0 (0)	69* (40*)	7 (1)	5 (5)
As	16:16 (6:10)	10 (6)	1.39 (1.79)	6–16 (< 5–20)	5–19 (2–20)	0.0208 (–)	6 (–)	0 (–)	22 (–)	23 (–)	49 (–)
Ba	16:16 (10:10)	56 (53)	1.59 (1.64)	25–128 (24–119)	22–140 (20–141)	0.0404 (0.0459)	29* (0)	0 (25)	10 (14)	39 (42)	22 (19)
Ca	16:16 (9:10)	599 (201)	1.80 (1.83)	200–2000 (< 100–600)	184–1948 (60–671)	0.0657 (0.0685)	0 (9)	17 (0)	0 (0)	82 (90)	1 (1)
Cd	1:16 (0:10)	<0.5 (<0.5)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)
Co	16:16 (10:10)	3 (6)	2.34 (2.24)	1–16 (1–17)	(0.5–15) (1–30)	0.1359 (0.1220)	0 (0)	0 (0)	83* (92*)	13 (4)	4 (4)
Cr	16:16 (10:10)	10 (10)	1.30 (1.43)	8–17 (6–19)	6–17 (5–20)	0.0130 (0.0244)	28* (53*)	0 (0)	43* (28)	7 (7)	22 (12)
Cu	16:16 (10:10)	10 (4)	1.81 (1.88)	4–32 (2–22)	3–31 (1–16)	0.0663 (0.0750)	0 (2)	0 (0)	73* (91*)	25 (6)	2 (1)
Fe	16:16 (10:10)	8962 (10071)	1.48 (1.58)	5300–27300 (6100–31000)	4077–19701 (4028–25180)	0.0293 (0.0396)	19 (35*)	0 (0)	66* (60*)	12 (3)	3 (2)
Hg	16:16 (10:10)	0.180 (0.060)	1.87 (1.72)	0.072–0.603 (0.029–0.121)	0.052–0.638 (0.019–0.169)	0.0742 (0.0559)	0 (0)	0 (55)	88* (38*)	7 (0)	5 (7)
K	16:16 (10:10)	595 (898)	1.79 (1.60)	200–2200 (500–2400)	186–1898 (353–2288)	0.0634 (0.0412)	0 (40*)	32 (0)	45* (27)	8 (10)	15 (23)
Mg	16:16 (10:10)	552 (805)	1.99 (1.82)	100–1700 (300–2100)	138–2195 (243–2670)	0.0899 (0.0678)	34 (75)	0 (2)	46* (3)	20 (19)	0 (1)
Mn	16:16 (10:10)	407 (719)	3.50 (2.76)	89–3693 (70–3186)	33–4988 (94–5490)	0.2959 (0.1949)	0 (0)	16 (0)	61* (96*)	22 (3)	1 (1)
Na	16:16 (10:10)	90 (100)	1.31 (1.35)	60–190 (60–170)	53–155 (54–183)	0.0137 (0.0173)	0 (39)	8 (7)	2 (0)	48 (21)	42 (33)
Ni	16:16 (10:10)	6 (5)	1.62 (1.96)	4–27 (2–29)	2–16 (1–21)	0.0435 (0.0858)	1 (28)	0 (0)	69* (60)	16 (5)	14 (7)
P	16:16 (10:10)	434 (226)	1.45 (1.62)	270–890 (100–410)	208–907 (86–594)	0.0256 (0.0438)	0 (0)	0 (30)	65* (23)	34 (46)	1 (1)
Pb	16:16 (10:10)	89 (26)	2.23 (1.92)	29–478 (11–67)	18–441 (7–97)	0.1216 (0.0799)	0 (0)	0 (0)	70* (36)	28 (61)	2 (3)
S	16:16 (10:10)	468 (130)	1.86 (1.47)	230–1580 (80–270)	136–1616 (60–283)	0.0724 (0.0282)	0 (0)	0 (26)	92* (69*)	7 (2)	1 (3)
Sr	16:16 (10:10)	6 (5)	1.45 (1.54)	3–15 (3–13)	3–13 (2–12.5)	0.0262 (0.0348)	0 (42*)	11 (0)	0 (32)	87 (24)	2 (2)
Ti	16:16 (10:10)	105 (113)	1.50 (1.87)	46–174 (29–223)	47–235 (32–397)	0.0306 (0.0741)	0 (0)	45 (0)	20 (80)	16 (12)	19 (8)
V	16:16 (10:10)	15 (15)	1.22 (1.31)	10–21 (11–24)	– (9–25)	0.0078 (0.0135)	0 (14)	0 (0)	17* (36)	2 (4)	81 (46)
Zn	16:16 (10:10)	58 (35)	1.47 (1.57)	32–119 (19–98)	27–124 (14–86)	0.0275 (0.0381)	0 (0)	26 (0)	18 (83)	54 (15)	2 (2)
pH	16:16 (10:10)	4.24 (4.87)	1.17 (1.08)	3.50–5.81 (4.40–5.55)	3.11–5.80 (4.17–5.69)	0.0046 (0.0011)	0 (11)	0 (56)	87* (25)	11 (2)	2 (6)

for explanations see Table I

Table III

Summary statistics for and variation in the element concentrations and pH in the soil horizon-A vs the horizon-B (in parentheses) in Wigierski National Park (NE Poland)

Element [mg kg^{-1}]	Ratio (W:N)	Summary statistics				Analysis of variance					
		Geom. mean	Geom. deviation	Observed range	Expected 0.05 range	Total log$_{10}$ variance	Levels				
							1	2	3	4	5
Al.	16:16	4318	1.49	1400–7200	1956–9532	0.0296	0	22	0	72	6
	(15:15)	(6059)	(1.32)	(3400–9300)	(3503–10479)	(0.0142)	(0)	(14)	(15)	(59)	(12)
As	1:16	< 5	–	–	–	–	–	–	–	–	–
	(1:15)	(< 5)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)
Ba	16:16	38	1.96	16–271	9–146	0.0857	12	0	22	56	10
	(15:15)	(30)	(1.38)	(15–53)	(16–58)	(0.0197)	(0)	(1)	(30)	(25)	(44)
Ca	16:16	984	4.53	200–30300	48–20241	0.4310	39*	0	18	43	0
	(15:15)	(474)	(2.56)	(200–10100)	(73–3094)	(0.1660)	(16)	(0)	(72*)	(12)	(0)
Cd	0:16	<0.5	–	–	–	–	–	–	–	–	–
	(0:15)	(<0.5)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)
Co	14:16	1	1.68	<1–4	1–4	0.0511	0	0	24	66	10
	(14:15)	(2)	(1.67)	(<1–4)	(1–5)	(0.0500)	(34)	(15)	(3)	(38)	(10)
Cr	16:16	5	1.44	2–10	2–10	0.0251	0	11	0	78	11
	(15:15)	(6)	(1.39)	(3–13)	(3–11)	(0.0206)	(7)	(0)	(40)	(39)	(14)
Cu	16:16	3	1.78	1–13	1–9	0.0629	21	0	33	44	2
	(15:15)	(2)	(1.46)	(2–8)	(1–5)	(0.0266)	(17)	(0)	(55*)	(24)	(4)
Fe	16:16	5803	1.34	3900–12600	3226–10438	0.0163	15	0	6	74	5
	(15:15)	(6521)	(1.40)	(3900–16900)	(3342–12722)	(0.0211)	(16)	(0)	(62*)	(18)	(4)
Hg	16:16	0.049	1.55	0.018–0.128	0.020–0.118	0.0364	28	0	0	62	10
	(15:15)	(0.020)	(1.58)	(0.007–0.041)	(0.007–0.045)	(0.0390)	(0)	(0)	(15)	(76)	(9)
K	16:16	455	1.28	300–900	–	0.0112	0	0	0	16	84
	(15:15)	(555)	(1.29)	(400–1000)	–	(0.0121)	(4)	(5)	(0)	(13)	(78)
Mg	16:16	756	1.67	300–1800	273–2097	0.0490	47	0	27	25	1
	(15:15)	(883)	(1.61)	(500–3500)	(339–2300)	(0.0433)	(35)	(0)	(47*)	(17)	(1)
Mn	16:16	374	2.48	58–1490	61–2305	0.1558	0	7	37	56	0
	(15:15)	(226)	(2.03)	(52–783)	(55–928)	(0.0942)	(0)	(0)	(52)	(48)	(0)
Na	16:16	96	1.17	80–140	–	0.0048	0	0	0	0	100
	(15:15)	(120)	(1.16)	(90–160)	–	(0.0040)	(0)	(0)	(0)	(0)	(100)
Ni	16:16	3	1.37	2–7	2–6	0.0186	23	8	0	35	34
	(15:15)	(4)	(1.49)	(2–10)	(2–8)	(0.0299)	(2)	(24)	(28)	(25)	(21)
P	16:16	357	1.94	170–2500	95–1345	0.0828	42*	0	14	44	0
	(15:15)	(274)	(1.37)	(190–530)	(147–511)	(0.0183)	(0)	(0)	(36)	(62)	(2)
Pb	16:16	19	1.38	8–28	10–36	0.0199	0	0	0	88	12
	(11:15)	(6)	(1.67)	(< 5–18)	(2–17)	(0.0496)	(0)	(0)	(31)	(64)	(5)
S	16:16	199	2.03	100–2100	48–819	0.0945	29	0	32	38	1
	(10:15)	(60)	(1.55)	(< 50–120)	(25–144)	(0.0359)	(1)	(0)	(0)	(97)	(2)
Sr	16:16	5	2.57	3–68	1–36	0.1678	28*	0	18	54	0
	(15:15)	(4)	(1.48)	(3–14)	(2–9)	(0.0292)	(3)	(0)	(76*)	(19)	(2)
Ti	16:16	115	1.45	39–212	55–241	0.0260	0	12	0	66	22
	(15:15)	(130)	(1.34)	(86–239)	(72–232)	(0.0161)	(30*)	(0)	(18)	(17)	(35)
V	16:16	9	1.48	3–18	4–19	0.0292	0	15*	0	64	21
	(15:15)	(10)	(1.40)	(6–24)	(5–19)	(0.0210)	(12)	(0)	(46*)	(12)	(30)
Zn	16:16	21	1.76	12–121	7–66	0.0609	1	8	0	90	1
	(15:15)	(16)	(1.39)	(9–36)	(8–32)	(0.0207)	(1)	(0)	(10)	(86)	(3)
pH	16:16	5.17	1.18	4.29–7.55	3.72–7.20	0.0051	20*	0	2	77	1
	(15:15)	(5.93)	(1.12)	(4.85–7.56)	(4.72–7.45)	(0.0024)	(6)	(0)	(48)	(43)	(3)

for explanations see Table I