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Trace element and sulphur stable isotope ratios in soils and vegetation of the Holy Cross Mountains

The results of trace element and sulphur stable isotope determinations performed on soils, lichens, mosses, pine needles, spring waters and industrial material from the Holy Cross Mts. region show that some elements are elevated due to pollution. The chemical analyses indicated the raised content of As, Cd, Hg, Mn, Pb, S and Zn, and somewhat Cu in the uppermost soil horizon. Of these elements, lead reaching 310 ppm is a concern. The remaining natural media also contain higher concentrations of many elements compared to those from other areas in the U.S.A. and Europe. Lichens, a classic bioindicator, are generally enriched in Cd, La, Li, Pb and S, and somewhat in Hg, Pb and Ti. A high level of sulphur (up to 0.128%) has been noted here. In order to record any fluctuations in the content of these and other elements, a two-year monitoring has been initiated.

INTRODUCTION

This report presents the preliminary results of trace element and sulphur isotope determinations on soils, vegetation (lichens, mosses and pine needles) and spring waters from Holy Cross Mountain National Park (HCMNP) (Świętokrzyski Park Narodowy) and adjacent areas (Holy Cross Mts. — HCM) (Fig.1). Analyses of stack dusts and some feedstock material (hard coal) from major industrial facilities located in the region have also been presented. The overall objective of this investigation was to determine the baseline concentration of trace elements and sulphur isotopes in the aforementioned media, as well as to outline the impact of potential industrial sources located in and near the Holy Cross Mts. region. The baseline results measured in this study will also serve as a reference point for comparison with ongoing monitoring in 1995–1996 whose purpose is to record fluctuations in the distribution pattern of these elements.

In Poland only soils were analyzed for trace elements and pH on a large scale, especially for different geochemical atlases (J. Lis, 1992; L. Lenartowicz, 1994; J. Lis, A. Pasieczna,

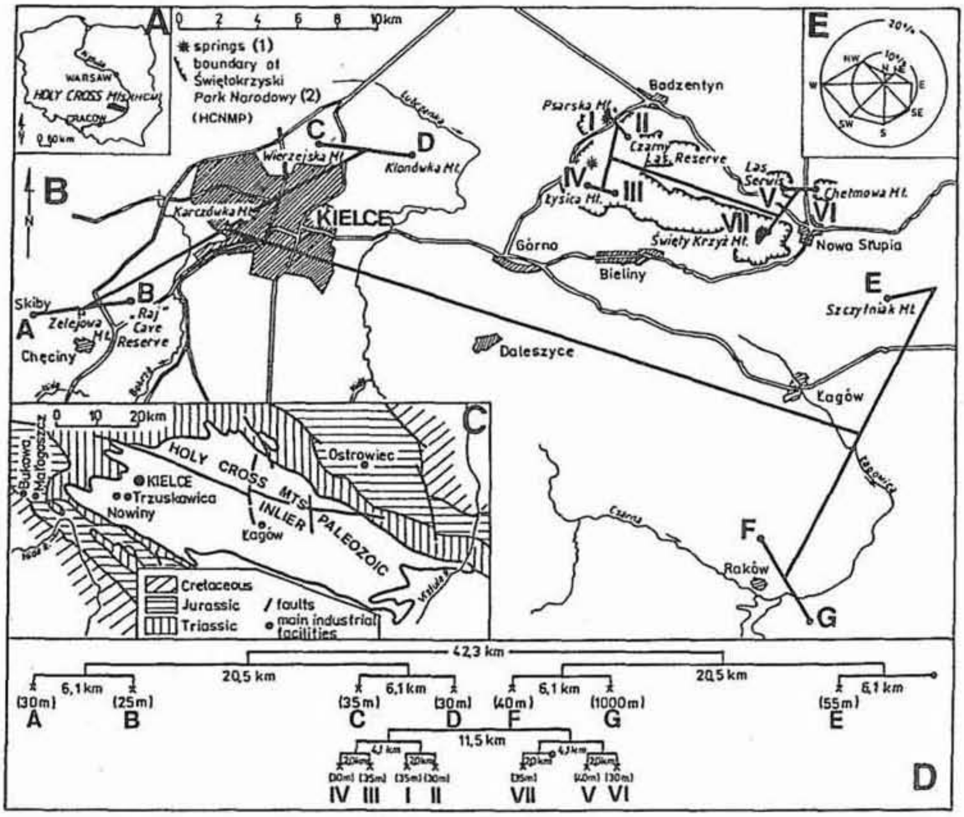

Fig. 1. Location of the study area (**A**); the Holy Cross Mts. and Holy Cross Mountain National Park (Świętokrzyski Park Narodowy) with barbell cluster (**B**); geologic sketch map with major local industrial facilities (**C**); nested design (**D**); wind rose (**E**)

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 (**A**); Góry Świętokrzyskie i Świętokrzyski Park Narodowy ze stanowiskami badawczymi wyznaczonymi metodą „sztangi" (**B**); szkic geologiczny wraz z lokalizacją większych zakładów przemysłowych (**C**); rozkład gniazdowy (**D**); róża wiatrów (**E**)

I–VII — stanowiska badawcze w Świętokrzyskim Parku Narodowym; A–G — stanowiska badawcze na pozostałym obszarze Gór Świętokrzyskich; 1 — źródła, 2 — granica Świętokrzyskiego Parku Narodowego

1995*a*, *b*, *c*). In addition, chemical analyses including some selected elements were done on lichens (J. Fabiszewski *et al.*, 1983; M. Świeboda, A. Kalemba, 1983), mosses (K. Grodzińska, 1983) and aquatic bryophytes (A. Samecka-Cymerman, A. J. Kempers, 1994). In the area of interest only a few principal elements (Ca, K, Mg, N, Na and P) were locally determined in lichens (S. Cieśliński, E. Jaworska, 1986). Regional biogeochemical investigation that includes trace element and stable sulphur isotope analyses on soils, lichens, mosses and pine needles, has not been carried out previously in Poland.

The Holy Cross Mts. are located in south-central Poland (Fig. 1). They take up an area about 65 x 35 km. The tallest mountain (Łysica Mt.) reaches 612 m a.s.l. The Holy Cross Mts. are made of the Palaeozoic inlier and the Permo-Mesozoic cover. The striking tectonic element is the Holy Cross Fault (WNW–ESE) which divides the whole region into two structural-palaeogeographic units, i.e., the Łysogóry (northern) and the Kielce (southern). The former is featured by a nearly continuous development of sediments spanning the Cambrian through the Lower Carboniferous. In turn, the Kielce unit contains numerous stratigraphic gaps. The lower portion of the Palaeozoic profile (Cambrian through Lower Devonian) is developed primarily as terrigenous sediments, whereas the upper (mostly Middle and Upper Devonian) as carbonate rocks topped by siliceous-clayey-terrigenous sediments (Lower Carboniferous). Permo-Triassic sequences are generally carbonate-terrigenous, whereas Jurassic and Cretaceous deposits primarily carbonate. Tertiary sediments (claystones, sandstones, limestones and gypsums) abut on the southern margin of the Holy Cross Mts.

Exposed Cambrian and Devonian rocks take up most of the study area. Of these rocks, Middle Devonian limestones are extracted on a large scale for building, road construction and metallurgy industries. Scattered and veined sulphide and barite mineralization occur primarily within Devonian, Upper Permian, and Lower and Middle Triassic, and somewhat Cambrian sediments (Z. Rubinowski, 1970, 1971; Z. M. Migaszewski *et al.*, 1995, 1996). HCMNP takes up the central part of the Łysogóry unit. The remaining study area occupies the Kielce unit, and the western and eastern parts of the Łysogóry unit (Fig.1).

In the Holy Cross Mts. a mosaic of soil types occurs. They include primarily rankers (not fully developed soils on quartzitic sandstones), arenosols (rusty soils), cambisols (brown soils), rendzinas (soils developed on carbonate rocks), and in some places chernozems, podsols and fluvisols. In general, they make up a thin layer averaging about tens of centimetres in thickness. Acidity of soils results from geologic, climatic and anthropogenic factors. In the region, neutral (pH 6.7–7.4), slightly acid (pH 6.0–6.7) and acid (pH 4.0–6.0) soils are ubiquitous; alkaline (pH 7.4–8.0) and very acid (pH 4.0–5.0) soils are scarce here (L. Lenartowicz, 1994; J. Lis, A. Pasieczna, 1995*c*).

In the Holy Cross Mts. winds from the western sector (NW, W, SW) are prevalent. In Kielce these winds make up 43.2% of the wind rose (Fig. 1). Southernly and southeasternly winds constitute 24.9% of this pattern (G. Żarnowiecki, 1993).

The study region shows environmental degradation which is reflected by the presence of impoverished coniferous tree, lichen and moss flora. The coniferous trees include spruce and pine represented only by several species among which *Abies alba* and *Pinus sylvestris* are the most common. Spruce *Abies alba* has steadily been dying out; however, recent observations seem to indicate that this process is being restrained. Similarly, pine *Pinus sylvestris* generally contains one- through three-year needle increments; no five- through seven-year increments characteristic of unpolluted environment are present.

The results of investigation performed on lichen flora of the Holy Cross Mts. have not been summarized so far. Nonetheless, these results indicated that the number of epiphytic (bark), epixylic (tree), epigeic (ground) and epilithic (rock) lichens has steadily been declining for more than 100 years (F. Berdau, 1876; F. Błoński, 1890; R. Kobendza, J. Motyka, 1928, 1929; R. Kobendza, 1939). Historical data reveal that all the pristine locations seem to have contained about 350–360 lichen species. In HCMNP as much as 197

Table 1

Summary statistics for and variation in the element concentration in the topsoil in HCMNP versus the remaining Holy Cross Mts. area (in parentheses)

Component	Ratio (m:n)	Summary statistics				Analysis of variance					
		Geom. mean	Geom. deviation	Observed range	Expected 95% range	Total $\log_{10}$ variance	Levels				
							1	2	3	4	5
Al	14:14	0.80	1.51	0.29-1.47	0.35-1.82	0.0315	26	0	45	28	<1
(%)	(14:14)	(0.43)	(2.13)	(0.15-1.47)	(0.10-1.96)	(0.1072)	(8)	(50)	(36*)	(6)	(<1)
As	14:14	9	1.68	5-22	3-27	0.0507	0	59	0	40	1
(ppm)	(9:14)	(9)	(2.38)	(<5-41)	(2-50)	(0.1414)	(5)	(6)	(78*)	(10)	(<1)
Ba	14:14	54	1.48	21-107	25-119	0.0295	2	20	29	49	<1
(ppm)	(14:14)	(48)	(2.30)	(14-215)	(9-252)	(0.1311)	(51)	(19)	(20*)	(10)	(<1)
Ca	13:14	0.07	2.23	<0.01-0.18	0.02-0.37	0.1209	0	22	3	75	<1
(%)	(10:14)	(0.10)	(8.67)	(<0.01-3.67)	(0.00-7.29)	(0.8796)					
Cd	8:14	0.5	1.55	<0.5-1.1	0.2-1.3	0.0365					
(ppm)	(9:14)	(0.7)	(1.83)	(<0.5-1.8)	(0.2-2.3)	(0.0691)					
Co	13:14	3	2.15	<1-16	1-15	0.1104	1	0	69*	30	<1
(ppm)	(12:14)	(2)	(1.98)	(<1-5)	(0-7)	(0.0883)	(52)	(0)	(38*)	(10)	(<1)
Cr	14:14	13	1.50	4-19	6-29	0.0310	0	49	16	34	1
(ppm)	(14:14)	(6)	(2.36)	(2-18)	(1-36)	(0.1386)	(4)	(69)	(25*)	(3)	(<1)
Cu	14:14	15	1.76	5-29	5-45	0.0598	0	54	6	40	1
(ppm)	(14:14)	(25)	(1.20)	(19-36)	(17-36)	(0.0064)	(0)	(20)	(47)	(28)	(5)
Fe	14:14	0.91	1.61	0.23-1.59	0.35-2.36	0.0429	0	0	76*	23	<1
(%)	(14:14)	(0.51)	(2.58)	(0.12-2)	(0.08-3.37)	(0.1691)	(7)	(48)	(42*)	(3)	(<1)
Hg	14:14	0.32	2.27	0.03-1.10	0.08	0.1266	0	40	0	60	<1
(ppm)	(14:14)	(0.16)	(4.02)	(0.01-0.83)	(0.01-2.54)	(0.3648)	(0)	(72*)	(0)	(28)	(<1)
K	14:14	0.13	1.41	0.06-0.22	0.06-0.26	0.0227	27*	0	37	35	1
(%)	(14:14)	(0.06)	(2.06)	(0.02-0.23)	(0.02-0.27)	(0.0983)	(0)	(38)	(54*)	(8)	(<1)
La	14:14	11	1.38	8-24	6-21	0.0197	0	84*	6	9	1
(ppm)	(14:14)	(6)	(1.67)	(3-14)	(2-18)	(0.0497)	(0)	(74)	(16)	(10)	(<1)
Li	12:14	4	2.12	<2-16	1-19	0.1063	14	0	78*	9	<1
(ppm)	(9:14)	(3)	(2.25)	(<2-15)	(1-14)	(0.1235)					
Mg	14:14	0.08	1.75	0.02-0.17	0.03-0.26	0.0585	20	0	54*	25	1
(%)	(14:14)	(0.06)	(4.35)	(0.01-1.63)	(0.00-1.13)	(0.4081)	(18)	(6)	(71*)	(4)	(<1)
Mn	14:14	351	3.33	19-2477	32-3882	0.2724	9	0	55	36	<1
(ppm)	(14:14)	(326)	(4.86)	(16-3020)	(14-7686)	(0.4713)	(68)	(0)	(20)	(12)	(<1)
Na	14:14	0.01	1.38	0.01-0.02	0.01-0.02	0.0199	60*	0	0	38	1
(%)	(14:14)	(0.01)	(1.00)	(0.01-0.01)	(0.01-0.01)	(0.0000)					
Ni	14:14	7	1.97	1-15	2-27	0.0869	13	0	65*	22	<1
(ppm)	(12:14)	(3)	(2.59)	(<1-12)	(0-22)	(0.1714)	(15)	(40)	(32*)	(13)	(<1)
P	14:14	0.044	1.58	0.014-0.068	0.018-0.110	0.0398	0	16	26	58	<1
(%)	(14:14)	(0.026)	(2.50)	(0.007-0.074)	(0.004-0.164)	(0.1582)	(0)	(59)	(32*)	(9)	(<1)
pH	14:14	4.5	1.13	3.7-5.6	3.5-5.7	0.0028	34	0	35	30	1
	(14:14)	(5.5)	(1.32)	(3.8-8.1)	(3.1-9.6)	(0.0149)	(0)	(97*)	(1)	(2)	(<1)
Pb	14:14	77	2.69	15-310	11-558	0.1848	0	62	9	29	<1
(ppm)	(14:14)	(48)	(3.25)	(5-211)	(5-505)	(0.2620)	(0)	(90*)	(4)	(6)	(<1)
S	14:14	0.043	2.02	0.007-0.116	0.010-0.173	0.0928	0	26	16	58	<1
(%)	(12:14)	(0.025)	(3.40)	(<0.005-0.128)	(0.002-0.289)	(0.2827)	(0)	(82*)	(12*)	(6)	(<1)
δ^{34}S	9:14	3.9	2.0	0.6-6.1	0.9-16.4	0.0968					
(‰)	(7:14)	(4.0)	(3.6)	(2.0-6.6)	(0.3-15.9)	(0.3128)					
Sr	14:14	8	1.38	4-14	4-16	0.0199	35	48*	0	14	2
(ppm)	(14:14)	(6)	(2.20)	(2-25)	(1-31)	(0.1179)	(45)	(40)	(8)	(6)	(<1)
Ti	14:14	135	1.77	58-420	43-419	0.0610	0	71	18	11	<1
(ppm)	(14:14)	(104)	(1.54)	(55-199)	(44-246)	(0.0352)	(0)	(98*)	(0)	(2)	(<1)
TIC	14:14	2.09	2.42	0.37-7.28	0.36-12.23	0.1475	0	0	62	38	<1
(%)	(14:14)	(0.91)	(3.48)	(0.07-4.04)	(0.07-10.98)	(0.2934)	(0)	(68)	(25*)	(6)	(<1)
TOC	14:14	4.08	2.21	0.95-11	0.83-19.96	0.1188	0	0	51	49	<1
(%)	(14:14)	(2.4)	(3.73)	(0.24-23.80)	(0.17-33.00)	(0.3271)	(0)	(73)	(19*)	(8)	(<1)
U	14:14	1.4	2.19	0.2-8.8	0.3-6.6	0.1165	0	38	0	62	<1
(ppm)	(14:14)	(0.9)	(2.5)	(0.2-4.0)	(0.1-5.5)	(0.1540)	(27)	(33)	(35*)	(5)	(<1)
V	14:14	17	1.53	5-27	7-40	0.0341	0	52	8	40	<1
(ppm)	(14:14)	(8)	(3.64)	(1-36)	(1-105)	(0.3145)	(11)	(68)	(17*)	(5)	(<1)
Y	14:14	4	1.36	3-8	2-8	0.0174	0	0	68*	31	2
(ppm)	(13:14)	(2)	(2.26)	(<1-11)	(0-13)	(0.1255)	(30)	(28)	(35*)	(7)	(<1)
Yb	14:14	0.3	1.41	0.2-0.6	0.1-0.6	0.0223	0	0	66*	33	1
(ppm)	(12:14)	(0.2)	(2.10)	(<0.1-0.8)	(0.0-0.9)	(0.1036)	(19)	(35)	(41*)	(4)	(<1)
Zn	14:14	60	1.74	12-109	20-184	0.0582	0	56	7	37	<1
(ppm)	(14:14)	(43)	(2.74)	(8-123)	(6-322)	(0.1917)	(42)	(49*)	(7)	(2)	(<1)

* — significant at 0.05 probability

Table 2

Summary statistics for and variation in the element concentration in the subsoil in HCMNP versus the remaining Holy Cross Mts. area (in parentheses)

Component	Ratio (m:n)	Summary statistics				Analysis of variance					
		Geom. mean	Geom. deviation	Observed range	Expected 95% range	Total $\log_{10}$ variance	Levels				
							1	2	3	4	5
Al (%)	11:11 (11:11)	1.16 (0.39)	1.71 (1.74)	0.55-3.02 (0.18-0.91)	0.39-3.39 (0.13-1.19)	0.0546 (0.0577)	20 (0)	0 (82)	77* (11)	3 (6)	<1 (<1)
As (ppm)	7:11 (4:11)	6 (5)	1.71 (1.58)	4-16 (<5-12)	2-17 (2-12)	0.0538 (0.0400)					
Ba (ppm)	11:11 (11:11)	57 (39)	1.46 (1.77)	26-108 (19-102)	27-121 (13-124)	0.0269 (0.0615)	10 (0)	0 (69)	65 (7)	24 (24)	<1 (<1)
Ca (%)	11:11 (7:11)	0.04 (0.02)	2.26 (3.48)	0.01-0.10 (<0.01-0.25)	0.01-0.18 (0.00-0.27)	0.1257 (0.2936)	69	10	1	19	<1
Co (ppm)	11:11 (11:11)	5 (2)	2.06 (1.83)	1-16 (1-4)	1-20 (0-5)	0.0980 (0.0686)	0 (0)	0 (60)	83* (31)	17 (9)	<1 (<1)
Cr (ppm)	11:11 (11:11)	14 (4)	1.67 (2.00)	6-34 (2-13)	5-40 (:1-18)	0.0492 (0.0907)	26 (0)	0 (90*)	69* (4)	4 (5)	1 (<1)
Cu (ppm)	11:11 (11:11)	7 (25)	2.17 (1.19)	2-22 (16-30)	2-35 (17-35)	0.1135 (0.0058)	3 (0)	0 (0)	84* (0)	13 (94)	<1 (6)
Fe (%)	11:11 (11:11)	1.11 (0.38)	1.95 (2.18)	0.41-3.55 (0.14-1.34)	0.29-4.24 (0.08-1.80)	0.0844 (0.1145)	20 (0)	0 (87)	79* (10*)	2 (2)	<1 (<1)
Hg (ppm)	11:11 (9:11)	0.13 (0.04)	1.60 (3.31)	0.04-0.2 (<0.01-0.21)	0.05-0.33 (0.00-0.44)	0.0421 (0.2705)	0 (0)	71 (77)	0 (12)	28 (11)	1 (<1)
K (%)	11:11 (11:11)	0.18 (0.06)	1.72 (1.89)	0.08-0.46 (0.03-0.14)	0.06-0.53 (0.02-0.22)	0.0552 (0.0761)	25 (0)	0 (92*)	51 (3)	24 (4)	<1 (<1)
La (ppm)	11:11 (11:11)	12 (6)	1.54 (1.94)	8-30 (3-15)	5-29 (2-24)	0.0349 (0.0828)	0 (0)	39 (93*)	52* (3)	8 (4)	<1 (<1)
Li (ppm)	10:11 (6:11)	7 (2)	2.40 (1.69)	1-31 (<2-6)	1-43 (1-6)	0.1446 (0.0520)	2	0	94*	4	<1
Mg (%)	11:11 (11:11)	0.13 (0.04)	1.85 (1.95)	0.04-0.32 (0.02-0.11)	0.04-0.43 (0.01-0.15)	0.0708 (0.0839)	21 (0)	0 (86)	71* (11*)	8 (2)	<1 (<1)
Mn (ppm)	11:11 (11:11)	265 (173)	2.10 (4.08)	78-1104 (29-1212)	60-1170 (10-2889)	0.1038 (0.3730)	0 (0)	57* (81)	0 (2)	43 (17)	<1 (<1)
Na (%)	11:11 (11:11)	0.02 (0.01)	1.54 (1.38)	0.01-0.03 (0.01-0.02)	0.01-0.04 (0.01-0.02)	0.0352 (0.0198)	44 (0)	49 (42)	1 (0)	5 (56)	1 (1)
Ni (ppm)	11:11 (11:11)	7 (2)	2.43 (1.79)	1-22 (1-5)	1-44 (1-7)	0.1487 (0.0645)	11 (0)	0 (43)	84* (5)	5 (52)	<1 (<1)
P (%)	11:11 (10:11)	0.019 (0.014)	1.87 (2.48)	0.006-0.060 (<0.005-0.050)	0.005-0.0661 (0.002-0.083)	0.0735 (0.1558)	0 (0)	42 (0)	27 (71)	31 (29)	<1 (<1)
pH	11:11 (11:11)	5.5 (6.0)	1.09 (1.16)	4.9-6.4 (4.9-7.8)	4.6-6.6 (4.5-8.1)	0.0014 (0.0042)	38 (0)	0 (96*)	0 (0)	60 (3)	2 (1)
Pb (ppm)	9:11 (7:11)	11 (13)	2.07 (3.21)	<5-28 (<5-72)	3-49 (1-138)	0.1002 (0.2563)	0	0	84*	16	<1
S (%)	11:11 (7:11)	0.009 (0.006)	1.40 (1.83)	0.006-0.015 (<0.005-0.017)	0.005-0.018 (0.002-0.021)	0.0214 (0.0688)	0 (2)	0 (84)	61 (11)	39 (3)	<1 (<1)
Sr (ppm)	11:11 (11:11)	8 (5)	1.68 (1.63)	4-19 (2-10)	3-24 (2-12)	0.0513 (0.0446)	57 (0)	0 (77)	35* (17)	7 (6)	1 (1)
Ti (ppm)	11:11 (11:11)	161 (130)	2.72 (1.80)	34-553 (58-262)	22-1190 (40-421)	0.1886 (0.0649)	0 (0)	0 (89)	98* (2)	2 (9)	<1 (<1)
TIC (%)	11:11 (9:11)	0.13 (0.08)	3.58 (5.16)	0.02-0.77 (<0.01-0.69)	0.01-1.68 (0.00-2.07)	0.3065 (0.5079)	0 (0)	0 (82)	31 (3)	69 (15)	<1 (<1)
TOC (%)	11:11 (11:11)	0.53 (0.35)	1.76 (2.68)	0.22-1.49 (0.09-1.48)	0.17-1.64 (0.05-2.48)	0.0601 (0.1828)	0 (0)	6 (92*)	22 (4)	73 (4)	<1 (<1)
U (ppm)	11:11 (11:11)	1.4 (0.6)	1.71 (2.09)	0.0-2.6 (0.2-2.0)	0.5-4.0 (0.1-2.6)	0.0540 (0.1020)	52 (0)	0 (84*)	44* (0)	3 (16)	<1 (<1)
V (ppm)	11:11 (10:11)	18 (4)	1.70 (3.67)	8-39 (<1-21)	6-52 (0-59)	0.0533 (0.3188)	32 (0)	0 (97*)	64* (2)	5 (1)	<1 (<1)
Y (ppm)	11:11 (11:11)	5 (2)	1.39 (1.86)	3-9 (1-4)	3-10 (1-7)	0.0202 (0.0723)	3 (7)	0 (81*)	32 (0)	63 (11)	1 (<1)
Yb (ppm)	11:11 (10:11)	0.4 (0.2)	1.44 (1.77)	0.2-0.7 (<0.1-0.3)	0.2-0.9 (0.1-0.5)	0.0251 (0.0611)	6 (0)	0 (85*)	27 (0)	66 (14)	1 (<1)
Zn (ppm)	11:11 (11:11)	34 (19)	1.76 (1.93)	14-77 (9-53)	11-104 (5-72)	0.0598 (0.0817)	9 (0)	0 (40)	76* (56*)	15 (4)	<1 (<1)

* — significant at 0.05 probability

species were originally recorded; this number has dropped to 129 or probably even less (S. Cieśliński, 1985, 1991). Irreversible changes are noted especially for epiphytic (bark) lichens. According to S. Cieśliński, K. Czyżewska (1991) and S. Cieśliński (pers. comm.), the number of these lichen species has decreased from about 200–250 to 70–100. Some taxonomic groups have become completely extinct. They included lichens primarily with leafy (foliose) and shrubby (fruticose) thalii, i.e., genera *Usnea, Bryoria, Ramalina, Evernia, Lobaria* etc.

This changes seem to have been connected mostly with human activity, i.e., old tree felling, soil, air and water pollution, collecting lichens for medical treatment, etc.

METHODS

SAMPLING DESIGN

Trace element and sulphur stable isotope spatial variation in soils was estimated for specific geographic intervals using a five-level, unbalanced, nested analysis-of-variance (ANOVA) design. Investigation (sampling) sites within HCM (Fig.1) were randomly located by means of a barbell sampling plan with a longer axis of about 42.3 km running WNW–ESE parallel to the extent of the Holy Cross Mts. (level 1), and progressively smaller axes of 20.5 km (level 2), 6.1 km (level 3) and 0.025–0.055 km; except for one place — 1.0 km (level 4). The level 5 referred to duplicated analyses of an individual sample. The same procedure was applied to HCMNP. The axial pattern was similar to that described above, but the very axes were of different length, i.e., 11.5, 4.1, 2.0 and 0.03–0.04 km, respectively. This sampling design helped determine whether or not element patterns in the examined medium were present, calculate element concentration baseline and detect differences between these two basic areas (Tabs. 1, 2). In all, 14 out of 16 sampling sites were designed for further investigation. All these sampling sites were marked with red oil paint.

The study area includes various habitats that seem to be the main reason why lichens, mosses and pine trees do not occur in each site. In addition, particular habitats contain a diverse lichen and moss species. Lichen taxon *Hypogymnia physodes* applied for the purpose of this investigation grows on a bark assigned to different birch-, oak-, pine-, rowan- and spruce-tree species. Thus, for instance, in one site lichens were derived from pine-trees, whereas in another from birch-trees. Considering this, the severe unbalancing of the design because of missing (or the lack of uniform) sites has potentially made all ANOVA results invalid for lichens, mosses and pine needles. For pine needles only summary statistics has been applied (Tab. 3), whereas for lichens and mosses observed concentration ranges have been given (Tab. 4).

In addition, 3 spring water samples were collected from sites I, IV and VII (Tab. 6).

INVESTIGATION SITES

Sampling was done at seven sites in HCMNP (I–VII) and at seven sites over a broader area in the vicinity of Kielce and south of HCMNP (A–G) (Fig. 1). The basement of the sites is made of Lower Cambrian clayey shales (F), Middle and Upper Cambrian quartzites

Table 3

Summary statistics for the element concentration in one (1994)- and two (1993)-year *Pinus sylvestri* pine needles in HCMNP versus the remaining Holy Cross Mts. area (in parentheses)

Component	One-year (1994) needles					Two-year (1993) needles				
	Ratio (m:n)	Geom. mean	Geom. deviation	Observed range	Expected 95% range	Ratio (m:n)	Geom. mean	Geom. deviation	Observed range	Expected 95% range
Al (%)	2:2 (6:8)	0.01 (0.02)	1.63 (1.92)	0.01-0.02 (<0.01-0.04)	0.01-0.04 (0.01-0.07)	2:2 (6:8)	0.01 (0.02)	1.63 (1.84)	0.01-0.02 (<0.01-0.04)	0.01-0.04 (0.00-0.05)
Ba (ppm)	1:2 (4:8)	2 (1)	4.02 (2.10)	<1-5 (<1-4)	0-30 (0-6)	2:2 (7:8)	5 (3)	3.34 (2.47)	2-11 (<1-8)	0-52 (0-18)
Ca (%)	2:2 (8:8)	0.31 (0.26)	1.07 (1.30)	0.30-0.33 (0.18-0.38)	0.27-0.36 (0.16-0.45)	2:2 (8:8)	0.78 ((0.62)	1.20 (1.27)	0.69-0.89 (0.42-0.94)	0.55-1.12 (0.39-1.00)
Cd (ppm)	2:2 (8:8)	0.6 (0.3)	1.91 (2.12)	0.4-1.0 (0.1-0.9)	0.2-2.3 (0.1-1.3)	2:2 (8:8)	0.7 (0.3)	1.52 (2.11)	0.5-0.9 (0.1-0.7)	0.3-1.5 (0.1-1.3)
Cu (ppm)	2:2 (8:8)	8 (8)	1.19 (1.28)	7-9 (6-12)	6-11 (5-14)	2:2 (8:8)	3 (4)	1.23 (1.26)	3-4 (3-6)	2-5 (2-6)
Fe (%)	0:2 (0:8)					1:2 (4:8)	0.01 (0.01)	1.29 (1.21)	<0.01-0.01 (<0.01-0.01)	0.01-0.01 (0.01-0.01)
Hg (ppm)	2:2 (8:8)	0.02 (0.02)	1.00 (1.73)	0.02-0.02 (0.01-0.05)	0.02-0.02 (0.01-0.05)	2:2 (8:8)	0.03 (0.03)	1.23 (1.23)	0.03-0.04 (0.02-0.03)	0.02-0.05 (0.02-0.04)
K (%)	2:2 (8:8)	0.90 (0.81)	1.10 (1.14)	0.84-0.96 (0.68-0.96)	0.74-1.08 (0.63-1.04)	2:2 (8:8)	0.40 (0.44)	1.35 (1.21)	0.32-0.49 (0.33-0.56)	0.22-0.72 (0.30-0.65)
La (ppm)	1:2 (0:8)	0.1	1.29	<0.1-0.1	0.0-0.1	1:2 (4:8)	0.1 (0.1)	1.29 (1.68)	<0.1-0.1 (<0.1-0.2)	0.0-0.1 (0.0-0.3)
Mg (%)	2:2 (8:8)	0.09 (0.10)	1.08 (1.13)	0.09-0.10 (0.08-0.12)	0.08-0.11 (0.08-0.13)	2:2 (8:8)	0.10 (0.08)	1.33 (1.45)	0.08-0.12 (0.04-0.13)	0.06-0.17 (0.04-0.17)
Mn (ppm)	2:2 (8:8)	635 (155)	1.14 (3.16)	577-698 (37-677)	485-831 (16-1550)	2:2 (8:8)	1358 (231)	1.48 (4.15)	1030-1790 (34-1450)	621-2967 (13-3983)
Ni (ppm)	2:2 (8:8)	12 (4)	1.57 (2.02)	9-17 (1-8)	5-30 (1-16)	2:2 (7:8)	6 (2)	1.39 (2.15)	5-8 (<1-8)	3-12 (0-7)
P (%)	2:2 (8:8)	0.240 (0.252)	1.09 (1.08)	0.230-0.260 (0.215-0.269)	0.210-0.290 (0.217-0.292)	2:2 (8:8)	0.133 (0.145)	1.23 (1.13)	0.115-0.154 (0.125-0.182)	0.088-0.201 (0.114-0.185)
Pb (ppm)	2:2 (5:8)	1 (1)	1.00 (1.20)	1-1 (1-1)	1-1 (1-1)	2:2 (8:8)	2 (2)	1.33 (1.74)	2-3 (1-4)	1-4 (1-7)
S (%)	2:2 (8:8)	0.077 (0.072)	1.09 (1.16)	0.072-0.081 (0.059-0.074)	0.060-0.090 (0.050-0.100)	2:2 (8:8)	0.067 (0.071)	1.04 (1.19)	0.065-0.069 (0.061-0.104)	0.060-0.070 (0.050-0.100)
δ^{34}S (‰)	2:2 (8:8)	4.8 (3.7)	1.01 (1.27)	4.8-4.9 (2.1-4.5)	4.8-4.9 (2.3-5.9)	2:2 (8:8)	4.4 (3.4)	1.10 (1.41)	4.1-4.7 (1.9-4.6)	3.6-5.3 (1.7-6.7)
Sr (ppm)	2:2 (8:8)	2 (1)	1.33 (1.56)	2-3 (1-3)	1-4 (1-3)	2:2 (8:8)	7 (4)	1.10 (1.54)	7-8 (2-7)	6-9 (2-10)
Ti (ppm)	0:2 (0:8)					2:2 (8:8)	1 (2)	1.63 (1.62)	1-2 (1-3)	1-4 (1-5)
Yb (ppm)	0:2 (7:8)	(0.01)	(1.13)	(<0.01-0.01)	(0.01-0.01)	1:2 (6:8)	0.01 (0.01)	1.29 (1.18)	<0.01-0.01 (<0.01-0.01)	0.01-0.01 (0.01-0.01)
Zn (ppm)	2:2 (8:8)	50 (51)	1.27 (1.17)	42-59 (39-61)	31-80 (37-70)	2:2 (8:8)	64 (53)	1.41 (1.37)	50-81 (32-92)	32-126 (28-99)

and quartzitic shales (C, D, E, III, IV, and VII), Silurian shales (II, V), Lower Devonian quartzitic sandstones (I, VI), Middle Devonian dolomites (A) and limestones (B) and Tertiary limestones (G). The slope of individual sites varies from 0 to 30° with a mean of 5–10°.

At the investigation sites, forest loamy and sandy soil cover occurs. Its thickness varies from tens of centimetres to about two metres, with a mean of about 40 cm. In HCMNP ranker soil type is prevalent; cambisols (V and VI) and chernozems (II) are scarce. In the second area of interest (HCM) rankers (C, D and E), arenosols (F and G) and rendzinas (A and B) are prevalent. In general, the soil profile consists of two (in places three) layers: humus-rich topsoil (A_1 horizon) and subsoil (B or (B) horizon) directly underlain by hostrock (C or D). The average thickness of topsoil is about 10 cm.

Table 4

Observed range of the element concentration in lichen species *Hypogymnia physodes* growing on a pine-tree, and moss species *Hypnum cupressiforme*, *Hylocomium splendens* and *Entodon schreiberi* in HCMNP versus the remaining Holy Cross Mts. area (in parentheses)

Component	Lichens	Mosses
Al (%)	0.05-0.09 (0.04-0.07)	0.05-0.07 (0.04-0.10)
As (ppm)	3-5 (<2-3)	<2-2 (<2-2)
Ba (ppm)	6-92 (8-40)	19-22 (10-31)
Ca (%)	0.08-2.24 (0.08-0.51)	0.22-0.35 (0.28-0.82)
Cd (ppm)	0.6-1.3 (0.5-1.0)	0.7-0.9 (0.5-1.0)
Cr (ppm)	2-6 (2-3)	2-4 (2-5)
Cu (ppm)	6-13 (6-14)	7-13 (8-12)
Fe (%)	0.09-0.26 (0.05-0.09)	0.05-0.09 (0.03-0.09)
Hg (ppm)	0.19-0.37 (0.11-0.18)	0.02-0.14 (0.05-0.11)
K (%)	0.14-0.33 (0.22-0.36)	0.42-0.60 (0.41-0.63)
La (ppm)	0.6-1.9 (0.6-0.8)	0.4-0.8 (0.3-1.0)
Li (ppm)	1-2 (1-1)	1-1 (<1-1)
Mg (%)	0.02-0.06 (0.02-0.04)	0.05-0.07 (0.05-0.09)
Mn (ppm)	44-525 (38-144)	122-386 (40-349)
Na (%)	<0.01-0.01 (<0.01-0.01)	0.01-0.01 (0.01-0.02)
Ni (ppm)	1-3 (1-2)	1-3 (1-3)
P (%)	0.059-0.129 (0.067-0.179)	0.116-0.140 (0.101-0.183)
Pb (ppm)	12-99 (14-46)	17-56 (12-43)
S (%)	0.091-0.128 (0.058-0.094)	0.068-0.095 (0.052-0.097)
$\delta^{34}S$ (‰)	3.2-5.4 (3.4-5.2)	2.8-3.9 (2.7-4.2)
Sr (ppm)	3-13 (3-5)	7-10 (6-11)
Ti (ppm)	18-73 (14-28)	1-18 (3-19)
V (ppm)	<10-10 (<10-10)	<10-10 (<10-10)
Y (ppm)	0.4-1.5 (0.4-0.7)	0.3-0.5 (0.2-0.6)
Yb (ppm)	0.04-0.11 (0.02-0.04)	0.03-0.05 (0.01-0.04)
Zn (ppm)	66-145 (71-170)	45-89 (44-72)

The investigation sites are located within diverse forest communities including pine, mixed coniferous and deciduous forests. Within HCMNP, the sites are located mainly in natural forest communities, whereas outside HCMNP some sites are situated in planted pine stands 15 to 20 years old. All sites are more than 300 m from hard-surfaced roads.

Species *Hypogymnia physodes* is the only lichen here featured by bigger thalli and a relatively large areal extent. Other lichen species with leafy and shrubby thalli, i.e., *Parmelia sulcata, Pseudevernia furfuracea* and *Cetraria chlorophylla*, occur in a very small amount and only in individual stands. Lichens with crusty thalli grow more commonly and are represented primarily by *Lecanora conizaeoides, Lepraria incana, Scoliciosporum chlorococcum* and *Hypocenomyce scalaris*. Other species are scarce and occur only in single stands.

Species *H. physodes* occurs on a bark of trees that grow in better shone places at margins of forest clearings, boulder fields, wood roads etc. At each site lichens were collected from within an area ranging from 10 x 10 to 100 x 100 m, primarily on several trees at a height of 0.25 to 2.0 m.

In general, the investigation sites do not contain much *H. physodes*. Moreover, at some sites (A, B, D, E, and VI) no *H. physodes* has been found on pine trees at all. It results from the pattern of local biotopic factors, but primarily from the character and pressure of anthropogenic stresses.

Mosses assigned to species *Entodon schreiberi* and *Hylocomium splendens* grow only at seven sites (D, E, F, III, IV, V, and VII). At one site (A) another species *Hypnum cupressiforme*, which grows within a young pine tree stand, was collected.

Pine species *Pinus sylvestris*, at places being out of reach (tall trees), occurs at most sites.

The much more detailed taxonomic characteristics of lichens, mosses and pine needles at particular sites (S. Cieśliński, Institute of Biology of the College of Education in Kielce) and the floral composition based on phytosociological survey (E. Bróż, the same Institute) have been stored in the Depository of the Świętokrzyskie Mts. Branch, Polish Geological Institute in Kielce.

FIELD SAMPLING, SAMPLE PREPARATION AND ANALYSIS

Samples were taken on June 28–30, 1994 during sunny days at a temperature of about 30°C. While collecting samples, and then during transportation and preparation, all measures were taken to reduce to minimum the influence of any outer contamination. To avoid all these disadvantages, plastic scrapers and shovels, stainless scissors, clean surgical gloves were used, smoking cigarettes was prohibited, etc., during sampling and elsewhere. Adhering bark fragments and other admixtures were removed with forceps and preliminary dried at an ambient temperature to avoid developing fungi. Soil, industrial dust and feedstock were stored in plastic and paper bags, organic material in paper bags, and spring water in special plastic bottles.

Soil samples composed of about 0.5–1.0 kg of material, were collected from each horizon (2 or 3) within an examined profile. Lichen, moss, and one- and two-year pine needle samples weighed about 30–50 g each.

Prior to the analyses, soil samples were pulverized in an agate blender and sieved. The fraction passing 2.0 mm was preserved. Part of the sample was subsequently ground with a ceramic blender to pass an 0.18 mm sieve. The same procedure was applied to industrial material.

Organic material was placed in teflon beakers, washed with deionized water and dried. This procedure was repeated three times. After that, the examined samples were placed on plastic colanders, washed with deionized water and preliminary dried at an ambient temperature. After oven-drying at about 40°C for about 24 hours, the samples were disaggregated using Fritsch's blender, then sieved. The fraction which passed a 2.0 mm sieve was ashed in an electric oven at 450°C.

The pivotal point that has the decisive influence on interpretation of obtained results, especially from soils, is digestion of samples. The complete digestion of a specific soil sample results in overlapping anthropogenic and geologic factors. Each soil and industrial dust sample (2 g) was digested with *aqua regia* (15 ml HCL + 5 ml HNO_3), evaporated (160°C), dissolved with concentrated hydrochloric acid (10 ml), and an insoluble residue was filtered. Soil and dust samples (0.1 g) for uranium determinations were digested with an acid mixture (1 ml HF + 5 ml HNO_3 + 3 ml $HClO_4$), evaporated until moist precipitates appeared (200°C), dissolved with 1N nitric acid (5 ml). The digestion procedure for plant ash samples (5 g) was the same as for soils.

In general, 133 samples were tested. Of this number, 10% was randomly selected for routine control analyses and 5% with reference to international standards. The samples were tested for 24 elements, i.e., Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, V, Y, Yb, and Zn using inductively coupled plasma-atomic emisssion spectrometry (ICP-AES) (spectrometer *Jobin-Yvon* model *JY 70 PLUS*), and FAAS method (spectrometer *PU 9100 X UNICAM*). The content of sulphur was selectively controlled using coulometric technique. Arsenic was determined both by ICP-AES method or continuous-flow, hydridegeneration, atomic absorption spectroscopy (HGAAS). Mercury was determined using automated, continuous-flow, cold-vapor, atomic absorption spectroscopic (CVAAS) method (spectrometer *Perkin-Elmer 4100 ZL* with a continuous-flow attachment *FIAS 100*). Total organic (TOC) and inorganic carbon (TIC) was detected only in soil, industrial material and water using automatic coulometric titration method (Coulomat *702 C/S*, Ströhlein, Germany). Uranium was determined by laser fluorometry using an analyzer *UA-3 Scintrex* (Canada). In some soil samples the content of fluorine was determined by potentiometric method (pehameter *PHM 64* Radiometer, Denmark with an ionselective fluoride electrode). In soil and industrial material, pH was determined by 1:1 water extraction using a pehameter *PH 204 Slandi* (Poland).

Stable sulphur and oxygen determinations were carried out on a modified mass spectrometer *MI-1305* (S. Hałas, Z. Skorzyński, 1981) on SO_2 gas. Sulphur was precipitated in the form of $BaSO_4$. The sulphate reacted with $NaPO_3$ under vacuum at 850°C; thus obtained SO_3 was then reduced to SO_2 on copper heated to 750°C (S. Hałas, W. Wołącewicz, 1981).

RESULTS AND DISCUSSION

Tables 1 and 2 present the results of summary statistics and ANOVA for trace element and sulphur stable isotope concentrations in topsoil and 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 $GM\text{x}GD^2$.

Aside from these data, the detection ratio, i.e., the number of samples above detectable concentration level (m) relative to the total number of samples (n), has been given. When the number of samples containing a specific element (and sulphur isotope) below lower limit of determination (censored) amounted to 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 lower limit 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 the calculation of the total $\log_{10}$ variance and its percentage split into five basic levels (R. L. Anderson, T. A. Bancroft, 1952). Because of the large proportion of the censored samples, Cd, $\delta^{34}S$, and partly (HCM) Ca, Li and Na were not included in ANOVA column for topsoil (Tab. 1). Nor were As, and partly (HCM) Ca, Li and Pb for subsoil (Tab. 2).

In HCMNP, the largest proportion of variability in topsoil was associated with smaller distances, i.e., the 4.1 km (level 2), the 2.0 km (level 3) and the 0.03–0.04 km (level 4). The exception was Na, and somewhat Sr, where their values varied much over the 11.5 km distance (level 1). The variability of K and pH concentrations was almost evenly split over the 11.5 km, 2.0 km and 0.03-0.04 km distance increments. In turn, the chemistry of subsoil in HCMNP only in some measure patterned that of topsoil. It varied primarily over the 2.0-km distance. Only Ca, Hg, Mn, Na, P, pH, Sr, TIC, TOC, Y and Yb recorded more than 42% of their variability at the remaining distance increments (11.5, 4.1 and 0.03–0.04 km). It should be stressed here that more than 71% of the total variability for Co, Fe, Li, Mg and Ni was associated with the level 3 (2.0 km) being similar to that in topsoil.

As for the remaining area (HCM), nearly all the components in topsoil recorded 67% or more of their variability at somewhat larger distances, primarily at the levels 2 (20.5 km) and 3 (6.1 km). This was not the case for Ba, Co, Mn, Sr and somewhat U, Y, Zn whose variance was also connected with the 42.3 km distance increment. In subsoil, nearly all the elements (except for Cu and P) recorded 40% or even much more of their variability at the level 2 (20.5 km).

Analytical error (level 5) linked to the sample type and the applied analytical method (sample chemical preparation + measurement errors) was negligible.

Tables 3 and 4 present the results of summary statistics (pine needles) and observed range (lichens and mosses) for trace element and sulphur stable isotope concentrations.

The results of performed biogeochemical investigations indicate a considerable pollution of the natural environment in the Holy Cross Mts., especially in their highest parts, most of which generally make up HCMNP (see geometric means of different element concentrations in Tables 1, 2).

The distribution of sulphur and trace elements in soil is a sum of their geochemical and biological circulation, and anthropogenic activity, which is reflected by their diverse (relative to plants) sulphur isotope composition varying from 0.6 to 6.6‰. Topsoil, like lichens and mosses is, in turn, distinctly enriched in heavy sulphur isotope (positive values). The similar distribution pattern of the sulphur isotope composition in all these media and industrial material indicates the common source of sulphur (Fig. 2)[1]. These data are different from those reported for soil 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 was, in turn, connected with the isotopic composition of the bedrock.

The content of Al, Ca, Fe, K, Mg, Na, P, TIC and TOC show local fluctuations linked mostly to the chemical composition of bedrock and biogeochemical cycle of these elements. Maximum concentrations of P, TIC and TOC have been noted in topsoil. The raised content of Ca and Mg has been observed in soils developed on limestones or dolomites, respectively.

In the Holy Cross Mts., the anthropogenic impact is apparently marked by the elevated levels of such elements as:

— As, Cd, Hg, Mn, Pb, S and Zn, and somewhat As and Cu in topsoil relative to subsoil; besides, topsoil commonly reveals lower pH (Tabs. 1 and 2);

— almost all (but especially Cr, Fe, Hg, La, Mn, Pb, S, Ti, U, V, Zn) in the highest parts of the mountains that take up the both study areas;

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[1] Sulphides linked to ore mineralization in the Holy Cross Mts. show primarily negative $\delta^{34}S$ values (Z. M. Migaszewski *et al.*, 1996).

Moreover, the content of some of these elements (Ba, Co, Mg, Mn, Ni, Sr, U, V, Y, Yb, and Zn) decreases in the southeastern HCM area, which is both poorly industrialized and remote from the principal industrial centers of the region and southwestern Poland (Fig. 1).

Of the aforementioned elements, sulphur is of particular interest. In some places, topsoil contains over twenty times more sulphur than subsoil, for instance: 0.128% versus 0.006% (Wierzejska Mt. — C/1). The highest content of sulphur is associated with the lowest pH values.

The geometric mean values of many trace elements (As, Cd, Cr, Cu, Hg, Pb, S and Ti, and somewhat Ba, Co, Mn, Ni and V) are higher in the Holy Cross Mts. region than in Poland (Tab. 5). Of all these elements, lead whose content reach even 310 ppm is a concern[2]. On the other hand, a relatively elevated level of lead (to 72 ppm) in subsoil may indicate a slightly raised regional geochemical background of this element. This inference seems to be supported by the results of many chemical analyses of Upper Palaeozoic and Lower Triassic rocks.

The only exception is site V (Las Service) where subsoil composed of Pleistocene tills is distinctly abundant in many heavy metals except for lead.

The above trend is also reflected by the chemical composition of spring waters from the HCMNP (Tab. 6). The total amount of

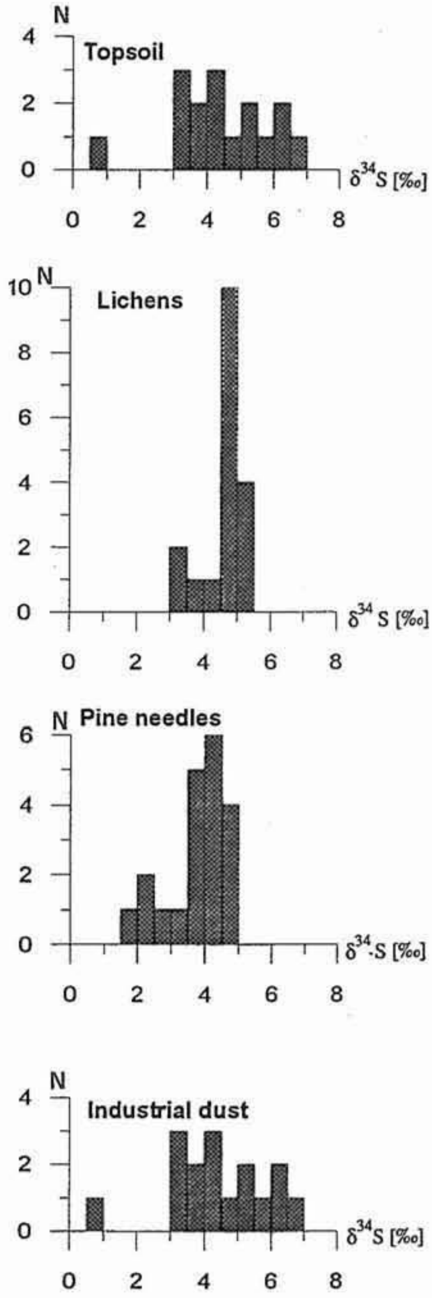

Fig. 2. The $\delta^{34}S$ distribution pattern in topsoil, *Hypogymnia physodes* lichens, *Pinus sylvestris* pine needles, and industrial (stack) dust from major regional industrial facilities

Rozkład wartości $\delta^{34}S$ w najwyższym poziomie glebowym, porostach *Hypogymnia physodes*, igłach sosny *Pinus sylvestris* oraz w pyłach kominowych większych zakładów przemysłowych

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[2] The highest level of lead in topsoil (peats) recorded in the region was 2100 ppm. It was closely connected with a narrow zone extending along both shoulders of E7 highway (L. Lenartowicz, 1990).

Table 5

Geometric mean and observed ranges for trace elements in topsoil from HCMNP, the remaining Holy Cross Mts. area (in 1994), Kielce forests (L. Lenartowicz, 1994) Upper Silesia (J. Lis, A. Pasieczna, 1995*b*) and Poland (J. Lis, A. Pasieczna, 1995*c*)

Element	HCMNP		HCM		Kielce forests		Upper Silesia		Poland	
	GM	Range	GM	Range	GM	Range	GM	Range	GM	Range
As (ppm)	9	5-22	9	<5-41	4.2	<5-20.0	<5	<5-238	<5	<5-3444
Ba (ppm)	54	21-107	48	14-215	-	-	54	2-1,777	32	<1-1777
Ca (%)	0.07	<0.01-0.18	0.09	<0.01-3.67	-	-	0.23	<0.01-13.47	0.17	<0.01-25.45
Cd (ppm)	0.5	<0.5-1.2	0.7	<0.5-1.8	0.6	<0.5-22.1	1.4	<0.5-253.3	<0.5	<0.5-253
Co (ppm)	3	<1-16	2	<1-5	2	1-20	2	<1-21	1.7	<1--46
Cr (ppm)	13	4-19	6	2-18	17	1-78	5	<1-95	4	<1-1873
Cu (ppm)	15	5-29	25	19-36	4	1-35	7	<1-805	5	<1-6401
Fe (%)	0.90	0.23-1.59	0.51	0.12-2.00	0.26	0.01-2.07	0.56	<0.01-5.06	0.50	<0.01-9.57
Hg (ppm)	0.32	0.03-1.10	0.16	0.01-0.83	0.03	0.02-0.62	0.08	<0.05-4.00	<0.05	<0.05-7.55
Mg (%)	0.08	0.02-0.17	0.06	0.01-1.63	-	-	0.06	<0.01-4.90	0.06	<0.01-4.90
Mn (ppm)	351	19-2477	326	16-3032	293	10-2700	186	2-7,000	173	<1-24270
Ni (ppm)	7	1-15	3	<1-12	5	1-46	4	<1-89	4	<1-146
P (%)	0.044	0.014-0.068	0.026	0.007-0.074	-	-	0.027	<0.005-0.476	0.033	<0.005-1.613
pH	4.5	3.7-5.6	5.5	3.8-8.1	5.7	3.6-7.7	6.2	2.2-9.7	5.9	2.1-9.7
Pb (ppm)	69	15-310	48	5-211	41	10-510	53	<3-16,972	16	<3-16972
S (%)	0.043	0.007-0.116	0.025	<0.005-0.128	-	-	0.015	<0.005-0.516	0.012	<0.005-3.263
Sr (ppm)	8	4-14	6	2-25	-	-	10	<1-708	8	<1-1298
Ti (ppm)	135	58-420	104	55-199	-	-	27	1-396	26	<1-1542
V (ppm)	17	5-27	8	1-36	-	-	8	<1-94	6	<1-266
Y (ppm)	4	3-8	2	<1-11	-	-	-	-	2	<0.5-62
Zn (ppm)	60	12-109	43	8-123	72	10-390	121	5-87,500	40	<1-91110

Note: soil samples for geochemical atlases (L. Lenartowicz, 1994; J. Lis, A. Pasieczna, 1995b,c) were digested with dilute HCl (1:4) prior to analysis

Table 6

Chemical and sulphur isotope analyses of spring waters from HCMNP

No.	Location	Al mg/l	Alkalinity mval/l	Ba mg/l	Ca mg/l	Cd mg/l	Cl mg/l	Conduct mS/cm	Cr mg/l	Fe mg/l	K mg/l	HCO_3 mg/l
1	I - Psarska Mt.	0.25	0.00	0.093	22.4	<0.002	8.48	0.2550	<0.01	0.087	1.6	0.0
2	IV - Święta Katarzyna	<0.04	0.03	0.011	5.6	<0.002	3.45	0.0764	<0.01	0.008	0.5	1.8
3	VII - Święty Krzyż Mt.	2.51	0.00	0.087	10.1	0.005	4.59	0.1700	<0.01	0.020	2.6	0.0

Table 6 continued

No.	Mg mg/l	Mn mg/l	Na mg/l	Ni mg/l	NH_4 mg/l	NO_3 mg/l	Pb mg/l	pH	$\delta^{34}S$ ‰	SiO_2 mg/l	SO_4 mg/l	Sr mg/l	Ti mg/l	TOC mg/l	V mg/l	Zn mg/l
1	6.07	0.320	4.3	0.05	0.07	14.1	<0.02	4.41	3.7	13.3	69.30	0.080	0.005	4.22	<0.01	0.049
2	1.66	0.007	1.9	<0.01	0.08	15.0	<0.02	5.18	5.5	7.6	3.82	0.013	<0.005	1.88	<0.01	0.016
3	1.71	0.856	1.8	0.01	0.07	14.9	<0.02	3.99	4.2	6.4	39.80	0.039	0.007	4.06	0.01	0.234

cations and anions is low varying from 33.280 to 126.350 mg/l. The $\delta^{34}S$ of these waters ranges from 3.67 to 5.50‰ and is similar to that reported for rainfalls from the area of Lublin (4.0–4.5‰)[3], which indicates their rapid circulation in the bedrock. The water from spring on Święty Krzyż Mt. (VII) contains somewhat higher concentrations of Cd (0.005 mg/l), Mn (0.856 mg/l) and Zn (0.234 mg/l), which exceeds several times those from the remaining springs. The high content of Cd, Mn and Zn is also observed here in soils, lichens and mosses. The waters described are acidic; pH varies from 3.99 (Święty Krzyż Mt.) to 5.18 (Święta Katarzyna).

Lichens are the best bioindicators of air pollution because they take up many nutrient elements, as well as sulphur and heavy metals. In the region, the only species present in adequate amounts for chemical and isotopic determinations, is *Hypogymnia physodes* (Tab. 4). The total sulphur concentration in the examined species varied from 0.091 to 0.128%, being higher than that in *H. physodes* from rural areas of Finland (below 0.07%) and *H. entomorpha* (0.006–0.064%) from Redwood National Park, California (L. P. Gough *et al.*, 1988*a*), and similar to that in *H. physodes* from areas around industrial facilities of southern Finland (0.085–0.283%) (S. Manninen *et al.*, 1991) and in *Parmelia sulcata* (0.092–0.170%) from Theodore Roosevelt National Park, North Dakota (L. P. Gough *et al.*, 1988*b*). The examined lichen flora from the Holy Cross Mts. region contains raised levels of Cd, La, Li, and somewhat Hg, Pb and Ti compared to those in the national parks mentioned above.

In the study region, *H. physodes* growing on a bark of different tree species reveals a diverse chemical composition even within the same site. Lichens that grow on deciduous trees show the raised content of Ba, Ca, Mn, Sr, Y, Yb, light sulphur isotope, and in some places K and Pb, as well as the decreased level of Hg, Fe and S compared to those on

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[3] S. Hałas (pers. comm.).

coniferous trees. The largest difference in the concentrations of many of these elements is noted between lichens growing on oak- and pine-trees (Tab. 7).

The total sulphur content in one (1994)- and two (1993)-year *Pinus sylvestris* pine needles from the Holy Cross Mts. is 0.065–0.081% resembling that in *P. sylvestris* pine needles from rural areas of Finland (0.053–0.092%) and in *Picea glauca* needles from the Kenai National Wildlife Refuge, Alaska (0.05–0.10%) (J. G. Crock *et al.*, 1992). *P. sylvestris* pine needles from areas around industrial facilities of southern Finland contain more sulphur (0.070–0.227%) (S. Manninen *et al.*, 1991). Nearly the same content of sulphur is observed in moss species *Hylocomium splendens*: 0.085% (Holy Cross Mts.) relative to 0.05–0.10% (KNWR).

The investigation of two- and one-year pine needles have enabled detection of fluctuations in the element pattern with time. Two-year pine needles show the raised levels of Ba, Ca, Hg, Mn, Pb, Sr, Ti, and Zn, and the decreased content of Cu, K, Ni, P and heavy S isotope and somewhat S relative to one-year pine needles. This trend was recorded on needles derived from individual pine-trees (sites G/1 and II). Moreover, it was also confirmed by the geometric mean values for pine needles from HCM and HCMNP (Tab. 3).

In addition, a diverse element uptake has been noted in the examined plants. For instance: Al, As, Ba, Cr, Fe, Hg, La, Li, Pb, Ti, Y and Yb, and somewhat S tend to concentrate in lichens and mosses,whereas Mg and Ni, and somewhat Mn and P in pine needles. Of these elements, Ti shows the highest level in lichens.

CONCLUSIONS

The preliminary results of biogeochemical investigation performed on soils, lichens, mosses, pine needles, and industrial dusts and feedstock enable drawing the following conclusions:

1. Some elements (As, Cd, Hg, Mn, Pb, S and Zn, and somewhat Cu) show raised concentrations in topsoil relative to subsoil. The concentration ratio of sulphur between these two media exceeds 20. The element spatial distribution pattern indicates that the western and the northern (highest) parts of the region are more polluted (Tabs. 1 and 2). The geometric mean values of most elements (especially As, Cu, Hg, Mn, S and Ti) in topsoil are higher than those determined for Poland or even for the highly industrialized Upper Silesian district (Tab. 5).

2. Lichens, mosses, and one- and two-year pine needles reveal nearly the same sulphur stable isotope distribution pattern (Z. M. Migaszewski, 1996). Compared to pine needles, lichens growing on a pine bark are slightly enriched in heavy sulphur isotope (Fig. 2). The $\delta^{34}S$ varies from 3.2 to 5.4‰ and reflects the mean value (2.5‰) for continental plants from the area of the former Soviet Union (F. V. Chukhrov *et al.*, 1980). This fact indicates that mixed local and imported SO_2 emissions (see wind rose in Figure 1) undergo rapid homogenization. However, the lack of any sulphur isotope data from flora of Poland precludes a detailed comparison.

3. All the examined flora contains a considerable amount of sulphur (Tabs. 3 and 4). Lichens show raised concentrations of Cd, La, Li, and somewhat Hg, Pb and Ti compared to those in other areas of the U.S.A. and Central Europe. One (1994)- versus two (1993)-year

Table 7

Trace element and sulphur stable isotope content in lichnes from deciduous vs coniferous trees (after Z. M. Migaszewski, 1996)

Sample symbol	As ppm	Ba ppm	Ca %	Cd ppm	Cu ppm	Fe %	Hg ppm	K %	La ppm	Mn ppm	P %	Pb ppm	S %	$\delta^{34}S$ ‰	Sr ppm	Ti ppm	Y ppm	Yb ppm	Zn ppm
C-birch	2	40	0.19	0.8	7	0.08	0.17	0.30	0.7	144	0.179	25	0.080	3.4	5	18	0.6	0.04	71
C-pine	-	18	0.08	1.0	7	0.09	-	0.22	-	53	-	16	-	4.5	3	-	-	-	170
F/1-birch	<2	13	0.49	0.8	6	0.05	0.13	0.30	0.8	108	0.087	33	0.058	4.7	5	15	0.7	0.04	138
F/1-pine	.3	8	0.15	0.9	8	0.09	0.17	0.23	0.6	38	0.067	14	0.094	4.8	3	19	0.4	0.02	98
I-oak	3	55	0.51	0.6	10	0.10	0.23	0.33	1.0	230	0.129	23	0.095	4.7	4	30	0.7	0.05	93
I-pine	3	10	0.10	0.9	8	0.10	0.24	0.24	0.6	51	0.083	18	0.097	4.9	3	28	0.4	0.04	100
II-oak	3	92	2.24	1.3	11	0.06	0.19	0.25	0.6	525	0.092	16	0.094	3.2	12	18	0.6	0.05	66
II-pine	3	11	0.25	1.1	10	0.09	0.21	0.26	0.6	76	0.080	18	0.098	5.0	4	26	0.5	0.04	108
IV-rowan	4	43	1.22	1.1	11	0.15	0.27	0.23	1.9	95	0.078	99	0.092	3.9	13	44	1.5	0.11	133
IV-spruce	5	25	0.20	0.9	12	0.23	0.33	0.20	1.0	66	0.085	39	0.119	4.2	5	46	0.6	0.06	113
VII-rowan	5	59	0.66	0.7	11	0.25	-	0.23	1.9	97	0.083	83	0.112	4.6	9	70	1.2	0.10	145
VII-spruce	5	30	0.11	0.9	13	0.26	0.27	0.19	1.3	44	0.079	48	0.128	4.8	4	73	0.7	0.07	120

Table 8

Chemical analyses of some industrial material from major production facilities of the region

Nos. Fig. 1	Ba ppm	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	Hg ppm	La ppm	Li ppm	Mn ppm	Ni ppm	Pb ppm	S %	Ti ppm	V ppm	U ppm	Y ppm	Yb ppm	Zn ppm
1(a)	34	3.1	5	26	27	0.81	0.10	8	13	221	18	94	0.509	87	50	0.2	10	0.8	100
1(b)	147	1.4	8	84	39	1.48	0.04	16	30	304	30	49	1.110	925	110	1.2	17	1.5	136
2 (a)	2	1.7	<1	3	2	0.06	0.01	2	3	77	<1	26	0.008	<10	30	0.1	3	0.3	45
2 (b)	49	1.2	2	13	8	0.28	0.01	4	7	108	5	8	0.171	152	50	-	6	0.8	76
3	30	17.4	1	36	27	0.88	0.10	8	16	130	12	418	0.575	73	40	0.3	7	0.6	273
4	2	0.4	1	6	<1	0.06	0.02	1	4	23	3	<1	0.024	<10	20	0.2	2	0.2	11
5a	323	0.6	17	44	258	3.22	0.10	16	55	569	45	34	0.429	580	90	13.5	16	1.4	103
5b	132	0.3	8	25	80	0.71	0.02	10	21	161	24	16	0.433	107	30	6.4	10	0.9	54
6	112	1.6	22	39	126	4.00	0.06	23	46	751	44	134	0.748	1330	90	14.3	22	1.9	370
7a	126	157.0	23	2760	1660	37.4	-	1	31	41600	518	9530	0.668	90	80	-	1	0.6	28600
7b	100	1320.0	20	1330	2390	26.4	-	1	32	19900	197	4220	0.767	366	50	-	1	0.6	228000

1 — Nowiny Cement Plant (a — stack dust, b — cement), 2 — Trzuskawica Lime Plant (a — limestone dust, b — lime dust), 3 — Małogoszcz Cement Plant (cement), 4 — Bukowa Lime Plant (stack dust), 5 — Kielce Heat Generating Plant (a — stack dust, b — hard coal), 6 — Ostrowiec Steelworks — heat generating plant (cyclone dust), 7 — Ostrowiec Steelworks: a — medium furnaces (ore dust), b — heavy furnaces (extractor dust); for detailed location see Figure 1C

pine needles revealed different concentrations of some elements. These differences may have resulted from combined element fixation during a 1993–1994 period, and changes in concentrations of certain elements in the air, i.e., an increase of Cu, K, Ni, P, S, and heavy sulphur isotope in 1994. A more detailed study concerning trace element, sulphur and sulphur stable isotope distribution pattern in lichens, and one-, two- and three-year pine needles is in progress.

4. The diverse content of elements in lichens collected from different tree species indicates that the chemical composition of a tree bark plays an important role, too (Tab. 7).

5. Some trace elements accumulated in excessive amounts, both in soils and plants, bring about disorders of very important vital organs and DNA structure, enzymatic disturbances and paralysis of the nervous system in many animals that live within a polluted area (A. Kabata-Pendias, H. Pendias, 1993). In the region some trace elements locally exceeded allowable limits for soils and plants given by A. Kabata-Pendias, H. Pendias:

— soils: As (>20 ppm) and Pb (>100 ppm),
— lichens: Cd (0.05–0.5 ppm), Hg (>0.05 ppm), Pb (30–300 ppm) and Zn (>100 ppm),
— mosses: Cd (0.05 ppm), Hg (>0.05 ppm) and Pb (30–300 ppm),
— pine needles: Cd (0.05–0.5 ppm) and Mn (400–1000 ppm).

The combined toxic content of these and other unspecified elements in plants explains various disorders observed in animals from HCMNP.

6. The investigation is ongoing, but the preliminary results of chemical analyses performed on soils, vegetation, stack dusts and feedstock seem to show the potential detrimental impact of some local industrial facilities on the natural environment of the Holy Cross Mts. (Tab. 8). This inference is also supported by the positive correlation between many elements in natural media and industrial material. The potential pollution sources are: the Ostrowiec Steelworks that affects especially northeastern part of the region (topsoil enriched in Cd, Cr, Cu, Fe, La, Mn, Ni, Pb, S, Ti and Zn, "lichen desert", scarce pine-trees, pine needles covered with industrial dust and fungi), as well as the Kielce Heat Generating Plant, and somewhat the Małogoszcz and Nowiny Cement Plants. The industrial dusts expelled into the air contain raised concentrations of many elements (Tab. 8). The high content of uranium in dusts derived from the Kielce and Ostrowiec heat generating plants (up to 14.3 ppm) is a concern. It may reflect a locally high concentration of this element in soils (Łysica Mt. — as much as 8.8 ppm). This problem, however, should be resolved by ongoing investigation. It is hard to assess the impact of pollution coming from the south and southwest, i. e., from the highly industrialized Upper Silesian-Cracovian area. It seems to play an important role here. Another inscrutable source of pollution is numerous small coal-fired household furnaces and industrial facilities with no dust filters or dust collectors. Their potential in the total regional pollution pattern seems to be great enough.

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PIERWIASTKI ŚLADOWE I STABILNE IZOTOPY SIARKI W GLEBACH I W ROŚLINNOŚCI GÓR ŚWIĘTOKRZYSKICH

Streszczenie

Wyniki oznaczeń pierwiastków śladowych i stabilnych izotopów siarki, wykonanych na glebach, porostach (*Hypogymnia physodes*), mchach, jednorocznych (1994) i dwuletnich (1993) igłach sosny (*Pinus sylvestris*), wodach ze źródeł oraz materiale przemysłowym z regionu Gór Świętokrzyskich (fig. 1, tab. 1–4, 6, 8), wskazały na podwyższoną koncentrację wielu pierwiastków. O antropogenicznym pochodzeniu zarejestrowanych zanieczyszczeń świadczy również pośrednio zbliżony skład izotopowy siarki w glebach, roślinności i pyłach przemysłowych (fig. 2).

Analizy chemiczne ujawniły wzrost zawartości As (do 41 ppm), Cd (do 1,8 ppm), Hg (do 1,10 ppm), Mn (do 3020 ppm), Pb (do 310 ppm), S (do 0,128%), Zn (do 123 ppm) i częściowo Cu (do 36 ppm) w najwyższym poziomie glebowym (A_1) (tab. 1 i 2). Stosunek koncentracji siarki między wymienionym poziomem a poziomem podścielającym (na ogół B lub (B)) przekracza niekiedy 20 (0,128 i 0,006% na Górze Wierzejskiej — stanowisko C/1). Średnie geometryczne zawartości wielu pierwiastków (szczególnie As, Cu, Hg, Mn, S i Ti) w poziomie glebowym A_1 są wyższe w Górach Świętokrzyskich i Świętokrzyskim Parku Narodowym niż na obszarze Polski, a nawet Górnego Śląska (tab. 5). Podobnie, maksymalne koncentracje Cr, Hg, La, Mn, Pb, S, Ti, V i Zn zanotowano w najwyższych partiach Gór Świętokrzyskich.

Wysokie zawartości wielu pierwiastków zaobserwowano również w roślinności (tab. 3 i 4). Porosty, będące klasycznym bioindykatorem, były na ogół wzbogacone w Cd, La, Li, Pb, S oraz częściowo w Hg, Pb i Ti w porównaniu z innymi obszarami USA i Europy Środkowej. Zwraca tu uwagę również wysoka zawartość siarki (do 0,128%). *Hypogymnia physodes* rosnąca na korze drzew liściastych zawierała podwyższoną zawartość Ba, Ca, Mn, Sr, Y, Yb, lżejszego izotopu siarki, niekiedy K i Pb oraz niższą zawartość Hg, Fe i S niż odpowiednio na korze drzew szpilkowych (tab.7). Dwuletnie (1993) igły sosny wykazywały wyższą koncentrację Ba, Ca, Hg, Mn, Pb, Sr, Ti, Zn i lżejszego izotopu siarki w porównaniu z igłami jednorocznymi (1994).

Niektóre z lokalnych zakładów przemysłowych (np.: Huta Ostrowiec, cementownie Nowiny i Małogoszcz) stanowią potencjalne źródło zanieczyszczeń w regionie (tab. 8).

Prowadzone badania, mające na celu uchwycenie fluktuacji zawartości pierwiastków śladowych w poszczególnych mediach, kontynuowane są w ramach dwuletniego monitoringu środowiska naturalnego na obszarze Gór Świętokrzyskich.