Environment Protection Engineering

Vol. 17 1991 No. 3–4

EWA PANEK*

HEAVY METALS IN THE SOIL AND BED-ROCK OF THE BABIA GÓRA NATIONAL PARK

Iron, manganese, zinc, copper, cadmium, lead, nickel and chromium contents in soil and bedrock on four height-plant levels in the Babia Góra National Park were studied. Lead, copper and chromium contents are very low in bedrock, whereas matrix rock is the natural source of the rest of the metals in the environment. Considerable enrichment of soil in lead, cadmium, zinc and copper in comparison with bedrock was found. Concentrations of the above-mentioned metals declined together with soil profile depth. There was also a significant differentiation in content of these metals in organic soil horizone which was dependent on localization, i.e. height-plant level.

1. INTRODUCTION

We witness a progressing deterioration of the natural environment in our country. Almost the whole territory of Poland is affected by industrial emissions. This refers particularly to southern Poland where the unique national parks are located [4], [9], [11]. Concentration of heavy metals is widely applied as the index of chemical pollution of the environment.

The present investigation aims at the characteristics of the anthropogenic impact exerted by the atmospheric immision on the natural environment of the protected mountainous areas in southern Poland. The paper takes into account heavy metals emitted by plants in considerable quantities or doing serious harm to the environment because of their toxicity. The investigations are based on the determination of the levels of chromium, zinc, cadmium, manganese, copper, nickel, lead and iron in the soil and bed-rock.

2. MATERIAL AND METHODS

The Babia Góra massif is characterized by a unique location under Polish conditions. Babia Góra is an isolated peak of a significant altitude (1725 m above sea

* Polish Academy of Sciences, Minerals and Energy Economy Research Centre, ul. Wybickiego 7, 31-261 Kraków, Poland.

level) as well as relative altitude (about 1000 m), located far from big industrial and urban centres. The part of the massif under study is characterized by geologically uniform bed-rock composed in the top parts and along the ridge of the Magura sandstone formations.

The investigations are concentrated only on the part of the Babia Góra National Park spreading along the eastern ridge of the massif between the Krowiarki pass and the summit of Babia Góra. It was a belt 6 km long and 500 m wide and the height difference was 800 m. The areas where samples of soil and plants were taken were located in four height-plant stands as follows: the stand of lower subalpine forest (altitude about 900 m above sea level), upper subalpine forest (1400 m above sea level), dwarf mountain pine (1500–1600 m above sea level) and the alpine stand (about 1700 m above sea level). These areas were found on both sides of the ridge and differed in the slope exposure. On a relatively small area there were a considerable variety of soil-forming factors as well as soils [1].

For the needs of the investigations eighteen soil pits were made, out of which 13 represented podzolic soils, podzols, podzolic rankers and the other 5 were brown and acid brown soils. The soil samples from the pits marked with numbers 1–13 were taken in the particular genetic levels. The samples from the other five soil pits were taken from the following depths: 0–2, 2–4, 4–6, 6–8, 8–10, 10–12, 12–17, 17–22, 27–32 cm, and in these pits bed-rock samples were not taken. From 13 pits 27 samples of the bed-rock material were taken. In each pit the bed-rock samples were taken as 1–4 rock fragments, according to the macroscopic differentiation of sandstone, including the colour, grain size and the weathering degree.

The air-dry, broken-up rock and soil material (after separating of the skeletal part of the soil) was ground in an agate mortar. 1g samples with 10 cm^3 of 60% $HClO_4$ were heated in Kjeldahl's flasks. After complete burning the contents of the flasks were diluted up to the volume of 25 cm^3 and passed through a hard filter. In the filtrate the content of selected heavy metals was determined by the method of absorptive atomic spectroscopy.

3. RESULTS AND DISCUSSION

The results of chemical analysis of 91 soil samples are presented in table 1.

In the organic soil levels and in the mineral levels of Babia Góra, the concentrations of iron ranges within 2300–19800 ppm (6700 on average) and 6100–21700 (13700 on average), respectively. The content of manganese amounted to 13–209 ppm (62 on average) in organic levels and 5–655 ppm (168 on average) in mineral levels. The content of zinc in the surface levels of the soil was close to its natural concentration in the upper level, i.e. to 23–174 ppm (58 on average), whereas its concentration in the mineral levels was 35 ppm on average. The maximum content of copper found in organic levels was 6.6 ppm on average and ranged from 2 to 34 ppm. In mineral soil levels the content of copper was between 1–20 ppm (4.8 on average).

Table

The content of heavy metals in soils of Babia Góra National Park

Mountain zone and height above sea level (m)	Profile no.	Genetic horizon	Depth (cm)	Heavy metal content ($m \cdot kg^{-1}$)							
				Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr
1	2	3	4	5	6	7	8	9	10	11	12
Alpine belt 1700	4	A_d	0–4	5400	52	23	2	40	0.7	7	158
		A_2	4–14	2900	37	traces	1	3	0.2	4	145
		B_h	14–22	13500	80	5	4	5	0.2	12	64
		B_s	22–42	15000	283	158	6	13	traces	30	74
		C	below 42	21700	354	57	4	6	0.2	60	30
	5	A_d	0–4	3100	29	36	4	64	0.4	5	121
		A_{1+2}	4–14	10300	83	3	4	20	0.3	13	65
		B_{h+s}	14–44	18500	389	41	4	30	0.1	33	82
		C	below 44	13700	566	46	6	8	0.2	42	77
	6	A_d	0–5	4100	20	62	5	117	1.2	5	50
		A_{1+2}	5–15	2700	20	26	1	14	0.3	3	111
		B_{h+s}	15–35	38800	162	26	9	12	0.6	41	79
		C	below 35	14100	382	36	4	8	0.3	35	74
Subalpine belt 1550	7	A_{LP+H}	0–8	2600	13	174	6	162	3.7	5	13
		A_2	8–18	1800	20	34	traces	122	0.4	4	143
		B_h	18–23	5000	31	51	3	142	0.5	7	114
		B_s	23–53	22600	140	53	8	8	0.6	33	122
		C	below 53	14500	303	45	5	5	0.4	35	45
	7A	$A_L A_d$	0–2	4800	73	76	13	231	1.3	7	45
		A_{FH}	2–4	3500	30	32	9	161	1.3	6	56
		A_{FH}	4–6	2500	25	21	6	105	1.3	6	49
		A_{FH}	6–8	3000	33	30	7	161	1.2	4	58
		A_{1+2}	8–10	traces	23	18	3	86	0.4	5	75
		A_{1+2}	10–12	2300	17	10	2	46	0.3	4	30
		B_s	12–17	3500	35	13	2	31	0.2	5	25
		B_s	17–22	4900	73	13	2	25	0.3	4	100
		B_s	22–27	7900	84	16	2	19	0.2	12	71
		B_s	27–32	20700	237	28	4	19	0.3	36	55
	8	A_{LF+H}	0–7	3400	17	56	6	222	0.9	4	76
		A/C	7–37	4300	23	29	2	47	0.3	4	103
		C	below 37	12300	209	34	4	11	0.2	18	83
	9	A_{LF+H}	0–10	3600	20	156	10	346	6.1	6	15
		A_2	10–30	1000	9	30	traces	9	0.2	2	77
		B_h	30–45	15200	47	36	3	20	0.4	14	56
		B_s	45–65	22000	121	60	7	16	0.4	28	98
		C	below 65	15600	253	37	9	4	0.2	49	73

1	2	3	4	5	6	7	8	9	10	11	12
Subalpine belt 1550	9A	A_LA_d	0–2	2300	82	135	19	293	2.9	9	33
		A_{F+H}	2–4	2500	20	47	9	126	2.1	3	48
		A_{F+H}	4–6	2300	15	28	6	119	2.0	1	88
		A_{1+1}	6–8	2500	10	43	5	173	1.9	2	13
		B_h	8–10	2200	16	40	4	142	1.8	3	41
		B_h	10–12	1900	9	21	2	37	0.7	3	34
		B_h	12–17	2700	5	15	2	28	0.5	1	125
		B_h	17–22	2000	20	12	2	18	0.5	traces	93
		B_h	22–27	1900	13	10	2	17	0.4	3	33
		B_h	27–32	2000	14	10	2	14	0.4	4	94
	13	A_{LF+H}	0–8	3600	103	97	11	225	3.6	3	36
		A_{1+2}	8–25	2500	36	24	2	80	0.8	1	125
		A/C	25–30	5200	40	8	2	23	0.5	6	117
		C	below 30	15300	103	24	5	11	0.3	25	61
	13A	A_LA_d	0–2	3300	64	87	21	280	2.2	10	20
		A_{F+H}	2–4	22600	107	94	34	293	3.8	13	30
		A_{1+2}	4–6	4800	31	32	9	155	1.2	6	67
		A_{1+2}	6–8	4400	20	10	3	70	0.9	6	70
		A_{1+2}	8–10	4300	16	18	3	61	1.0	6	52
		B_{h+s}	10–12	5800	32	15	3	29	0.9	6	84
		B_{h+s}	12–17	7100	9	10	2	28	0.5	1	71
		B_{h+s}	17–22	5100	31	11	3	23	0.7	8	35
		B_{h+s}	22–27	7200	41	14	2	17	0.5	8	84
		B_{h+s}	27–32	7100	30	11	1	14	0.3	6	115
Upper mountain zone 1400	1	A_{LF+H}	0–4	6900	49	51	7	84	1.1	8	153
		A_{1+2}	4–12	8500	38	1	2	8	0.2	4	220
		B_s	12–40	18100	40	14	6	2	0.2	33	130
		C	below 40	20000	145	70	8	5	0.4	75	42
	2	A_{LF+H}	0–10	2500	38	54	5	79	2.0	4	150
		A_{1+2}	10–30	2500	28	23	3	2	0.4	3	197
		C	below 30	10000	195	48	4	8	0.2	20	83
	3	A_{LF+H}	0–8	19800	100	83	6	29	1.1	3	122
		A_{1+2}	8–15	2000	28	traces	2	4	0.3	3	204
		C	below 15	7400	104	25	4	6	0.3	10	45
Lower mountain zone 950	10	A_{OL}	0–5	10300	173	77	6	42	0.5	18	110
		A_1	5–7	11900	122	79	6	34	0.6	17	61
		(B)	7–48	16100	655	67	6	15	0.4	22	49
		C	below 48	15300	357	41	6	5	0.2	37	53
	10A	A_{OL}	0–2	9500	157	28	4	35	1.1	11	88
		A_1	2–4	10800	112	27	4	28	0.5	11	51
		(B)	4–6	15900	139	28	6	20	0.5	15	61
Lower mountain zone 950	10A	(B)	6–8	15100	76	19	3	20	0.5	8	47
		(B)	8–10	17100	79	18	3	28	0.5	10	87
		(B)	10–12	18100	134	20	4	16	0.4	9	60
		(B)	12–17	20200	154	24	4	10	0.3	10	79

1	2	3	4	5	6	7	8	9	10	11	12
Lower mountain zone 950		(B)	17–22	17000	206	26	5	17	0.6	12	89
		(B)	22–27	19700	164	26	4	8	0.5	14	37
		(B)	27–32	17800	196	38	4	20	0.5	20	65
	11	A_{OL}	0–5	10400	53	101	10	88	0.5	13	66
		A_{1+2}	5–13	7200	65	55	4	20	0.1	12	53
		B_{h+2}	13–20	8600	49	46	6	45	0.3	8	47
		B_{h+2}	20–45	9500	65	44	5	22	0.2	8	53
		B_{h+2}	45–50	1400	5	25	traces	16	0.3	8	43
		C	below 50	6100	76	27	1	4	0.1	10	119
	12	A_{OL}	0–10	15100	209	27	14	199	1.3	25	97
		A_{1+2}	10–12	11300	150	123	6	56	0.5	12	37
		(B)	12–37	32300	532	39	20	36	0.6	57	59
		C	below 37	15700	585	43	6	8	0.2	31	36
	12A	A_{OL}	0–2	8200	104	118	21	257	1.0	10	26
		A_{F+H}	2–4	7800	59	110	16	275	1.6	11	36
		A_{F+H}	4–6	15700	89	119	16	262	2.6	14	63
		A_1	6–8	10700	40	59	11	85	1.6	7	52
		A_1	8–10	9800	47	28	7	55	1.0	11	44
		(B)	10–12	21600	179	34	9	56	0.9	21	66
		(B)	12–17	22500	362	39	11	28	0.8	28	51
		(B)	17–22	15000	422	32	9	15	0.9	34	47
		(B)	22–27	15600	479	47	9	16	0.8	37	47
		(B)	27–32	20800	483	55	11	20	0.8	41	45

KABATA-PENDIAS and PENDIAS [6] take 20 ppm Pb as the average concentration of lead in non-polluted loamy soils, while CONNOR and SHACKLETTE [3] take the value of 18.7 ppm Pb as its average content in non-polluted soils in USA. In comparison with these data, the concentrations of lead in the surface soil levels of Babia Góra were usually very high and in the organic levels they were ranged from 29 to 346 ppm (105.5 ppm on average). It was at least twice as high as the lead content in the mineral levels, i.e. 2–142 ppm (24 on average). The content of cadmium in the surface soil levels of Babia Góra is low and is usually within the values accepted as normal. Nevertheless, in some cases in the surface levels the content of cadmium was a few ppm, i.e. 0.4–6.1 ppm (1.3 on average). In the mineral soil level cadmium appeared in trace amounts, up to 1.8 ppm (0.4 ppm on average). The content of nickel ranged between 1 and 25 ppm in the organic levels and from trace up to 57 ppm in mineral levels. These amounts are close to those given by KABATA-PENDIAS and PENDIAS [6] for natural soils of Poland. The content of chromium in soil is related to its level in the matrix. Chromium in Polish soils formed out of sedimentary rocks is estimated as 29–60 ppm. These amounts are lower or close to those found in the soils of Babia Góra. In the organic levels, chromium was between 20 and 158 ppm (85.3 on average) and in the mineral levels, between 34 and 130 ppm (92.8 on average).

To sum up, it should be stated that the concentrations of lead and cadmium in the surface soil levels of Babia Góra exceeded their natural levels, whereas in the case of zinc, copper and chromium they approached the upper level of the natural content typical of non-polluted areas [3], [5], [6], [8].

The data concerning the content of heavy metals on the areas in the neighbourhood of the Babia Góra massif, i.e. Beskid Żywiecki [9], [11] as well as Beskid Śląski and Gorce [9], do not differ from the data gathered in the course of the present investigations, although in some cases they are a little higher. The maximum content of copper in the soils of Beskid Żywiecki formed on the basis of the Magura sandstone is 94 ppm in the surface levels and 65 ppm in deeper levels, while in the Babia Góra soils it is 34 and 20 ppm, respectively. The above observations refer also to zinc, nickel and particularly to manganese; the concentrations of manganese in the soils of Beskid Żywiecki exceeds a few times the amounts in the respective depth levels of the Babia Góra soils. According to SZCZUBIAŁKA [11], the concentration of lead in the surface levels is within 45–780 ppm. Neglecting extremely high concentrations, it can be assumed that the content of lead in the soils of Beskid Żywiecki is similar to its content found in the soils of Babia Góra and is indicative of a very high surface accumulation.

The discussion is focussed on the distribution of the metals in question in the soil profiles, i.e. the changes in their concentrations with the depth as well as the spatial differentiation of heavy metal concentrations in surface soil levels on the area investigated.

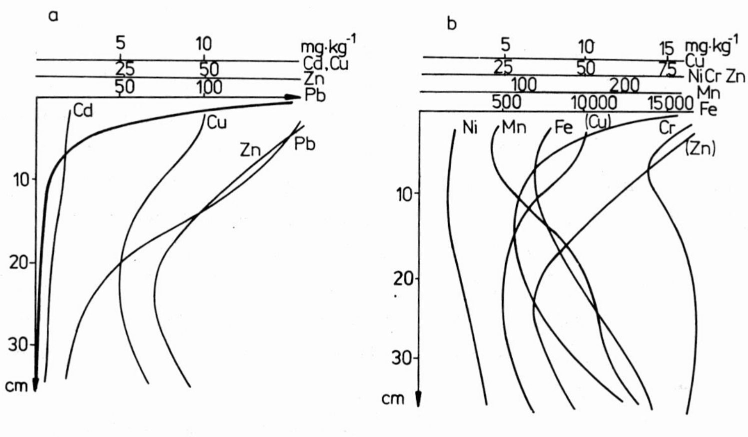

Fig. 1. Diagrams of the distribution of heavy metals in soil profiles: a – diagram in which surface enrichment with metals originating from the accumulation of atmospheric pollution is taken into account, b – diagram in which the main source of heavy metals in the soil is the matrix
— curves obtained on the basis of results of the present investigations, ▬ curves after MARTIN and COUGHTREY [10]

When investigating the changes in concentrations of heavy metals together with the soil depths, two typical diagrams of metal distribution [10] were taken as the basis. The first diagram (fig. 1a) reflects the surface enrichment of soil with a given metal as the result of air pollution, when the matrix does not contain this metal. The other diagram (fig. 1b) refers to a situation when the matrix itself is the carrier of the metal and is responsible for the surface enrichment of soil with this metal. On the basis of the results presented in this paper, the appropriate diagrams of changes in concentrations of the particular metals in soil profiles were made compared with the above diagrams. The distribution of non-ferrous metals corresponds to diagram 1a, which especially refers to lead and cadmium in the soils of Babia Góra, whereas the distribution of the concentration of iron, manganese and nickel complies with diagram 1b.

The differentiation of the particula heavy metal concentrations were analysed in organic levels of Babia Góra soils. The spatial differentiation of heavy metal concentrations in surface levels was presented in the diagrams illustrating the changes in concentrations together with the altitude. The diagrams were constructed on the basis of four heights of plant stands. The diagrams of the distributions of the particular heavy metal concentrations in the surface levels were almost identical (e.g. 2a). The concentrations of the above metals increase with the altitude, and reach their maxima on the upper border of the dwarf pine stand. The next diagram (fig. 2b) refers to this group of metals whose main source is the bedrock. The shape of this diagram is different compared with the previous one. The maximum concentrations of non-ferrous metals correspond with the minimum concentrations of the other metals.

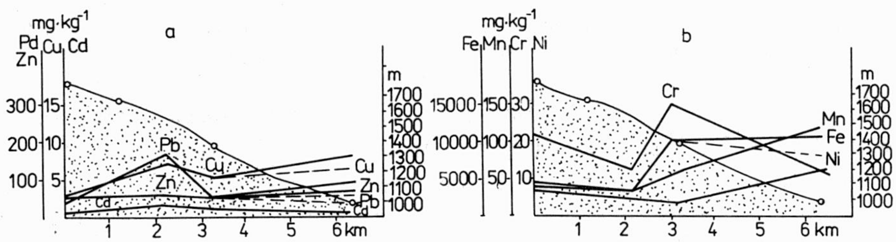

Fig. 2. Contents of heavy metals in organic levels of the Babia Góra soils within the particular height-plant stands: a – curve for Zn, Pb, Cu and Cd, b – curve for Fe, Mn, Ni and Cr —— curve of the metal concentrations representing all the samples, - - - curve of the metal concentrations without the samples taken in the immediate neighbourhood of the road

The examinations of the bed-rock represented by the Magura sandstone showed a relatively considerable homogeneity of the content of such metals as lead, copper or cadmium. Their contents were low (4–11 ppm Pb, 1–9 ppm Cu) and in the case of cadmium even close to the trace content (0.1–0.5 ppm). Such low concentrations imply that the bedrock is not the source of the above metals in soil. On the other hand, the matrix is the carrier of the other metals, i.e. iron (6100–21700 ppm), manganese (76–585 ppm), zinc (24–70 ppm), nickel (10–75 ppm) and chromium (30–83 ppm) (table). According to KORAB and DURKOVIC [7], considerable differences in the content of manganese may result from the differences in the content of the binder, mainly silty substance and rare pieces of foreign rocks in sandstone, containing minerals rich in this metal.

The bedrock on the area examined can be the carrier only of some of the metals in question and, having a uniform chemical composition of the metals analysed, it cannot be the factor which brings about the differentiation of the concentrations of these metals in soil.

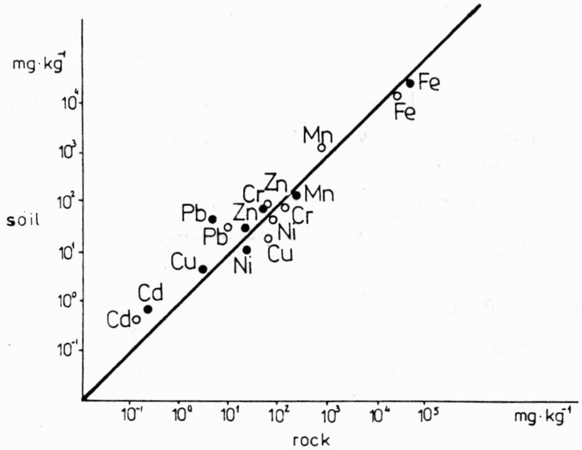

Fig. 3. Relations between the contents of the selected heavy metals in the soil and bedrock • – on the basis of own investigations, o – according to BOWEN [2]

In the present investigation of the relations between the heavy metal concentrations in the bedrock and soil, the diagram constructed by BOWEN [2] on the basis of the average concentrations of heavy metals in the earth's crust and in non-polluted soils was used. The values referring to the environment of Babia Góra were shown in this diagram (fig. 3). When analysing the diagram with reference to the Babia Góra National Park, we can conclude that in relation to the bedrock the soils are enriched with lead, cadmium, zinc, copper and chromium, while concentrations of nickel, manganese and iron are impoverished. One of the more significant differences between Babia Góra and a non-polluted area is a considerable increase in the concentration of lead in the soils of Babia Góra.

4. CONCLUSIONS

1. The contents of lead, copper and cadmium in the matrix are low and therefore the bedrock is not responsible for the accumulation of these metals in soil and plants. The bedrock is the natural source of iron, manganese, zinc, nickel and chromium.

2. In comparison with the bedrock, enrichment of soil with lead, cadmium, zinc and chromium as well as the impoverishment on nickel, and manganese were found. A significant accumulation of lead and, to a lesser degree, of zinc and cadmium took place in the surface soil levels.

3. The contents of heavy metals in surface soil levels differ considerably, depending on the location of the areas investigated. The maximum concentrations of lead, zinc, copper and cadmium were found in th: dwarf pine stand.

4. The results obtained are indicative of the pollution of the natural environment in the Babia Góra National Park with lead and also, to a lesser degree, with zinc and cadmium.

BIBLIOGRAPHY

[1] ADAMCZYK B., *Charakterystyka gleb Babiogórkiego Parku Narodowego,* [in:] *Park Narodowy na Babiej Górze. Przyroda i człowiek.* ZOPiN PAN, Studia Naturae, 29 (1983), 95–120.

[2] BOWEN H.M.J., *Environmental chemistry of the elements,* London Acad. Press, London 1979, quoted from [10].

[3] CONNOR J.J., SHACKLETTE H.T., *Background geochemistry of some rocks, plants and vegetables in the conterminous United States,* Geol. Survey Prof. Paper 574F (1975), pp. 168.

[4] GRODZIŃSKA K., *Zanieczyszczenie górskich parków narodowych metalami ciężkimi.* ZOP PAN, 43 (1980), 9–27.

[5] KABATA-PENDIAS A., PIOTROWSKA M., *Całkowite zawartości mikroelementów w glebach Polski,* Materiały IUNG, Puławy, 8 (1971), 7–47.

[6] KABATA-PENDIAS A., PENDIAS H., *Pierwiastki śladowe w środowisku biologicznym,* Wyd. Geolog., Warszawa 1979, pp. 299.

[7] KORAB T., DURKOVIC T., *Geologia dukielskiej jednotki (flys wyhodneho Slovenska).* Geol. Ustav. D. Stura. Bratislava 1978, pp. 194.

[8] LITYŃSKI T.H., JURKOWSKA, *Żyzność gleby a odżywianie się roślin.* PWN, Warszawa 1982, pp. 643.

[9] MACIASZEK W., *Mikroelementy* (Mn, Zn, Cu, B, Mo) *w glebach leśnych wytworzonych ze skał fliszu karpackiego.* Rocz. Gleb. 34 (1983).

[10] MARTIN M.H., COUGHTREY P.J., *Biological monitoring of heavy metal pollution. Land and air,* Applied Science Publishers, London, New York, 1982, pp. 475.

[11] SZCZUBIAŁKA Z., *Badania zawartości mikroelementów i niektórych metali ciężkich w glebach leśnych terenów górzystych przy użyciu analizy spektralnej,* Probl. Agrof., 12 (1974), 75–83.

The investigations were carried out at the Institute of Botany of the Polish Academy of Sciences in Cracow.

METALE CIĘŻKIE W GLEBIE I PODŁOŻU SKALNYM BABIOGÓRSKIEGO PARKU NARODOWEGO

Badano stężenia żelaza, manganu, cynku, miedzi, kadmu, ołowiu, niklu i chromu w glebie i podłożu skalnym w obrębie czterech pięter wysokościowo-roślinnych Babiogórskiego Parku Narodowego. Zawartości ołowiu, miedzi i kadmu w podłożu skalnym sa bardzo niskie, natomiast skała macierzysta jest naturalnym źródłem pozostałych metali ciężkich. Stwierdzono wyraźne wzbogacenie gleb w ołów, kadm, cynk i miedź względem podłoża skalnego. Koncentracje tych metali malały wraz z głębokością profilu glebowego. Zaobserwowano istotne zróżnicowanie koncentracji badanych czterech metali w poziomie organicznym gleby. Było ono uzależnione od lokalizacji stanowisk badawczych w czterech piętrach wysokościowo-roślinnych.

ТЯЖЕЛЫЕ МЕТАЛЛЫ В ПОЧВЕ И СКАЛЬНОМ ОСНОВАНИИ БАБИОГУРСКОГО ЗАПОВЕДНИКА

Исследованы концентрации железа, марганца, цинка, меди, кадмия, свинца, никеля и хрома в почве и скальном основании в пределах четырех высотно-растительных уровней Бабиогурского Заповедника. Содержания свинца, меди и кадмия в скальном основании очень малы, зато материнская порода является натуральным источником остальных тяжелых металлов. Было установлено резкое обогащение почвы свинцом, кадмием, цинком и медью по отношению к скальному основанию. Концентрации этих металлов уменьшались вместе с гчубиной профиля почвы. Наблюдалось существенное дифференцирование концентрации исследуемых четырех металлов на органическом уровне почвы. Оно зависимо от локализации испытательных стендов на четырех высотно-растительных уровнях.