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METAL CONTENT IN TERRICOLOUS MOSSES IN POLLUTED AREAS

Abstract. Four terricolous moss species *Brachythecium rivulare* B.S.G., *B. mildeanum* (Shimp.) Milde, *Ciriphyllum piliferum* (Hedw.) B.S.G., and *Rhytidiadelphus squarrosus* (Hedw.) Warnst. were analysed for Zn, Cd, Pb, Cu, Ni, Fe, and Zr content using atomic absorption spectrophotometry and X-ray fluorescent analysis. The moss samples were collected in parks of the city of St. Petersburg and its outskirts.

To compare the accumulation rate and contamination differences of moss species in the sampled areas, an accumulation coefficient, the ratio of the metal content in moss species from collection sites to that from the control plot (40 km away from St. Petersburg), was used. The general heavy metal pollution index as the sum of accumulation coefficients was also calculated.

In general, it can be concluded that the estimated concentrations of heavy metals in five sampled terricolous moss species reflect the contamination state on the study area even when the levels of Zn, Cd, Pb, Cu, and Ni are low in environment. The sampled terricolous moss species have a low value for biomonitoring Mn, Fe, and Zr pollution.

Key words: heavy metals, terricolous mosses.

Naturally occurring terricolous mosses and other bryophytes are used as bioindicators of regional and local air pollution with heavy metals (e. g., Rühling, Tyler, 1969, 1971, 1973; Groet, 1976; Скрипниченко et al., 1978; Grodzińska, 1978). These mosses have been valuable in estimating air pollution around industrial centres and local emission sources, as well as in cities (e.g., LeBlanc et al., 1974; Lötschert et al., 1975; Groet, 1976; Folkeson, 1981). In the present study the accumulation of eight heavy metals in four terrestrial moss species growing in the area affected by industrial emissions has been investigated.

Materials and Methods

The study was carried out in the parks of the city of St. Petersburg and its outskirts. Moss species were collected in the control background plot I located at 40 km from industrial emission sources and in plots II, III, IV, and V situated in a polluted area. The tree layer in the parks examined was dominated by the following deciduous and coniferous species: *Tilia cordata* Mill., *Betula pubescens* Ehrh., *Acer platanoides* L., *Quercus robur* L., *Picea abies* (L.) Karst., *P. pungens* Engelm., and *Pinus sylvestris* L.

Four moss species viz. *Brachythecium rivulare* B.S.G., *B. mildeanum* (Schimp.) Milde, *Ciriphyllum piliferum* (Hedw.) B.S.G., and *Rhytidiadelphus squarrosus* (Hedw.) Warnst. were sampled at open areas avoiding direct influence of tree cover as much as possible. Samples were picked in May 1979. Green portions of mosses were taken for analysis. The mosses were dried at 60 °C and extraneous material was carefully removed. Then the samples were washed shortly with cold ethanol and

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after desiccation in an air flow they were shaken repeatedly. This procedure reduced the contamination of the samples with mineral particles. The content of metals was determined by atomic absorption spectrophotometry (AAS Perkin-Elmer, model 303) and by an X-ray fluorescence analysis (spectrometer FRS-2, USSR) as was done in a previous study (Парибок et al., 1985).

Results and Discussion

The ash content and the concentrations of Zn, Cd, Pb, Cu, Ni, Fe, and Zr in the moss species from plots II, III, IV, and V were higher than those in the control plot I (Table). The concentration of zinc in mosses was great in plots III and V, that of lead especially in plot IV, cadmium in plots IV and V, copper and nickel in plot V. These differences among the plots reflected the impact of local emission sources. Iron and zirconium concentrations seem to be related with the general pollution in the site rather than a particular emission source. Manganese was the only metal to be found in rather similar concentrations in the mosses from contaminated plots II, III, IV, and V and from the control plot I.

Metal content in mosses, p.p.m. dry weight

Plots	Ash, %	Zn	Cd	Pb	Cu	Ni	Mn	Fe	Zr
				Brachythecium rivulare					
I	8.0	91	0.32	15.9	9.5	5.0	101	793	9.8
II	8.5	194	0.60	21.7	26.4	26.6	98	1020	14.2
III	10.1	275	0.61	31.3	33.5	31.3	103	1720	21.4
IV	11.2	251	0.78	42.6	47.0	25.1	118	2130	25.6
				Brachythecium mildeanum					
I	8.2	84	0.33	16.8	9.9	4.8	99	833	9.2
II	9.3	186	0.56	25.5	31.7	27.8	107	1180	13.4
III	10.1	269	0.61	33.3	34.3	30.2	111	1820	22.3
				Ciriphyllum piliferum					
I	8.3	90	0.33	18.3	9.2	5.5	144	995	11.8
II	8.0	177	0.52	23.7	28.7	32.9	128	1040	11.5
V	9.3	303	0.80	35.5	71.8	98.8	123	1490	16.7
				Rhytidiadelphus squarrosus					
I	7.0	78	0.31	21.7	10.5	4.4	139	838	9.8
II	10.7	165	0.62	35.6	32.8	28.8	122	1150	13.8
III	10.8	276	0.76	45.4	39.5	38.9	114	1730	21.8
IV	12.2	244	0.98	65.9	57.3	25.2	140	2320	23.8
V	9.9	316	0.99	49.4	94.8	132	143	2080	21.5

Species of the same genus *B. rivulare* and *B. mildeanum*, which have quite similar morphological features, accumulated equal quantities of the metals studied. In plots III, IV, and V the concentrations of Cd, Pb, Cu, and Ni were higher in *R. squarrosus* than in other species. This can be due to a denser sward formed by the moss in these plots that favoured the retention of particulate matter and solutes.

Heavy metal accumulation in moss species from the contaminated plots was characterized by the accumulation coefficient C_a calculated as the ratio of the metal content in mosses from plots II, III, IV, or V to that from the control plot I (Fig. 1). Similar species *B. rivulare* and *B. mildeanum* showed almost the same accumulation coefficient values for the eight metals analysed. Higher C_a values of Cu, Ni, Pb, Cd, and Zn were obtained for *R. squarrosus* especially from plot V.

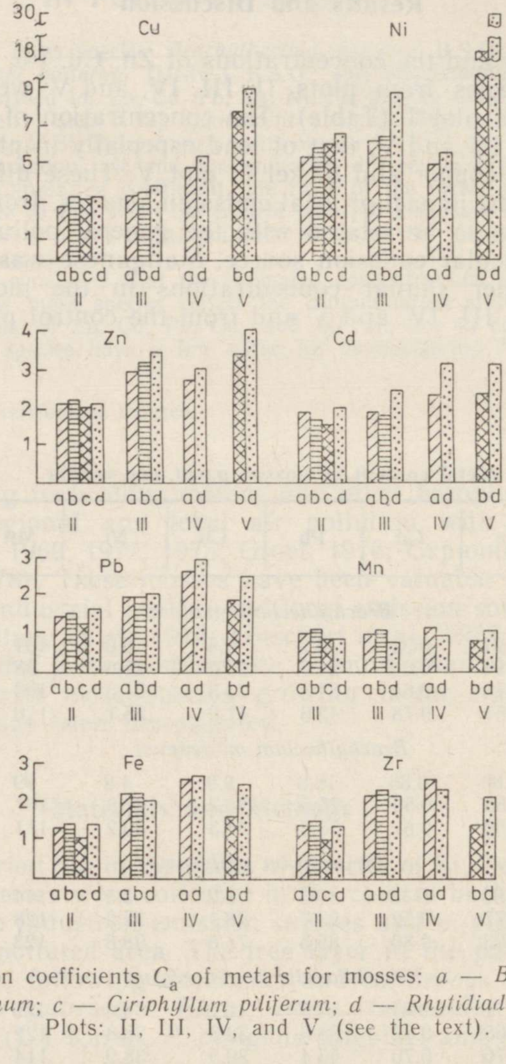

Fig. 1. Accumulation coefficients C_a of metals for mosses: *a* — *Brachythecium rivulare*; *b* — *B. mildeanum*; *c* — *Ciriphyllum piliferum*; *d* — *Rhytidiadelphus squarrosus*. Plots: II, III, IV, and V (see the text).

The contamination of plots was calculated by the average C_a values for the studied moss species (Fig. 2). Plot II was a relatively "clean" one among the others; plot III was polluted especially by Zn and Ni; plot IV especially by Pb and Cd; plot V by Ni, Cu, and Zn.

The general heavy metal pollution index for a plot was calculated as the sum of accumulation coefficients of five metals in the given plot (Mn, Fe, and Zr were not included). The pollution index values, calculated for *B. rivulare*, *B. mildeanum*, and *C. piliferum*, were as follows: plot II — 13.5; plot III — 15.7; plot IV — 17.8; plot V — 33.9; for *R. squarrosus*: II — 15.4; III — 20.7; IV — 20.4; V — 48.6.

Some samples of snow and soils collected in plots I, IV, and V were analysed for Cu, Ni, Zn, and Mn. The concentrations of these four metals

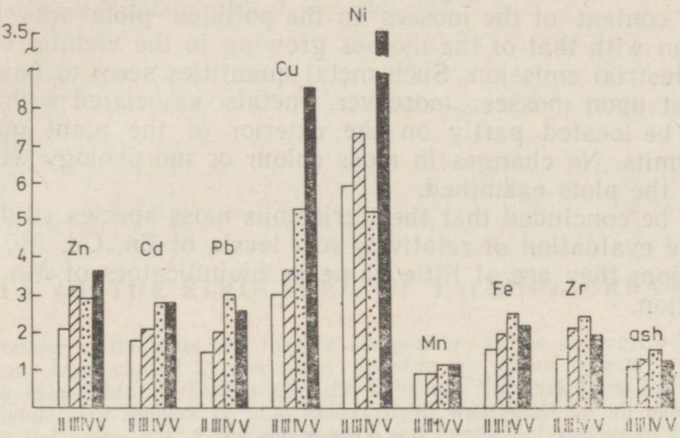

Fig. 2. Average accumulation coefficiens C_a of metals and ash for moss species. Plots: II, III, IV, and V (see the text).

in the samples from plots IV and V were higher than those from the control plot I. Thus, the higher contents of Cu, Ni, and Zn in the mosses corresponded to the increased contents of these metals in the precipitation and soils. No relationship was found between manganese content in mosses and manganese concentration in snow and soils. In all the plots examined the manganese concentration was quite similar in the mosses collected in May (Table). However, the manganese content in the mosses taken in September in plots IV and V was 2—3 times lower than in the control plot I; the content of other heavy metals was, on the contrary, higher. A similar inverse relationship has been found in herbs and woody plants in an urban-industrial area (Парибок et al., 1983; Парибок et al., 1982). Apparent inverse relationship between manganese and heavy metal contents in epiphytic and terricolous mosses has been reported in regional and local pollution studies (e. g., Rasmussen, 1977; Grodzińska, 1978; Pilegaard et al., 1979; Folkeson, 1981; Pakarinen, 1981).

The absence of manganese accumulation in mosses in the contaminated plots can be explained by a weaker binding and retention ability of manganese to moss tissues as compared with other heavy metals (Pb, Cu, Ni, Zn, etc.) amongst which manganese has the lowest affinity for the exchange sites (Rühling, Tyler, 1970; Nieboer, Richardson, 1980). Manganese is known to be leached quite easily by acid rains and displaced by soluble heavy metal cations.

Correlation coefficients (r) for the relationship between metal concentrations and ash content in moss species were as follows: Zn — 0.40; Cd — 0.57; Pb — 0.33; Cu — 0.46; Ni — 0.24; Mn — 0.26. High correlation coefficients between metal and ash contents were obtained only for Fe and Zr: 0.81 and 0.83, respectively. A close correlation between Fe and Zr concentrations in mosses was found ($r=0.97$). It is probable that the increased accumulation of Fe and Zr in the mosses of the polluted plots is related to the contamination of samples by soil particles. It is known that iron and especially zirconium concentrations are usually much greater in soils than in plants (Mitchell, 1960; Shacklette, 1965) and that is why the contamination of mosses by soil particles increases their Fe and Zr contents. It follows that terricolous mosses are of little value for the assessment of air pollution with Fe and Zr, at least under low contamination levels.

Metal content of the mosses in the polluted plots was not great in comparison with that of the mosses growing in the vicinity of sources of heavy industrial emission. Such metal quantities seem to have no hazardous effect upon mosses; moreover, metals associated with mosses are known to be located partly on the exterior of the plant out of the cell interior limits. No changes in moss colour or morphology were observed in any of the plots examined.

It can be concluded that the terricolous moss species studied are useful for the evaluation of relatively low levels of Zn, Cd, Pb, Cu, and Ni air pollution; they are of little value as bioindicators of Mn, Fe, and Zr air pollution.

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