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## CHEMICAL ANALYSIS OF BIVALENT TRACE METALS IN THE SURFACE LAYER OF RAISED BOGS

*(Presented by U. Kirso)*

In recent years there have been carried out several investigations of the possibilities to use the upper layer of raised (ombrotrophic) bogs for studying the regional atmospheric concentration of trace metals since they get their nutrients mainly from the atmosphere. Such studies were undertaken in Finland [1-6], Norway and Sweden [7, 8], and Denmark [9, 10].

The territory of the Estonian SSR is located in the zone of raised bogs. Some of them exist from the end of the postglacial period that is more than 10 000 years [11]. The study of the Estonian raised bogs was started in 1981 under the sponsorship of the Ministry of Forestry and Nature Protection. The distribution of mercury, cadmium, lead, copper, zinc and manganese was studied in 15 samples of various bogs (Fig. 1).

Characteristic of these bogs is the stratification of vertical structure of plant cover, consisting mainly of bog mosses. From the point of view of investigating atmospheric deposits it is of utmost importance to divide the upper layer of the bog into sublayers or horizons with different characteristics (pH, E, the water level). In this paper we shall present the results of these studies and discuss the suitability of such samples as ecointicators of the atmosphere.

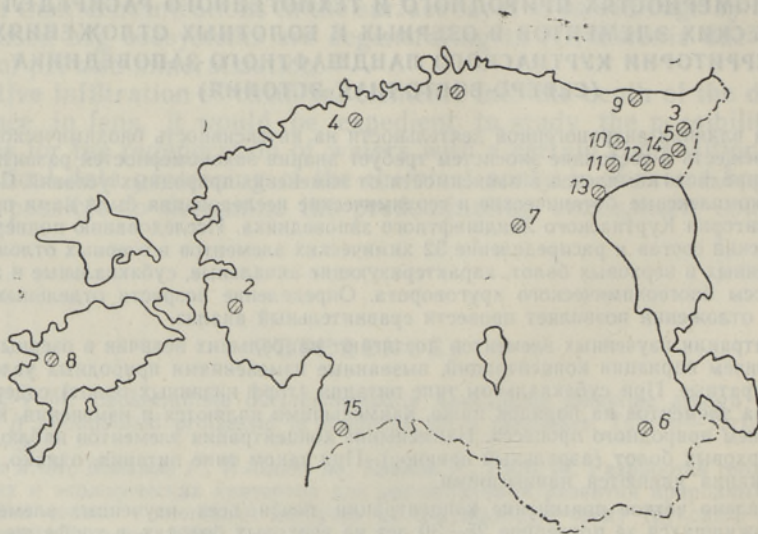


Fig. 1. Location of the bogs. 1 — Laukasoo, 2 — Tuhu, 3 — Poroni, 4 — Rae, 5 — Permisküla, 6 — Meenikunno, 7 — Endla, 8 — Vedruka, 9 — Valaste, 10 — Ratva, 11 — Roostoja, 12 — Remniku, 13 — Rannapungerja, 14 — Kivinõmme, 15 — Nigula.

## Sample preparation and chemical analysis

The upper layer (0–30 cm) was sampled with a 60 cm long sampler (section  $15 \times 15 \text{ cm}^2$ ). The core was cut into three samples, 10 cm thick each. The samples were sealed into plastic bags. Water level in the peat profile was measured. The samples were weighed and dried in a dust-free room. The air-dried samples were weighed and their density was calculated. A mean sample of about 50 g was separated, dried at  $40^\circ\text{C}$ , and ground in the laboratory mill. The humidity of the sample at  $40^\circ\text{C}$  was determined separately. Further the sample was treated with a 1:1 mixture of conc.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  for Hg and with a 1:10 mixture of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  for Pb, Cd, Cu, Zn and Mn. The analyses were performed by the atomic absorption method with a Pye Unicam SP9-700 instrument. The results are given as the means of several (two at least) replicate samples on  $40^\circ\text{C}$  dry weight (DW) basis in  $\text{mg}\cdot\text{kg}^{-1}$  (ppm), and in  $\text{g}\cdot\text{m}^{-3}$ .

The volume weight of the peat stand was calculated by

$$D = \frac{1000 \cdot m}{S \cdot h},$$

where  $D$  — volume weight ( $\text{kg}\cdot\text{m}^{-3}$ ) of the peat;  $m$  — dry weight of the sample, g;  $S$  — sample area,  $\text{cm}^2$ ;  $h$  — peat profile depth, cm. The metal concentration in the peat was calculated by  $C_v = \frac{C \cdot D}{1000}$ , where  $C_v$  — concentration of the metal in peat,  $\text{g}\cdot\text{m}^{-3}$ ;  $C$  — concentration of the metal in peat,  $\text{mg}\cdot\text{kg}^{-1}$  DW;  $D$  — volume weight of the peat stand,  $\text{kg}\cdot\text{m}^{-3}$ .

P. Pakarinen has used the concentration of the metals, the quantity of dry matter in a 1 mm layer of an area of  $1 \text{ m}^2$  and the annual net production of sphagnum moss for calculating the annual metal consumption in  $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  [1]. In the present study the annual length increment of moss was not measured and therefore the calculations of the annual metal consumption could not be carried out.

## Results and discussion

The mean concentrations of trace metals in the upper layer of the bog (0–10 cm from the top) determined for 30 different cores in 15 locations (Fig. 1) do not differ significantly from the data obtained in other Northern European countries (the Table).

Mean concentrations of trace metals in the upper layer (0–10 cm) of raised bogs in Northern Europe

Location	N of samples	Concentration, ppm						Reference
		Hg	Cd	Pb	Cu	Zn	Mn	
Estonian SSR	30							This work
min		0.10	0.02	6.3	0.9	18.1	13.6	
av		0.68	0.63	18.9	3.8	53.7	75.4	
max		2.17	1.81	38.0	13.7	80.2	232.6	
Finland	40							[2]
min				3.8	2.8	16.9	53	
av				14.6	5.4	32.4	261	
max				64.6	12.2	60.0	653	
Norway	4							[2]
min				5.3	5.0	16	37	
max				31.0	7.3	33	185	
FRG	30							[2]
Denmark	2	0.23						[9]

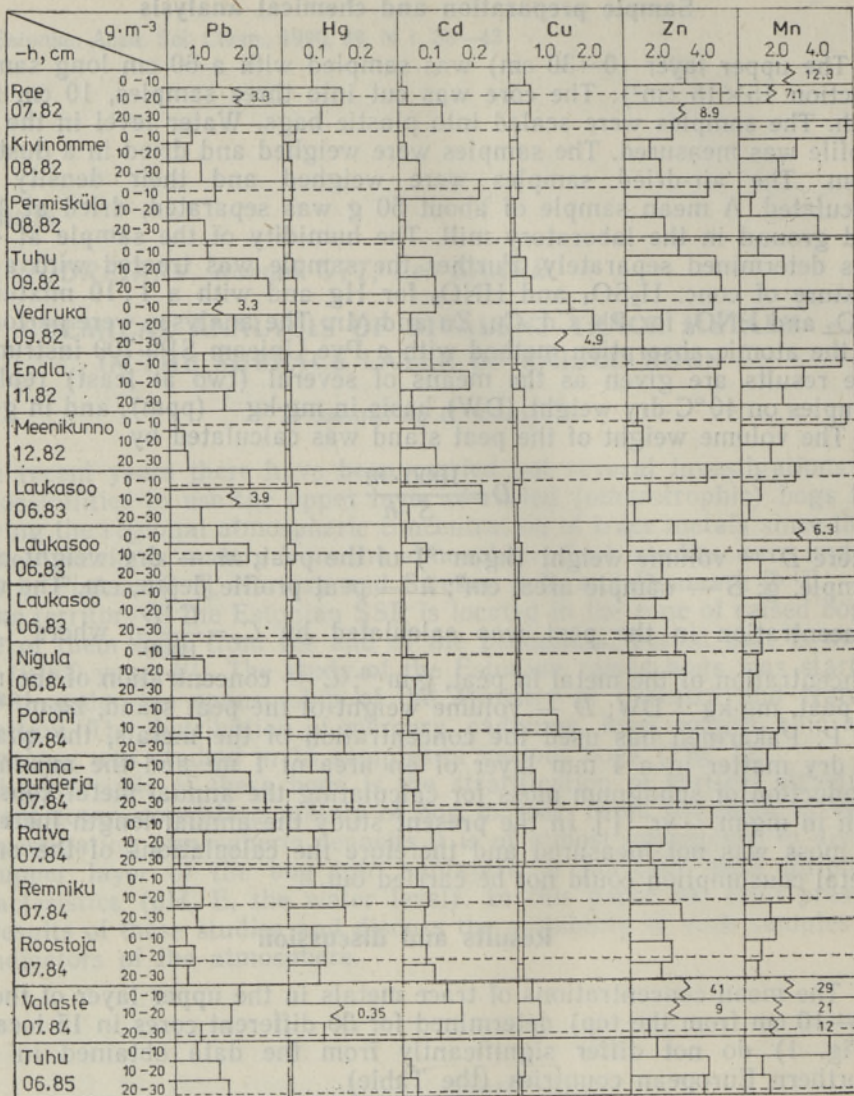


Fig. 2. Distribution of metals ( $\text{g}\cdot\text{m}^{-3}$ ) in 15 bogs in separate layers ( $-h=0-10$  cm;  $10-20$  cm;  $20-30$  cm) at different water levels (---).

A comparison between the concentrations of the elements in the layer  $0-10$  cm and in the whole layer  $0-30$  cm indicates the cyclic release and retention of the elements. The changes in the chemical composition of metals in the investigated bog profile are summarized in Fig. 2. It can be seen that the elements react differently. The changes seem to be closely related to the water level and, therefore, to the aeration of the peat. The distribution of the elements depends on the stability and solubility of their compounds. Metals can enter the bog either as soluble ions or molecules in aerosols and as particulate matter. The initial fate of metals in the upper layer of the bog depends on the form of the atmospheric input, while the subsequent changes of the metals are the results of chemical and biological processes in the "biomass pool". Characteristic features of the bog ecosystem are the alternating aerobic and anaerobic conditions connected with the cyclic movement of the water level, highly acidic medium (pH

3—4), release of hydrogen sulphide from decomposing plants and reduction of sulphate-ion, low redox potential, high concentration of organic matter and the cation-exchanging properties of mosses.

**Lead** is one of the most common trace metals in the atmosphere of urban and industrial regions. Because of the industrial activities (melting and battery factories, automobile gasoline additive, paint pigments and plastics, burning of fossil fuels, etc.) the present-day concentration of lead in the atmosphere is much higher than that of the natural background caused by forest fires, sea salt spray, volcanoes, etc. The flux of the lead to the soil from natural sources is calculated to be  $2.04 \cdot 10^{-5} \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  [12]. J. O. Nriagu has reported data on the atmospheric load of lead in different locations: in polluted areas and urban districts the mean deposition rate of lead is generally more than  $20 \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ , and in rural and remote areas  $5\text{--}20 \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  or less than  $5 \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ , respectively [13]. T. J. Chow and M. S. Johnstone have estimated the average annual deposition in the western hemisphere to be  $1.1 \text{ ng} \cdot \text{m}^{-2}$  [14]. In South Canada the average annual deposition rate of lead is  $3.0 \text{ mg} \cdot \text{m}^{-2}$ , in France  $17.0 \text{ mg} \cdot \text{m}^{-2}$  and in the United Kingdom it was  $17\text{--}69 \text{ mg} \cdot \text{m}^{-2}$  in 1972—1973 [12]. Using our data on the lead content in snowpack during the years of 1983—1985 in several parts of Estonia, the lead atmospheric deposition rate was calculated to be in the range of  $2\text{--}20 \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  (total fallout about  $700 \text{ mm year}^{-1}$  and the snow period of three months).

The main forms of lead in the atmosphere are as follows: lead carbonate and/or basic carbonate (58%), lead oxide (21%), lead sulphate and/or basic sulphate (8.2%), lead chloride (5.4%) [15]. J. M. Pierrard suggested that lead oxide PbO might be the most expected end-product in the atmosphere [16]. After L. J. Schnider about 2% of airborne lead is organic lead [17]. The soluble lead aerosols which enter the aerobic upper layer of a bog may be bound to the sediments, to the moss (by cation-exchange mechanism) or form a complex with fulvic and humic acids. In the anaerobic conditions lead will form insoluble in the acid medium lead sulphide. When the water level is lowered and the medium is changing to aerobic, the lead sulphide will be oxidized into the more mobile lead sulphate. Therefore the maximum concentration of lead can be found near the water level. New quantities of lead from the atmosphere will concentrate on the surface and the cycle will repeat. We compared the lead behaviour at various water levels (Fig. 2) and the results support the idea. The histogram of the concentration distribution (Fig. 3) indicates good agreement between the arithmetic mean concentration and the median.

**Mercury** background concentration in the atmosphere is about  $1 \text{ ng} \cdot \text{m}^{-3}$ . The main forms of mercury in the atmosphere are elemental Hg and organic  $(\text{CH}_3)_2 \text{Hg}$ . The atmospheric deposition rate of mercury has to be  $1 \text{ } \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  that follows from the mercury accumulation rate at the Greenland Ice Sheet that is 2—3 orders of magnitude lower than in urban or industrial districts. In Estonia mercury has the atmospheric deposition rate  $0.09\text{--}1.2 \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ . The increase of mercury concentration is due to burning of fossil fuels, heating ceramic materials and/or increasing rate of degassing of mercury from agricultural soils. The accumulation of mercury in the bog upper layer depends on the redox conditions in it. In the aerobic medium mercury could be bound to the sphagnum mosses through cation-exchange. This process must be preceded by formation of soluble forms of mercury. It is one of the possible ways for the methylation of the mercury. M. Lodenius et al. have pointed out humus which can cause a non-biological methylation and so enhance its bioaccumulation [6]. This may be an explanation to the high accumulation rate in the upper layer of bog as compared with the background concentration of

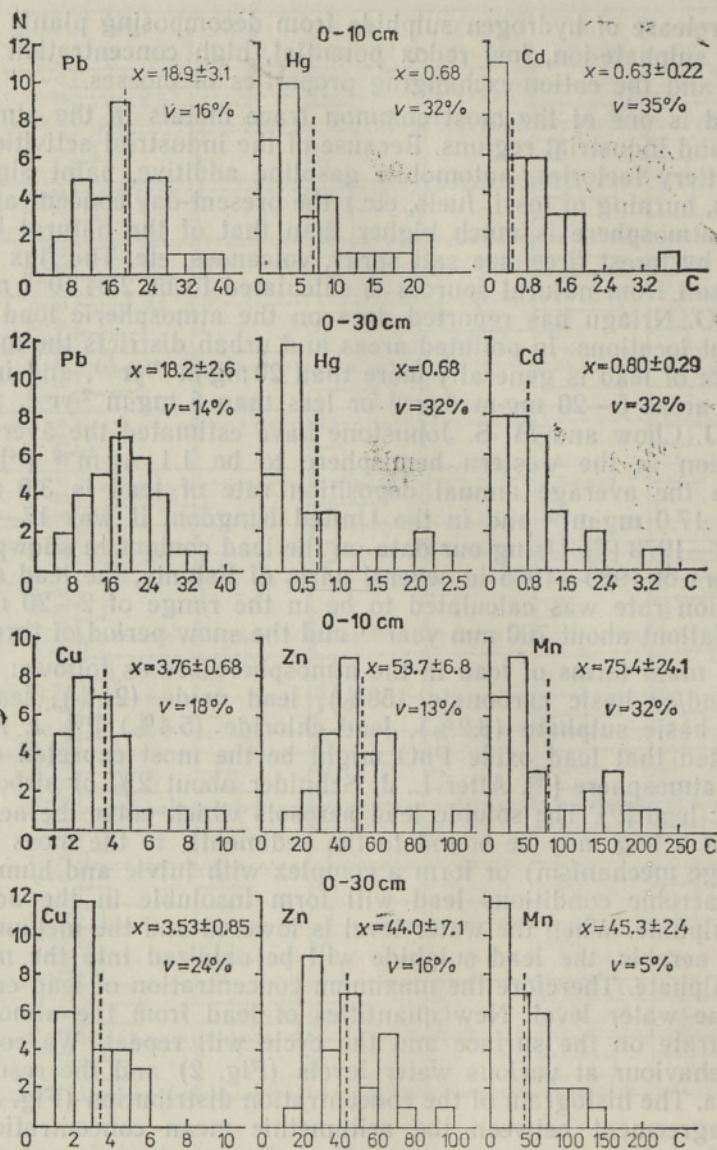


Fig. 3. Histogram of the distribution of metals ( $\text{mg} \cdot \text{kg}^{-1}$  DW) in the upper layers of the bog (0-10 cm and 0-30 cm) and the arithmetic mean ( $\bar{x} \pm SD$ ) of concentration ( $N$  — the number of samples;  $C$  — concentration of the metal in peat,  $\text{mg} \cdot \text{kg}^{-1}$ ).

mercury in the atmosphere. The anaerobic upper layer has a high hydrogen sulphide concentration and low pH value. In these conditions metals are fixed as insoluble sulphides, the more so the smaller is their solubility product:

	HgS	CuS	CdS	PbS	ZnS	MnS
$K_s$	$4 \cdot 10^{-53}$	$3.5 \cdot 10^{-42}$	$1 \cdot 10^{-29}$	$1 \cdot 10^{-29}$	$7 \cdot 10^{-26}$	$1.4 \cdot 10^{-15}$

Formation of highly insoluble mercury sulphide immobilizes it in various redox-conditions. Low solubilities of the sulphides of mercury and copper are seen in the distribution patterns. The relative immobility of mercury (and also of copper) sulphide makes possible to use the bog profile as a record of the history of the atmospheric deposition of these metals.

**Copper** is one of the most widely used metal. Copper pollution can be observed near the copper processing plants. K. Wachowska-Serwatka and J. Serwatka have shown that the copper deposition rate near the emission point in the distance not more than 1 km is  $9.0 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  and in the distance of 1—5 km  $1.3 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  [18]. Our data show that the deposition rate of copper in Estonia varies in the range of  $1.0\text{--}5.0 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  that is lower than in South Finland ( $6.0 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) [3]. As indicated earlier, the distribution of copper is mainly determined by the formation of its insoluble sulphide. So the mobility of copper is limited and does not depend essentially on the water fluctuation.

**Cadmium and zinc** are rather similar in their chemical, physical and geochemical properties, but differ significantly in their biological properties. Zinc is an essential element for life, while cadmium, even in minor concentration, is toxic. Zinc forms great deposits (sulphides, oxides) in nature ranking fourth among metals in annual world consumption. Cadmium is produced mainly as a coproduct of zinc. However, its production has increased lately due to electronic industry. Compounds of cadmium are widely used in dye and plastic industry. Besides, metallic cadmium is used in galvanoplastic coating and in alloys. Cadmium enters the atmosphere also through burning fossil fuels. In Estonia zinc and cadmium atmospheric deposition rates are  $9\text{--}64 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  and  $0.1\text{--}2.4 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ , respectively. In South Finland the mean deposition of zinc is  $28.8 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  [3]. Zinc and cadmium could be bound to the moss in the aerobic as well in the anaerobic conditions. Thus their uniform distribution throughout bog profile is quite common.

**Manganese** is one of the most widely distributed trace metals in nature. Its content in the earth crust (0.085%) is surpassed only by iron. Manganese is necessary for life and is present in every organism. As a result of human activities, manganese can be concentrated in the industrial and urban districts. The main contributors of manganese are the metallurgy (Mn alloys, steel), battery and dye industries. Manganese is used also as an additive to automobile fuels and oils. H. L. Windom has estimated the manganese concentration in the atmosphere above the Central Atlantic as  $1.2 (0.03\text{--}27) \text{ mg}\cdot\text{m}^{-3}$  and atmospheric flux to coastal water in the North Sea at the level of  $9.4 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  [19]. The atmospheric deposition rate in South Finland is given by P. Pakarinen as  $5.7 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  [3]. The atmospheric deposition rate in Estonia, according to our data, is in the range of  $0.8\text{--}32 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ . The accumulation rates (retention) in the plant cover of ombrotrophic bog area ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) are: 33.6 in Finland, 24 in Sweden, 95 in Denmark, 26.6 in Harz (FRG) [3]. These data indicate the high accumulation of manganese in the plant cover of the bog in respect to atmospheric flux. The distribution of manganese in the bog upper layer is controlled by the redox potential of the peat. In anaerobic and acidic conditions ( $E \approx 0.075 \text{ V}$ ,  $\text{pH} = 3\text{--}4$ , Jacobsen, 1981), manganese occurs in the reduced two-valent form, which is soluble and easily exchangeable by bioorganic cation-exchanging systems. Some authors suggest that manganese is an important micronutrient for mosses [20]. Manganese has the maximum concentration in the upper layer being independent of the fluctuation of water.

In this paper the behaviour of individual metals is discussed. However, the movement and accumulation of metals can be influenced by the competition between metals in biochemical reaction. Some authors have shown that a rise in the concentration of lead is correlated with a decrease in the concentration of manganese [2]. In our investigations the decrease in the concentration of manganese in the upper layer in Permisküla bog can be the result of observed rise of the concentration of cadmium (Fig. 3).

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### RABA PINNASES LEIDUVATE KAHEVALENTSETE MIKROMETALLIDE KEEMILINE ANALÜÜS

Metalliliste elementide käitumine kõrgraba pinnases sõltub nii elementide iseloomust kui ka raba omadustest: aeroobse ja anaeroobse keskkonna vaheldumisest sõltuvalt vee-taseme kõikumisest, happelisest reaktsioonist, divesiniksulfiidi vabanemisest taimede lagunemisel ja sulfaationide taandumisel, madalast redokspotentsiaalst, kõrgest orgaanilise aine sisaldusest ja sammaltaimede katioonivahetuslikest omadustest.

Elavhõbeda, kaadmiumi, plii, vase, tsingi ja mangaani sisaldust Eesti rabades on 15 erinevas paikkonnas uuritud aastatel 1981—1988. Elavhõbeda ja vase liikumine raba ülemises 30 sentimeetris on vahelastuvate sulfiidide tekke tõttu aeglane. Plii kontsenteerub põhjavee tasandi läheduses ja liigub koos sellega. Kaadmium ja tsink on suhteliselt ühtlaselt jaotunud kogu uuritud raba profiilis. Mangaan kontsenteerub raba pealiskihis. Uuritud elementide kontsentratsioonide aritmeetilised keskmised ja muutumise piirid ei erine oluliselt teistest Põhja-Euroopa kohta saadud andmetest ja on järgmised ( $\text{mg} \cdot \text{kg}^{-1}$  kuivaines): Hg 0,68 (0,10—2,17), Cd 0,63 (0,02—1,81), Pb 18,9 (6,3—38,0), Cu 3,8 (0,9—13,7), Zn 53,7 (18,1—80,2), Mn 75,4 (13,6—232,6).

## ХИМИЧЕСКИЙ АНАЛИЗ ДВУХВАЛЕНТНЫХ МИКРОЭЛЕМЕНТОВ В ПОВЕРХНОСТНОМ СЛОЕ ВЕРХОВОГО БОЛОТА

Миграция металлических элементов в почвах верховых болот зависит как от типа элемента, так и от типа болота: от перемены аэробных и анаэробных условий в зависимости от колебания уровня грунтовых вод, кислотности среды, освобождения сероводорода при разложении растений и восстановлении сульфат-ионов, содержания органического вещества и катионообменных процессов во мхах.

Содержания ртути, кадмия, свинца, меди, цинка и марганца в 15 болотах разных районов Эстонии исследовались в течение 1981—1988 г. Миграция ртути и меди в верхнем слое (30 см) замедлена из-за образования малорастворимых сульфидов. Свинец концентрируется вблизи уровня грунтовых вод и перемещается вместе с водой. Кадмий и цинк распределяются в исследованном слое относительно равномерно. Марганец концентрируется в самом верхнем слое. Арифметические средние концентрации и пределы концентраций заметно не отличаются от данных, полученных для других стран Северной Европы, и являются следующими, мг · кг<sup>-1</sup> сухого вещества: ртуть 0,68 (0,10—2,17), кадмий 0,63 (0,02—1,81), свинец 18,9 (6,3—38,0), медь 3,8 (0,9—13,7), цинк 53,7 (18,1—80,2), марганец 75,4 (13,6—232,6).