Major and Trace Elements in Peat from Bogs of East Latvia

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Trace element concentrations in different natural sorbents can be used not only as indicators of environmental pollution, but also to characterize the quality and application possibilities of the selected material. From this perspective, an important objective of research is analysis of trace element accumulation in peat. In this study, trace element concentrations and their occurrence in peat samples from seven peat bogs of industrial importance located east Latvia were studied. It was found that trace element concentrations in the upper layer of the peat profiles are most affected by industrial airborne pollution, but the concentrations of trace elements in the bulk peat mass are comparatively low.

Keywords: accumulation, major and trace elements, peat, pollution.

INTRODUCTION

Not only a significant part of carbon (Coccozza et al., 2003) within its biogeochemical cycle is accumulated in the form of peat, but also major and trace elements assimilated during the life of wetland's biota as well as from atmospheric precipitation. Many studies consider anthropogenic pollution the main source of major and trace elements (Martinez Cortizas et al., 2002; Coggins et al., 2006; Shotyk et al., 2001); however, usually only upper peat layers have been analyzed. Presence of trace elements in peat is of importance considering the increasing use of peat in agriculture and industry because excessive amounts of trace element can reduce the application potential of the mined peat. If peat is used as fuel, trace elements concentrated in ash can influence their utilization possibilities.

Trace element accumulation in peat has been studied throughout the world, and human activities are often considered the major source of peat pollution (Ukonmaanako et al., 2004; Shotyk et al., 2001) The upper layers of peat profiles are most heavily contaminated (Shotyk et al., 2001). A significant impact of natural geochemical processes on trace element accumulation has been stated (Syrovetnik et al., 2004). For better understanding of the factors influencing trace element accumulation in peat, it is important to study their concentrations in remote areas where there is no direct impact on the point sources.

The objective of this article is to study the characteristics of major and trace metal accumulation in peat from bogs in east Latvia depending on peat properties and the impact of local and regional pollution sources on the metal accumulation characteristics.

MATERIALS AND METHODS

Site Location

Peat sampling has been carried out in seven representative raised bogs in east Latvia (Fig. 1). In the study, sampling sites throughout the territory of Latvia were selected to represent the possible minimum impact of direct pollution sources (roads, railway, cities, industry) in human-unaffected territories. Several of the sampled bogs are of industrial importance (Table 1).

Table 1. **Characterization of sampling sites**

Peat bogs	Total area, ha	Industrial output area, ha
Baltmuiža	1380	358
Borovka	1113	643
Kņava	1240	882
Lielais Aknīstes	1050	810
Skrebeļi	3475	1845
Tīrais	727	727
Teiči	19,394	0

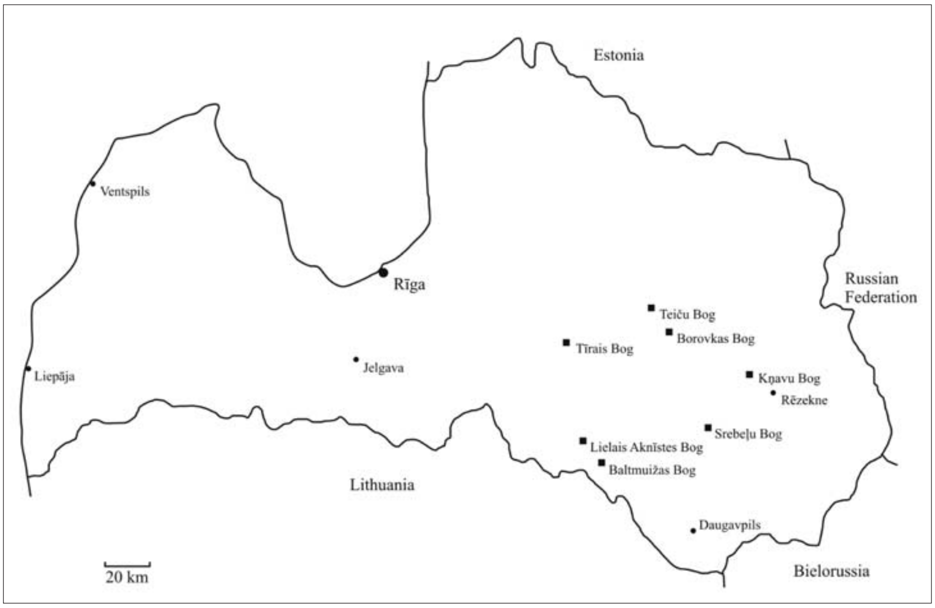

Figure 1. **Sampling sites**

Sampling

Studies of coring and peat sampling have been accomplished in the cupola area of each bog, where the surface peat layers are elevated up to 2–4 m above the edge of the bog and have not been influenced by peat sliding (as suggested by Shotyk et al., 2001). The peat samples (34 cm long monoliths) were put in polyethylene film to preserve nature moisture and brought to the lab. The first slice (+3 to 0 cm) corresponded to the living plant material on the bog surface. To determine metal concentration in peat from the 7 studied bogs, in each site three peat cores were sampled using a peat sampler (ϕ = 8 cm). Excess surface vegetation was removed *in situ* to facilitate penetration of the peat surface. Samples of peat were taken from a depth of at least 204 cm up to 374 cm.

Peat Sample Preparation and Analysis of Metals

The study was carried out using air-dried peat. Analysis was performed using A class vessels, calibrated measuring instruments and equipment.

Analytical quality reagents were used without further purification. All chemicals used in this study were of high purity. For preparation of solutions, high purity deionized water was used throughout.

Glass and quartz vessels utilized in the study were pre-cleaned treating them with $K_2Cr_2O_7$ and concentrated sulphuric acid mix.

All peat samples were analyzed in triplicate.

Major elements and trace metals and elements were determined after acid digestion (Krachler et al., 2001; Tan, 2005). A peat sample was digested heating 1.5 g of peat with 15 ml conc. HNO_3 at 95 °C for 2 hours. The sample was filtered through filter previously washed with 0.5% conc. HNO_3 solution, then the filtrate was diluted to the volume of 65 ml with deionized water. Metal (Ca, Mg, Fe, Mn, Zn, Cu, Cd, Pb, Co, Cr, Ni, Mo, V, Se, Sr) concentrations were measured with inductively coupled plasma optical emission spectrometer OPTIMA 2100 DV ICP/OES by Perkin Elmer.

Data Treatment

Statistical analyses were performed using SPSS 16 software. Fitting of the obtained data to normal distribution was checked with the Kolmogorov-Smirnov test. In further analysis non-parametric methods were used. Relationships between different characteristics were assessed with the Spearman rank correlation coefficients. In all cases, the significance level was $p = 0.05$.

RESULTS AND DISCUSSION

Major and Trace Element Concentrations in Peat from East Latvia

The values of element concentration (Fig. 2) found in peat in East Latvia and their intervals are in general similar to those reported for Estonia, the United Kingdom, Russia, Norway, Australia, and other countries (Syrovetnik et al., 2004;

Jennifer and Hao, 1993; Markert, 1991; Simon and Thomas, 2003; Frontasyeva and Steinnes, 2005; Orru and Orru, 2006; de Vleeschouwer et al., 2007); at the same time, the data reflect the local processes that influence the element concentrations in the peat mass. The local conditions may influence major elements (Mg, Fe, Ca), which are found in lower concentrations than in Norway, Russia, and the United Kingdom. The trace element concentrations in the main peat mass, which is of industrial importance, are low, especially if compared with element concentrations reported by other countries (Table 2), thus proving the high market value of the peat mined in Latvia. The low concentrations found in peat from east Latvia can be explained considering the absence of major local pollution sources (metal ore processing, building material industries, chemical industries, and others) and the comparatively large distance from major pollution sources.

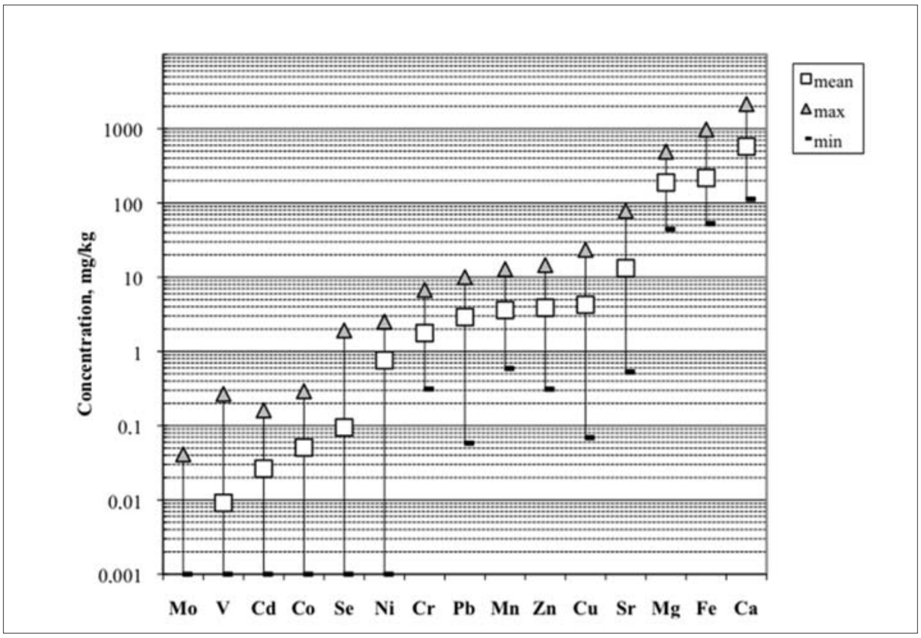

Figure 2. **Concentrations of major and trace elements in peat from bogs in east Latvia**

The correlation matrix calculated for 15 elements analyzed in the peat from east Latvia is presented in Table 3. The element pairs Mn-Fe, Ca-Mn, Co-Mn, Fe-Sr, Fe-Ni, Fe-Ca were all significantly correlated. Strongest correlations were between the element pairs of evidently natural origin, for example, Fe-Mn, Mg-Ca, Fe-Mg (Table 3). Correlations such as Cu-Cr, Cd-Co, Fe-Ni, Fe-Pb might be attributed to industrial activity and long-range transport of pollutants (Percy and Borland, 1985). In the case of some elements (Cu, Zn, Mn, Ni), both anthropogenic and natural sources could be of imortance.

Table 2. **Concentrations of major and trace elements (mg/kg) in peat from seven bogs in Latvia and in other countries**

Element	Estonia	United Kingdom	Russia	south Norway	north Norway	Australia	Baltmuiža Bog	Borovka Bog	Kņavas Bog	Lielais Aknistes Bog	Skrebeļi Bog	Tīrais Bog	Teiči Bog	Average in east Latvia
Cu	102.1	54.8	26.3	5.6	1.6	4.2	0.87	10.71	0.45	0.95	13.04	1.00	2.73	4.26
Pb	200.0	358	15	23.2	6.9	28.6	2.08	3.71	4.27	2.53	3.20	0.92	3.82	2.90
Zn	446.5	56.2	59.6	19.6	12.3	11.3	1.94	7.64	0.76	1.17	7.00	2.46	7.96	3.88
Cd	17.4	2.09	-	1.2	0.24	2.7	0.041	0.069	0	0.002	0.044	0.007	0.045	0.03
Ni	46.6	10.9	-	1.4	2.6	-	0.64	1.61	0.15	0.28	1.35	0.33	1.35	0.76
Cr	-	15.9	-	0.8	0.9	-	1.38	2.38	0.67	1.83	3.59	0.68	1.91	1.77
Fe	1155	3.52	1783.3	1130	727	1686	177.4	467	116.9	285.3	162	114.1	273.3	217.5
Co	-	-	-	1.16	1.06	-	0.067	0.186	0	0.009	0.054	0.013	0.081	0.05
Mn	146.5	25.4	68.6	3.6	4.3	-	5.04	5.43	1.96	4.24	1.86	4.57	2.89	3.61
Ca	-	80.8	-	-	-	-	584	865	262	593	438	868	450	575
Mg	-	246	-	-	-	-	202	163	91	204	256	211	188	188

Table 3. **Correlation coefficient matrix of major and trace element analyses in peat from east Latvia**

	Fe	Mg	Ca	Sr	Mn	Pb	Cu	Zn	Co	Ni	Cd	Cr	V	Se
Mg	.274*													
Signif.	.026													
Ca	.512**	.471**												
Signif.	.000	.000												
Sr	.594**	.183	.760**											
Signif.	.000	.141	.000											
Mn	.559**	.513**	.723**	.591**										
Signif.	.000	.000	.000	.000										
Pb	.165	.211	–.165	–.106	.151									
Signif.	.187	.089	.186	.398	.227									
Cu	.114	.077	–.045	–.041	–.136	–.004								
Signif.	.363	.541	.721	.744	.275	.973								
Zn	.194	.322**	–.075	.181	.016	.482**	.462**							
Signif.	.119	.008	.550	.145	.896	.000	.000							
Co	.668**	.183	.383**	.624**	.361**	.154	.279*	.475**						
Signif.	.000	.141	.001	.000	.003	.216	.023	.000						
Ni	.557**	.314*	.207	.426**	.133	.249*	.499**	.726**	.747**					
Signif.	.000	.010	.095	.000	.288	.043	.000	.000	.000					
Cd	.314*	.426**	.117	.291*	.243*	.557**	.187	.740**	.623**	.620**				
Signif.	.010	.000	.350	.018	.049	.000	.132	.000	.000	.000				
Cr	.369**	.464**	–.027	–.066	.017	.347**	.442**	.591**	.404**	.686**	.532**			
Signif.	.002	.000	.833	.601	.892	.004	.000	.000	.001	.000	.000			
V	.152	.189	–.027	.139	.038	.498**	.016	.506**	.349**	.306*	.624**	.282*		
Signif.	.224	.129	.828	.266	.761	.000	.899	.000	.004	.012	.000	.022		
Se	–.025	.324**	–.121	–.213	–.115	.291*	–.052	.386**	.076	.341**	.374**	.580**	.124	
Signif.	.840	.008	.333	.086	.358	.018	.677	.001	.543	.005	.002	.000	.320	
Mo	.012	.042	–.026	.047	–.010	.258*	.086	.282*	.079	.057	.440**	.010	.314*	–.027
Signif.	.923	.735	.837	.707	.935	.036	.495	.022	.528	.647	.000	.936	.010	.831

* – Correlation is significant at 0.05 level (two-tailed).

** – Correlation is significant at 0.01 level (two-tailed).

Variations of Major and Trace Element Concentrations in the Peat Profiles

For in-depth studies of the metal accumulation pattern in peat sections, three raised bogs in eastern part of Latvia were selected.

Concentrations of major and trace elements in the peat sections of the three studied bogs in Latvia demonstrate high variability (Fig. 3–7). Variability of both major elements, possibly of natural origin (Ca, Mg, Fe), and trace elements, presumably of anthropogenic origin (Pb, Cu, Cd, Ni, Cr, etc) is equally high.

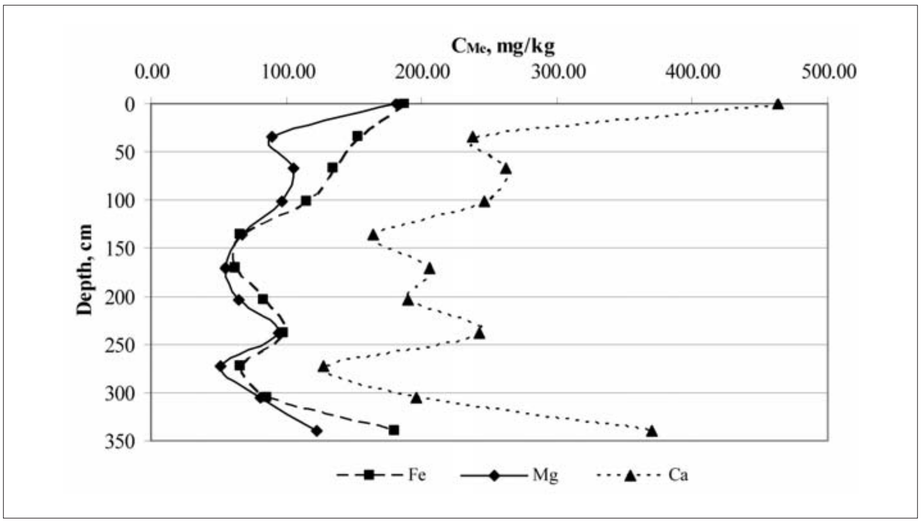

Figure 3. **Fe, Mg, Ca concentrations (mg/kg) in the peat core from the Kņavas Bog**

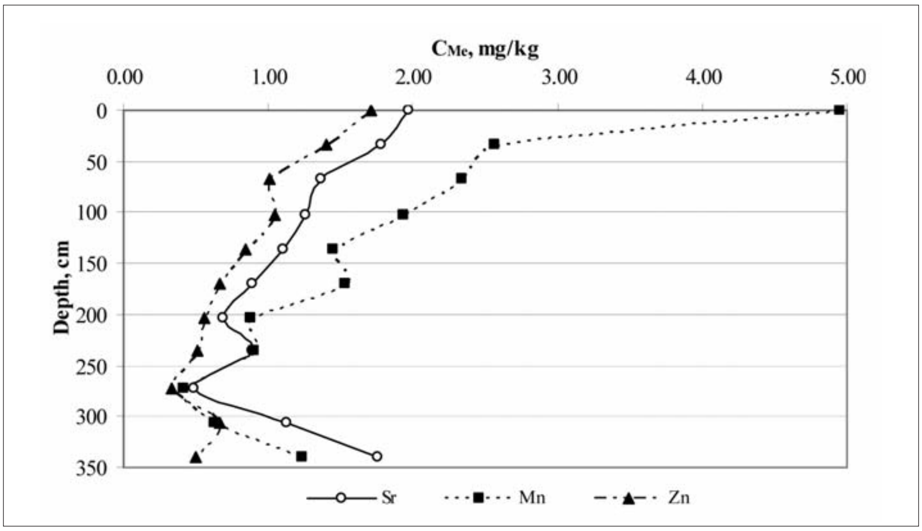

Figure 4. **Sr, Mn, Zn concentrations (mg/kg) in the peat core from the Kņavas Bog**

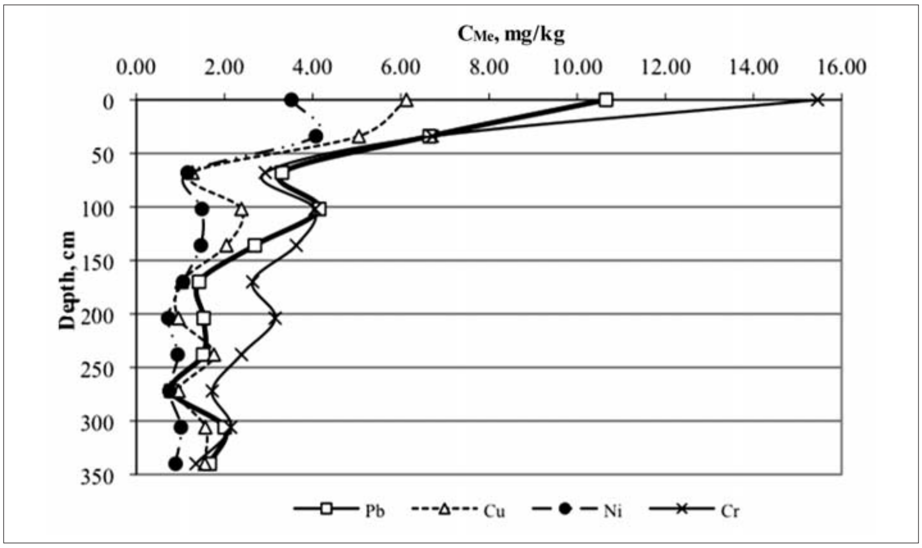

Figure 5. **Pb, Cu, Ni, Cr concentrations (mg/kg) in the peat core from the Skrebeļi Bog**

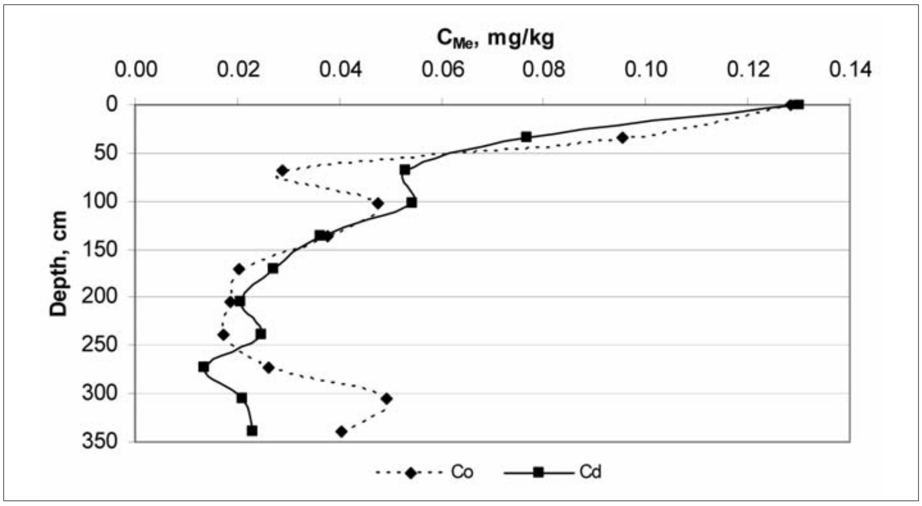

Figure 6. **Co, Cd concentrations (mg/kg) in the peat core from the Skrebeļi Bog**

Peat profiles serve as an archive of major and trace elements. As it was discovered, for most of the studied elements the concentrations are significantly higher in the upper layers of the studied bogs, and the major source could be atmospheric precipitation, as well as release of trace elements during the decay of living plants. We could suppose that the mobility of the studied elements is rather low; at the same time, binding to respective functional structures within peat comparatively strong as far as the leakage from the accumulation (upper) layer at the bog top does not happen and the distribution of concentrations in lower peat layers is low. The changes of major and trace element concentration at first can influence the biogenic recycling and low mobility of these elements, also considering the changes of the water table (Gorres and Frenzel, 1997). Changes of concentrations of the studied elements in all studied bogs are of similar character: higher concentrations at the upper layers and a decrease of the element concentration starting from a depth of 50 cm up to 100 cm. The concentrations of several elements (Fe, Sr, Zn, Mn, Ca, Mg) increase again starting from a depth of 2–3 m, most probably due to supply of groundwater. The behavior of Fe could be related to high stability and mobility of Fe^{+2} ions under reducing conditions to the extent that under such conditions these ions are readily soluble and may be transported upward with the groundwater flow until conditions favor oxidation to the immobile Fe^{+3}. Fe and Mn behavior is also influenced by redox conditions, and these elements may behave similarly in peat. The enrichment in element concentrations in the peat profiles is not limited to the uppermost layer of recent origin, where active moss growth and decay processes take place, involving metabolic mobilization of nutrients (including such elements as Ca, Mg, Cu, Zn).

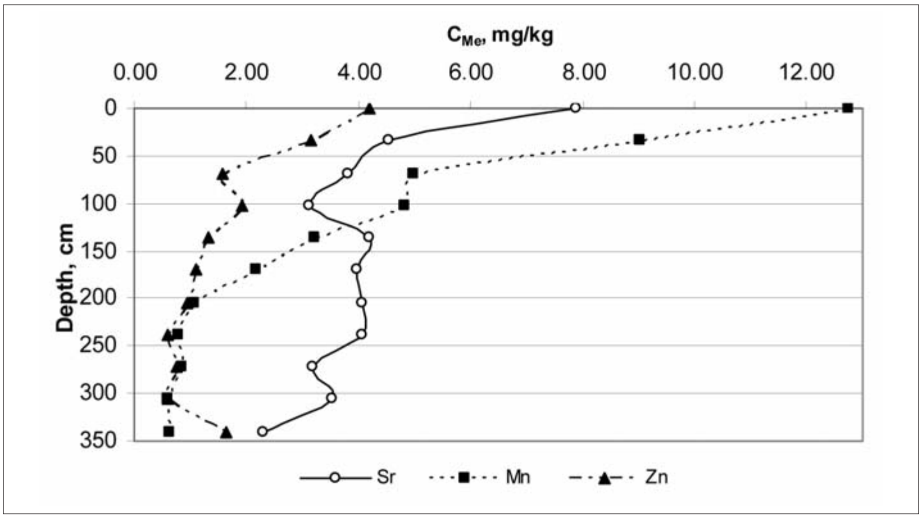

Figure 7. **Sr, Mn, Zn concentrations (mg/kg) in the peat core from the Lielais Aknīstes Bog**

The tendencies of changes of concentrations of evidently anthropogenic elements (Pb, Cr, Cd, and others) are similar at both sites: concentrations within the bulk of the peat section are stable (and they can be considered background concentrations for corresponding elements in peat), but then steeply increase towards the surface, slightly decreasing again at approximately 10–20 cm below the surface.

CONCLUSIONS

The trace element concentrations in bogs located in the eastern part of Latvia are low, especially in comparison with regions where intensive industrial activity has influenced trace element accumulation in the upper peat layers. Low concentrations of trace elements are considered an indicator of the good quality of the mined peat.

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