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Peat properties, major and trace element accumulation in bog peat in Latvia

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Abstract In this study the trace and major elements and the character of their accumulation in peat, with a particular emphasis on peat properties and the impact of local and regional pollution sources on the character of element accumulation in the ombrotrophic bogs in Latvia, have been analysed. The values of the element concentrations in peat taken from 44 bogs in Latvia reflect the local processes of element concentrations in the peat mass indicating accumulation of trace elements, apparently of anthropogenic origin (Pb, Cd, Co, Ni and others), in the upper layers of the peat profiles. In addition they indicate accumulation of several elements (for example, As, Cr, and others) in deeper layers of bog, possibly due to the feeding pattern, depending on the saturation of the groundwater. The trace element sorption capacity onto peat is influenced by the peat properties and depends on the concentration of oxygen containing functional groups in peat and is growing with an increasing degree of decomposition and humic/fulvic acid ratio of the peat humic matter. Peat seems to be largely unsaturated in respect to metal ions, but the peat sorption capacity can be correlated with the presence of nitrogen containing ligands and humic/fulvic acid ratio.

Keywords *Peat, trace and major elements, accumulation, pollution.*

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INTRODUCTION

World wide bogs are treated as an important nature value. They have been formed by an accumulation of peat—a light brown–to–black organic material, built up from partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees under waterlogged conditions. The developed surface area and large number of acidic functional groups common to peat, determine the ability to bind trace elements included in remains of living organic mater, either both as a sedimentary, deposited, particulate matter or as sorbed or complexed metal ions (Brown *et al*. 2000).

The major sources of metals in the peat mass thus can be attributed to atmospheric precipitations, metals present in the peat forming plants as well as in supply from groundwater and atmospheric precipitations. The ability of peat to accumulate trace metals depends on the affinity of metal ions to bind with the common functionalities in the structure of peat and, as a consequence of this, the affinity of metals can be arranged in the sequence Hg>Cu>Pb>Ni>Zn>Co>Cd>Mn (Rinquist & Ohorn 2002).

Other factors influencing trace metal accumulation in peat can be identified as pH in the bog waters, the presence of low molecular weight complexing substances (for example, carboxylic acids), as well as a number of other dissolved substances (for example, sulphate ions or hydrogen sulphide) (Tipping *et al.* 2003). As it has been demonstrated in numerous studies carried out over the last decades, significant increases of accumulation of trace metals in peat have been observed. This has been due to an increasing anthropogenic pollution, as far as peat forming plants are concerned and peat serves as an efficient trap for trace elements brought in with atmospheric precipitations or wastewaters from local sources in the adjacent areas (Martinez Cortizas *et al.* 2002; Coggins *et al.* 2006; Shotyk *et al*. 2001; Kalnina *et al.* 2003). It has been stated that peat can serve as a good indicator of recent and as well as historical changes in the pollution loading (Shotyk *et al.* 2002). At the same time, the metal accumulations in peat are highly regional and therefore it is important to analyse trace elements regionally with regard to their distance from the pollution forming source.

Another reason why trace metal analysis in peat mass is important is their possible environmental and human health implications in cases where peat is used as fuel, or in agriculture or in other applications to the extent that in such case the accumulated trace metal amounts can be released in concentrated forms (from ash) and could contaminate the environment. Also, a significant amount of organic carbon in the form of peat is being stored, and thus peat use could play a significant role in the trace metal biogeochemical cycling.

The metal accumulation in peat have been studied in the West European countries quite widely (Damman 1978; Martinez Cortizas *et al.* 2002; Ukonmaanako *et al.* 2004; Coggins *et al*. 2006; Shotyk *et al*. 2001; Shotyk *et al*. 2002; Shotyk 2002), as well as in various territories in the vicinity of pollution sources including those also in Latvia's neighbouring country Estonia (Syrovetnik *et al.* 2004; Orru & Orru 2006). In Latvia the area of peat lands covers 10.7 % of the entire territory and raised bogs occupy 41.7% of the whole area covered by peatlands (Pakalne & Kalnina 2005). There are numerous raised bogs where peat mining is of a definite industrial importance (Snore 2004), but, at the same time, the territory of the country is relatively unpolluted as attested by the moss monitoring results (Nikodemus *et al*. 2004).

The objective of this article is to study the trace metal accumulation characteristics in peat, with respect to its properties and the impact of local and regional pollution sources on the metal accumulation characteristics in the ombrotrophic bogs.

MATERIALS AND METHODS

Peat sampling has been carried out in 44 representative raised bogs in Latvia (Fig. 1). For choosing the sampling sites of importance certain locations of the bog on the territory of Latvia were selected to ensure geographical coverage representativeness of the sampling sites with respect to geomorphological setting (Pakalne & Kalnina 2005). Several of the sampled bogs are of industrial importance (Olaines, Stružānu, Seda bogs).

Multidisciplinary proxy studies have been done in 2 ombrotrophic bogs located in the central part of Latvia's Riga District: Eipurs and Dzelves Krona (Fig.1). These bogs are located in the lowlands (coastal and middle Latvia lowlands), however they are of similar origins, but largely differing lithology. Eipurs, Dzelves Krona bogs have developed due to ground paludification. Both bogs studied recently are typical raised bog types including a number of bog lakes and pools. Not presently, nor historically the studied bogs have been affected by direct pollution sources.

Fig. 1. Sampling sites - ■; sites for in–depth studies: ○ A – Eipurs Bog; B – Kronu–Dzelves Bog.

The characteristics of the Eipurs Bog are as follows:

1) It is in the transformation process from raised bog to the *Pinus sylvestris* forest;

2) The maximal depth of the peat layer in the bog is 4.70 m;

3) The vegetation of the bog is dominated by *Pinus sylvestris* reaching up to 5–6 m height and pines cover up to 35 % of the bog territory.

4) The area of the bog is covered with shrubs (dominated by *Calluna vulgaris*, *Ledum palustre*). Among other dominant species *Eriophorum vaginatum, Rubus chamaemorus*, but more rarely *Cladina spp.* can be mentioned. Among the mosses the *Sphagnum* species (*S. fuscum, S. magellanicum*) dominate.

5) The territory of the bog is surrounded by a vegetation common to transition mires represented by the presence of *Carex lasiocarpa, Carex rostrata, Andromeda polifolia*, *Oxycoccus palustris* and dominating *Ledum palustre*; and *Eriophorum vaginatum*, whereas in some places *Drosera rotundifolia* can be found.

Kronu Dzelves Bog belongs to the developing raised bogs and is included in the list of *Natura–2000* protected areas. At the sampling area the communities of common raised bog with knolls covered by the *Sphagnum* moss and surrounded by ditches and small bog lakes can be found. The ground is covered by *Sphagnum* species such as *S. fuscum, S. magellanicum;* more rarely *S. rubellum.* From higher plants and shrubs

Eriophorum vaginatum, Oxycoccus palustris, Drosera rotundifolia, Calluna vulgaris can be mentioned; more rarely *Empetrum nigrum*. The trees are dispersed and dwarf forms of pines, reaching the height 2 –4 m, can be found only in few bog islands. Yet, more rarely also *Betula pubescens* can be found.

SAMPLING

The study of (in bogs Eipurs; Kronu Dzelves) coring and peat sampling has been accomplished in the cupola area of each bog, where the surface peat layers are elevated up to 2–4 m beyond the edge of the bog and has not been influenced by peat sliding (as suggested by Shotyk *et al.* 2001, and Coggins *et al.* 2006). The peat samples (50 cm long monoliths) were put in a special cartridge and wrapped in polyethylene film to preserve nature moisture, brought to the lab and sliced into 5 cm sections using a stainless steel knife. The outside edges were systematically discarded, as those could have been contaminated during the sampling. The first slice (+3 to 0 cm) corresponded to the living plant material on the bog surface. For survey of the metal concentration in the peat in the remaining 42 studied bogs in each site three peat cores were sampled using a corer (φ = 10 cm). Excess surface vegetation was removed *in situ*, to facilitate penetration of the peat surface. Samples of peat were taken to a depth of at least 50 cm. In the case of industrially mined bogs (where the surface layer already has been removed), the upper layer (~ 20 cm) was removed and the sampling done starting from that depth.

Peat sample preparation and analysis of physical and chemical properties

The peat material was oven dried at 105 ºC in Teflon bowls and ground in a centrifugal mill. The ash content, expressed as a percentage of the initial dry weight, was determined by combustion at 550 ºC for 12 h; all peat samples were analysed in duplicate.

The ^{14}C dating was done at the Institute of Geology of the Tallinn Technical University (Estonia). Elemental analysis (C, H, N, S, and O) was carried out using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). Carbon, hydrogen, nitrogen, and sulphur concentrations were determined using a combustion gas chromatography technique. The measured data were corrected for moisture and ash. The elemental compositions of all peat samples were determined as the mean value of three measurements.

All the reagents used in the analytical procedures were of analytical grade. Cleaning of plastic and glassware was carried out before the procedure by soaking in 14 % (v/v) HNO_3 for 24 h and then rinsing with Millipore water.

Major elements and trace metals and elements were determined after acid digestion (Krachler *et al.* 2001). Acid digestion consisted of a two step dissolution in Savilex beakers: 1) 100 mg of peat sample were transferred into beakers placed in the heating block (Biosan, Latvia) and digested with 5 ml of nitric acid 65 % cc. (Merck) and 1 ml of H_2O_2 30 % p.a. at 130 °C for 12 hrs for the organic matrix dissolution; 2) addition of 5 ml of nitric acid 65 % cc. (Merck) and 0.5 ml HF suprapur (Merck) for additional 6 hrs at 130 °C. After reaching room temperature, the completely clear, homogeneous solutions in the digestion vessels were quantitatively transferred into 10 ml calibrated flats and filled up to the mark with 10 % HCl.

Metal (Fe, Mn, Zn, Cu, Mg, Ca, Cd, Pb, Co, Cr, Ni, Mo) and As concentrations were measured by graphite furnace atomic absorption (GFAAS) (Perkin-Elmer AAnalyst 200) with background correction. Na, K was measured using flame photometer PAZ-3 with air-propane flame. Trace element (Se, V, Sr) concentrations were measured by total-reflection X-ray fluorescence spectrometry (TXRF). The acid digested peat sample were pre–spiked with 100 ng/ml Ga(III) as internal standard and dried (30 µl aliquots) on pre-cleaned quartz glass carriers, mostly resulting in homogeneous and transparent "polymer" films. The analytes were determined with a TXRF spectrometer (Röntec PicoTAX TXRF (Röntec GmbH); excitation: Mo tube operated at 50 kV and 1 mA, (live time 1000 s) equipped with a Ni/C reflection module (reflectivity 80%) and Be detector (area – 10 mm^2, thickness – 7.5 µm). Quality assurance was done using reference materials: NIST SRM 1547 peach leaves, NIST SRM 1575 pine needles, CRM 482 lichen. Accuracy was between 1 – 10 % for major elements and 1 – 2 % for trace elements. Detection limits were lower than 1 mg/kg for major elements. Detection limits for trace metals and other trace elements were lower than 1 µg/kg.

Peat decomposition analysis

Peat decomposition degree is a very important peat characteristic for evaluation of the element accumulation character. That analysis has been carried out by using centrifuging method according to Standard GOST 10650-71.

Peat botanical composition and pollen analysis

Peat botanical composition is closely related to plant feeding conditions, characteristics of bog depression, relief, underlying deposits and groundwater mineralisation degree, which substantially affect peat decomposition degree, moisture and physical-mechanical properties (Tyuremnov 1976).

Pollen analysis principally is based on a well-known method described by Moore and Webb (1978). Pollen data help to estimate time of peat formation, climate changes and vegetation development in the region as well as, to interpret peat properties (botanical composition, decomposition degree, moisture etc.).

Sorption capacity (after Sun *et al.* 2004)

To remove absorbed major and trace elements acid washing was done treating 5.00 g of peat with 0.1 N HNO_3 in glass beaker overnight, careful washing with Millipore water until removal of H^+ ions and drying at 105 °C. 1.00 g of acid washed peat was thoroughly mixed into 100 ml of 100 mg/l of $Cu(NO_3)_2$ in a glass bottle. The peat suspension was shaken for 24 h at a 20 °C and 175 rpm to ensure that adsorption equilibria were established. After filtration the Cu concentration in the filtrate was determined by GFAAS, and the sorbed Cu amount calculated as a difference. Each sorption experiment was done in triplicate.

Data treatment

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

RESULTS AND DISCUSSION

Major and trace element concentrations

The absolute values of the element concentration and their intervals (Fig. 2) found in peat in Latvia is in general similar to that reported for Estonia, Sweden, Belgium and other countries (Frontasyeva & Steinnes 2005; Orru & Orru 2006; de Vleeschouwer *et al.* 2007), but, at the same time the data reflect the local processes affecting element concentrations in the peat mass. This may be related both with respect to major elements (Na, K) which are found in lower concentrations than for example in Norway where sea salt aerosol containing precipitations influence their elevated concentrations, but also in respect to elements such Ca, Mg, Fe.

In the peat bulk mass, which is of industrial importance, the trace element concentration is comparatively low, especially if compared with element concentrations in other countries (Table 1). This aspect may be of importance considering the industrial uses of peat in agriculture. It can be assumed that the found concentrations of trace elements in peat ash composition (if the peat is used as fuel) especially if compared with the concentrations of major elements (Mg, Fe, Ca), could not pose significant harm.

The correlation matrix calculated for 13 elements analysed in the peat from Latvia is presented in Table 2. The element pairs Mn-Fe, Ca-Mn, Co-Mn, Fe-As,

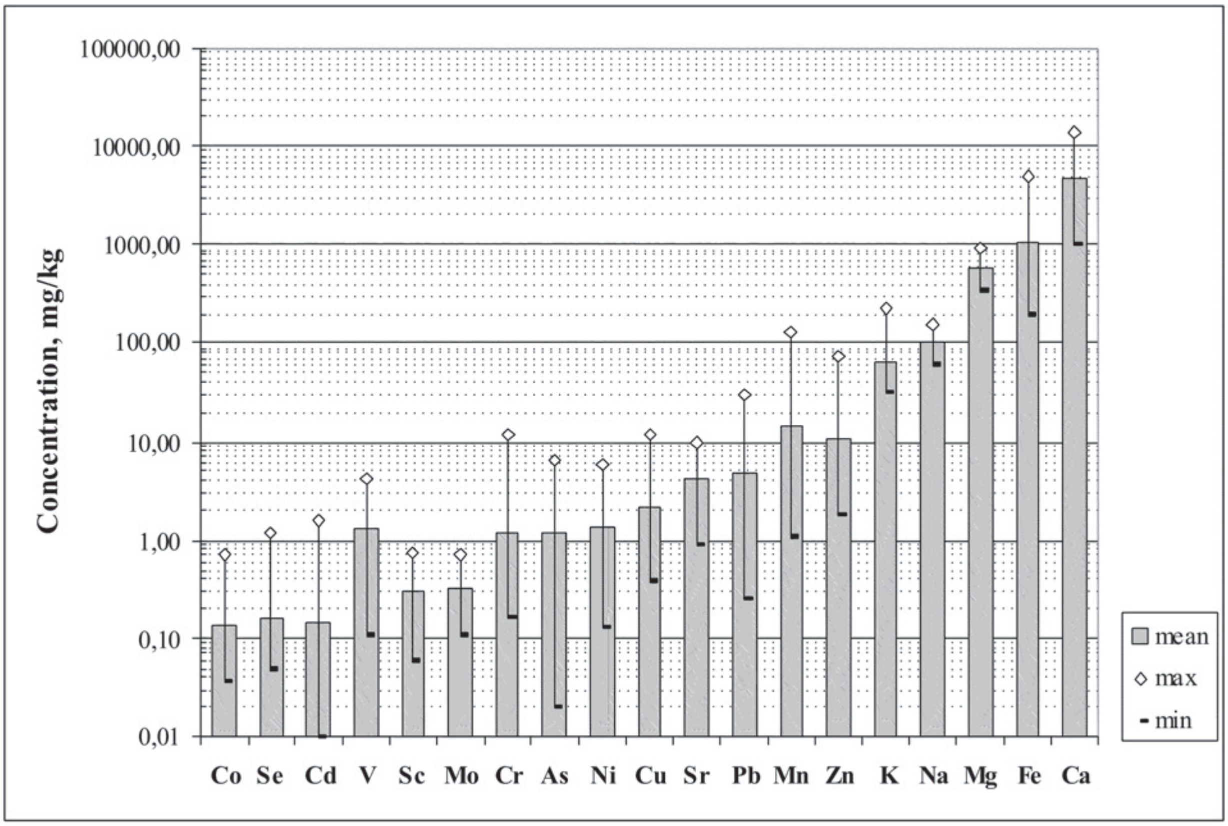

Fig. 2. Concentrations of major and trace elements in peat from Latvia.

Table 1. Major and trace element concentrations (mg/kg) in peat from 44 bogs in Latvia and in other countries.

Element	This study	Peat, Norway[i]	Peat, Estonia[ii]	Peat, Belgium[iii]
Na	101	698	na	na
Mg	569	2210	na	na
K	65	1465	na	na
Ca	4784	3830	na	na
Sc	0.31	0.52	na	na
V	1.33	3.75	0.51	na
Cr	1.17	12.5	0.39	na
Mn	14.47	75.4	14.16	na
Fe	1062	2050	na	na
Co	0.14	0.93	0.09	na
Ni	1.38	4.30	0.71	14.2
Cu	2.19	5.00	1.36	8.4
Zn	10.6	48	8.54	106
As	1.19	0.50	0.89	na
Se	0.16	0.37	na	na
Mo	0.32	0.85	0.21	na
Ag	0.07	0.06	na	na
Cd	0.14	na[iiii]	0.19	na
Pb	4.77	na	9.62	61.6

[i] Frontasyeva and Steinnes 2005; [ii] Orru and Orru 2006; [iii] de Vleeschouwer et al. 2007; [iiii] na – not analysed.

Fe-Ni, Fe-Ca Na-K were all significantly correlated. Strongest correlations were amongst the element pairs of evidently natural origin, for example, Na-K, Fe-Mn, Fe-Ca (Table 2). Correlations such as Cu-Cr, Fe-Ni, Fe-Pb might be attributed to industrial activity and long-range transport of pollutants (Percy & Borland 1985). At the same time for some elements (Cu, Zn, Mn, Ni, As) of importance could be both anthropogenic both natural sources.

Variation of major and trace element concentrations

One of the aims of this study was to determine whether the element distribution in profiles of ombrotrophic *Sphagnum* bogs can help to indicate anthropogenic activity (not only lead accumulation as it has already found in many other studies, for example, by Martinez-Cortinas *et al.* 2002; Shotyk *et al*. 2001; Shotyk 2002) and to what degree the variability of peat properties influence trace metal accumulation patterns. For in-depth studies of the metal accumulation pattern in peat sections, two raised bogs in central part of Latvia have been selected. The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate both, differences and similarities, of the studied bog development and peat properties. Kronu Dzelve Bog has been formed by the paludification process of the sandy ground manifesting itself in groundwater level increase and wet conditions in the small depression. The raised bog cotton grass peat layer covers the sandy bottom, which overlays by pine-cotton grass peat. The upper part of the peat section is represented by 3.2 m thick *Sphagnum fuscum* peat layer with decomposition degree 9 to 17 % (Fig. 3). Botanical composition is not very changeable. The composition of main peat forming species is very similar throughout the whole section and vary in small intervals: *Sphagnum fuscum* (60–75%), *Eriophorum vaginatum* 10–15%, *Sphagnum rubellum* 10–15% and dwarf shrubs 10–15%. The botanical composition of peat does not reveal vegetation and climate changes during bog development therefore pollen data are important as climate change indicators.

Completely different is the botanical composition of Eipurs Bog, though its origin is similar (Fig. 4),

Table 2. Correlation coefficient matrix of major and trace element analyses in peat in Latvia.

	Fe	Mn	Zn	Cu	Mg	Ca	Cd	Pb	Co	Cr	Ni	As	Na
Mn	**0.93**												
Zn	**-0.27**	-0.02											
Cu	**0.45**	**0.42**	-0.12										
Mg	0.11	**0.21**	-0.03	0.04									
Ca	**0.90**	**0.83**	**-0.32**	**0.52**	0.14								
Cd	0.08	**0.23**	**0.37**	**0.39**	0.06	0.16*							
Pb	**-0.20**	-0.03	**0.61**	0.03	-0.15	**-0.29**	**0.50**						
Co	**0.79**	**0.73**	-0.08	**0.30**	**-0.25**	**0.58**	0.04	0.05					
Cr	**0.45**	**0.47**	0.05	**0.70**	-0.03	**0.49**	**0.49**	0.20*	**0.32**				
Ni	**0.77**	**0.75**	-0.11	**0.59**	0.15*	**0.86**	**0.42**	-0.02	**0.52**	**0.64**			
As	**0.83**	0.77	-0.07	**0.48**	-0.01	**0.71**	**0.23**	0.10	**0.80**	**0.48**	**0.75**		
Na	**-0.42**	**-0.33**	0.15*	**-0.28**	**0.48**	**-0.52**	-0.08	0.08	**-0.46**	**-0.29**	**-0.44**	**-0.41**	
K	**-0.42**	**-0.25**	**0.30**	-0.14	**0.49**	**-0.52**	0.13	**0.33**	**-0.40**	-0.12	**-0.32**	**-0.39**	**0.75**

* Correlation is significant at the 0.05 level (2-tailed); **Bold** – correlation is significant at the 0.001 level (2-tailed).

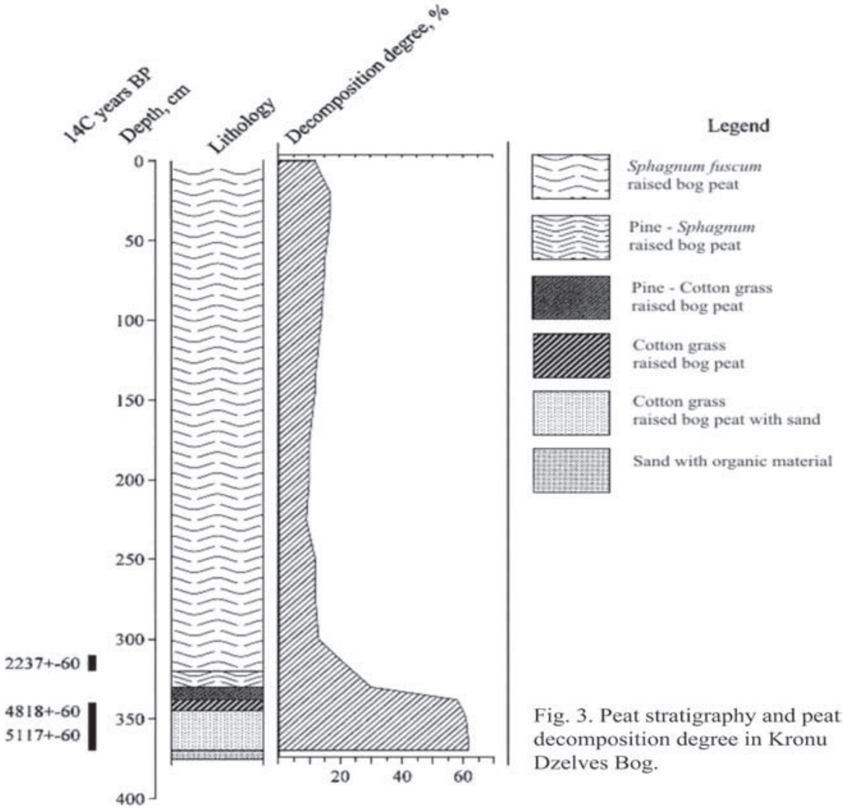

Fig. 3. Peat stratigraphy and peat decomposition degree in Kronu Dzelves Bog.

although it has been formed at least three thousand years earlier than Kronu Dzelves Bog.. The lowest part of Eipurs is formed by fen wood-grass peat, *Hypnum* and sedge-*Hypnum* peat (Fig. 4) which is covered by transition type wood peat. The upper part is represented by 3.45 m thick raised bog peat of different types and decomposition degree. For example, well decomposed (40–42 %) raised bog cotton grass–sphagnum peat in the depth interval 1.18–1.34 m and pine–cotton grass peat (decomposed 48 %) occur at the depth interval 1.34–1.39 m (Fig. 4), which point to a lower groundwater level in bog, so that apparently better conditions for peat decomposition had taken place. There is not enough data to decide whether it was due to the climate change or some other local condition, which could have caused groundwater level decrease. Although these bogs are located comparatively close, there was no signs of dryer conditions in Kronu Dzelve Bog, which demonstrated that local conditions for peat formation in both bogs have been different. Pollen data indicate that the start of peat formation at Eipurs Bog took place during the late Preboreal (at the Eipurs Bog) and the development of peat in Kronu Dzelves Bog - during the late Atlantic Time and at the beginning the Subboreal. The surface vegetation of the studied bogs is typical for ombrotrophic bogs in Latvia.

The elemental composition of the studied peat cores are summarized in Fig. 5, and Table 3. The ash contents in the studied bogs range between 0.30 ± 0.05 % and 6.10 ± 0.05 %, with an average content of 1.8 ± 0.05. The C concentration range from 40 to 55 % and H from 5.4 to 6.7 %, N from 0.5 to 1.5 %, S from 0.2 to 1.7 %, O from 38 to 49 %. The elemental composition of peat in the Eipurs Bog is comparatively variable and reflect the changes in the peat decomposition degree and peat type. C concentration in peat is increasing starting from the depth of 1 m up to the level of 53 % and then again decreasing. H concentrations demonstrate significantly higher variability, but changes of N concentrations (increased in the upper and lower horizons of the bog, but also dem-

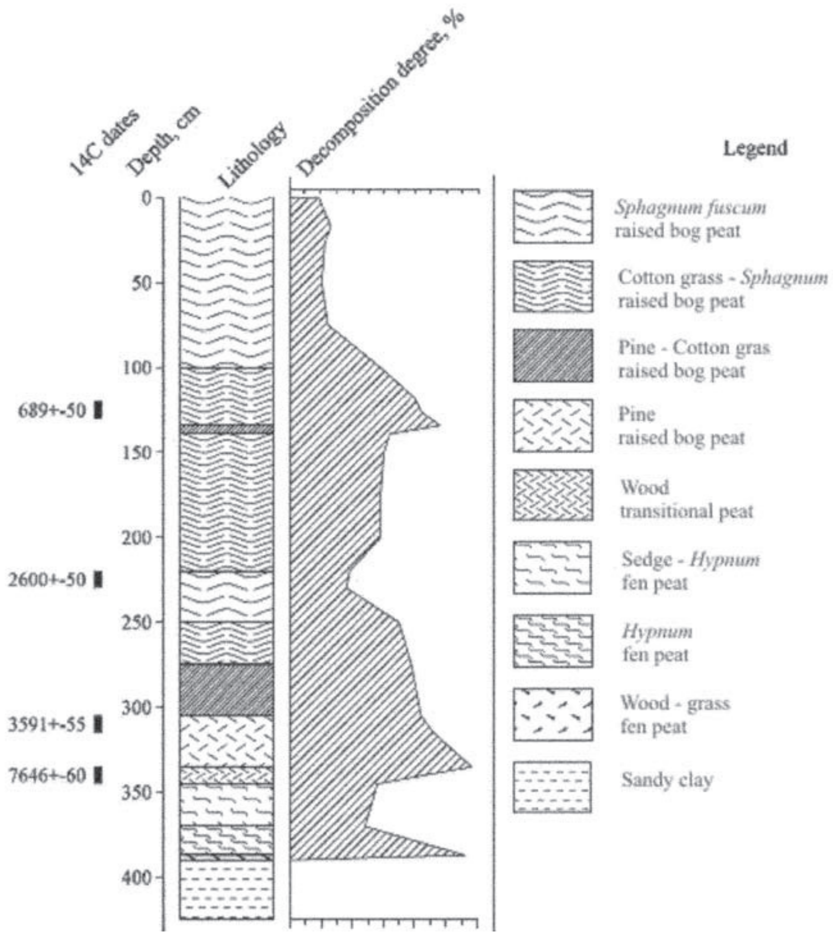

Fig. 4. Peat stratigraphy and peat decomposition degree in Eipurs Bog.

onstrating increased values coinciding with the changes in the peat composition and formation conditions) could be associated with changes in the peat botanical composition and their degree of decomposition. S concentrations are significantly lower just in few upper centimetres of the peat bog, but comparatively stable along the peat section. At the same time the elemental composition (Table 3) of Kronu Dzelves Bog is significantly different and largely reflects the peat section composition: the C content in the upper layers is much lower (~ 45 %) and comparatively uniform up to depth of 3.25 m, but then rapidly increases reaching 55 % for highly decomposed peat.

To characterize the peat composition, element ratios have been used (Fig. 6). C/N ratio is an index of the humification process at first due to specific microbial activity in anaerobic, acidic environment. This ratio can be efficiently used as a measure of peat composition and degradation. The decreasing C/N ratios indicate increasing peat decomposition and *vice versa*. H/C ratio is an index of molecular complexity and it ranges from 1.6 to 1.2. It is relatively constant with respect to depth; below 50 cm, it decreases. On the other hand, O/C ratio is considered an indicator of carbohydrate and carboxylic contents and can be directly related to aromatization of the organic mater forming peat. O/C ratio decreases with depth, however, in layers with a higher decomposition degree also values of this indicator are high.

The trace element accumulation in peat is directly related to the record of human impact both from the regional, as well as from global perspective (Shotyk 2002). The history of the human impact on territory of Latvia is related to comparatively low level of industrial activity (especially, if compared with many regions in the Southern and Central Europe) since farming and land clearing in this area was a dominant

Table 3. Peat decomposition degree and elemental composition of peat in Kronu Dzelves Bog.

Depth, cm	Decomposition, %	C %	H %	N %	S %
-5	12	44.77	5.91	0.73	0.89
-105	14	45.68	5.78	0.53	0.88
-160	12	46.05	5.81	0.55	0.88
-205	10	45.53	5.60	0.47	0.81
-240	9	44.84	5.47	0.45	0.88
-305	13	47.42	5.75	0.76	0.87
-320	12	45.73	5.55	0.62	1.22
-325	24	44.73	5.44	0.60	0.64
-335	30	52.10	5.20	1.51	0.73
-340	38	52.70	5.20	1.70	0.77
-350	> 60	55.53	6.20	1.23	1.19

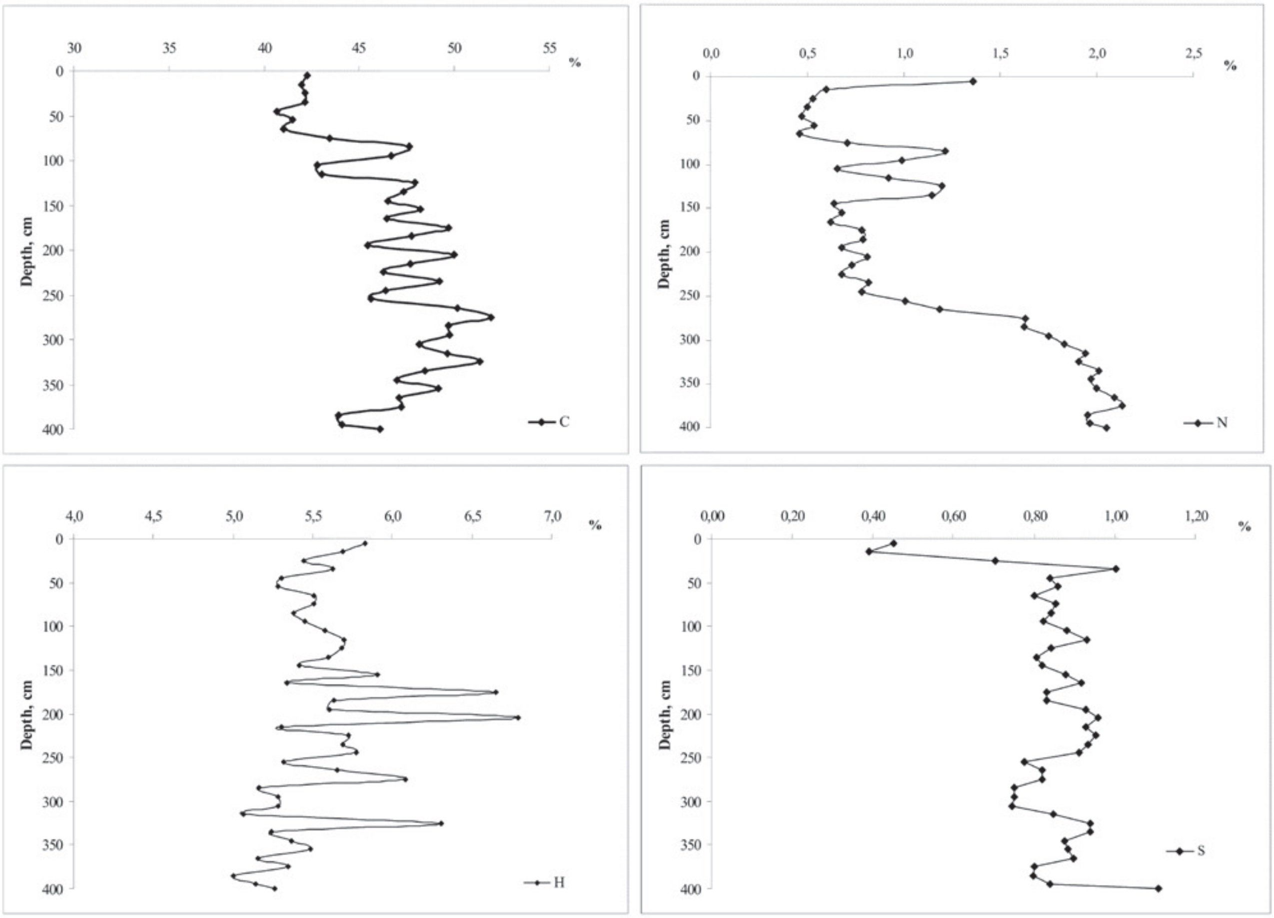

Fig. 5. Elemental composition of Eipurs Bog peat.

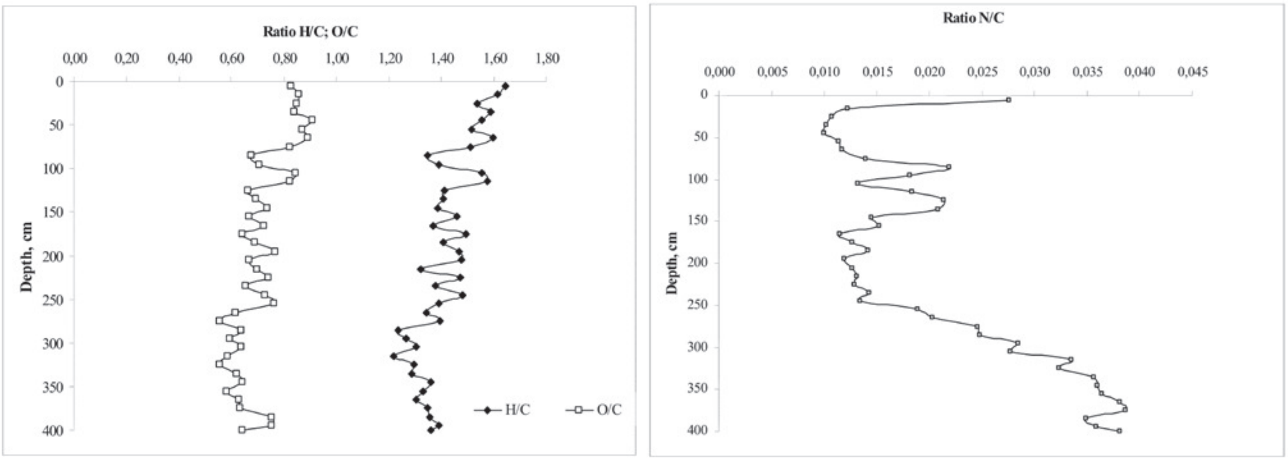

Fig. 6. Element ratio in peat from Eipurs Bog.

form of agriculture for centuries. Only in the second half of the 19th century intensive development of industrial production began, first in Riga and few other biggest cities, but, again, it could be assumed that the loading on environment, especially with respect to the pollution with trace elements was not very intense. The situation changed after World War II, but starting from the 90 ties of the 20th century, large scale industrial production ceased again.

Concentrations of the major and trace elements in the peat sections of the studied bogs in Latvia demonstrate high variability (Figs. 7–10). Variability of the concentrations of the studied elements is equally high both for major elements, possibly of natural origin (Na, K, Ca, Mg, Fe etc), both with regard to the concentrations of trace elements presumably of anthropogenic origin (Pb, Cu, Cd, Ni, As).

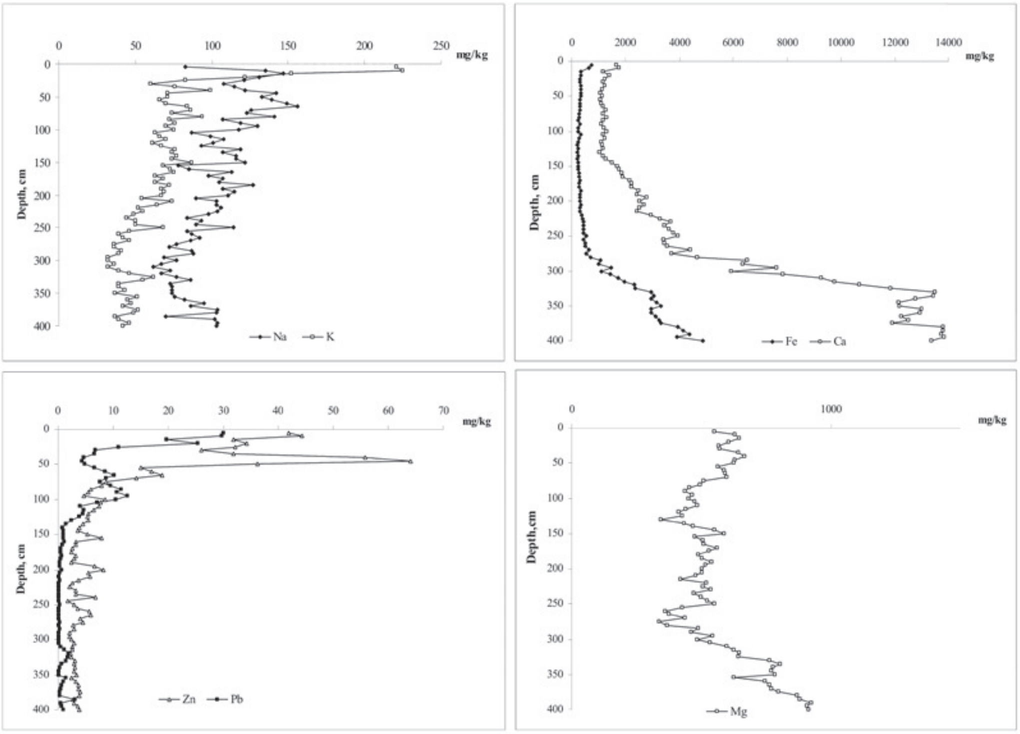

Fig. 7. Na, K, Fe, Ca, Zn. Pb, Mg concentrations (mg/kg) in peat core from bog Eipurs.

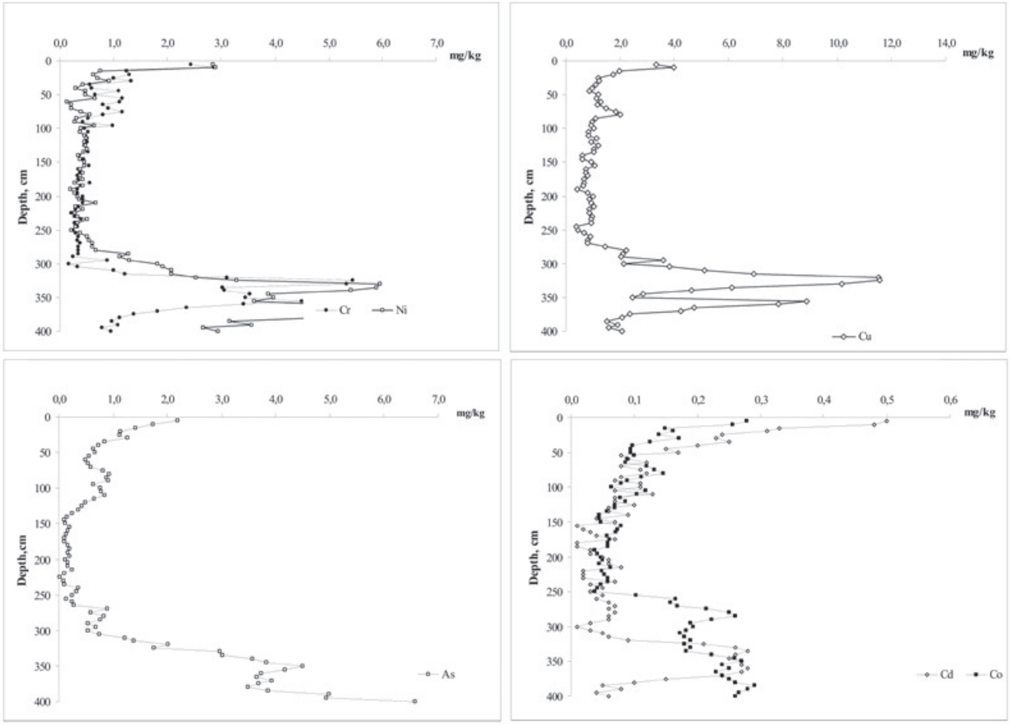

Fig. 8. Cr, Ni, Cu, As, Cd, Co concentrations (mg/kg) in peat core from bog Eipurs.

Peat sections serve as an archive of storable profiles of major and trace elements. As an exception to this can be considered Na and K, as far as these elements are mobile, but their source could be atmospheric precipitations (sea salt and soil born dust), released during the decay of living plants. As it is seen in the example of bog Eipurs peat section, the Na and K concentrations (Fig. 7) are elevated to the top layer, then gradually decrease and slightly increase at the bottom layer. The profile of the Na and K changes at first can influence their biogenic recycling and high mobility of these elements considering also the changes of the water table (Gorres & Frenzel 1997). Changes of concentrations of other naturally occurring elements Fe, Ca, Mg, Mn in Eipurs Bog (Fig. 7) or in Kronu Dzelve Bog (Fig. 9) have similar character: low concentrations at upper layer and increased concentrations in Eipurs Bog starting from depth ~ 3 m, but in Kronu Dzelve Bog 2.5 m. The behaviour of Fe could be related to high stability and mobility of Fe^{+2} ions under reducing conditions as far as under such conditions these ions are readily soluble and may be transported upward with the groundwater flow until conditions favour oxidation to the immobile Fe^{+3}. Fe and Mn behaviour is also influenced by redox conditions and these elements may behave similarly in the peat. The enrichment in element concentration in the peat profiles are not limited to the uppermost peat layer of recent origin where active moss growth and decay processes take place involving metabolic mobilization of nutrients (including also K, Fe, but also elements as Ca, Mg, Cu, Zn).

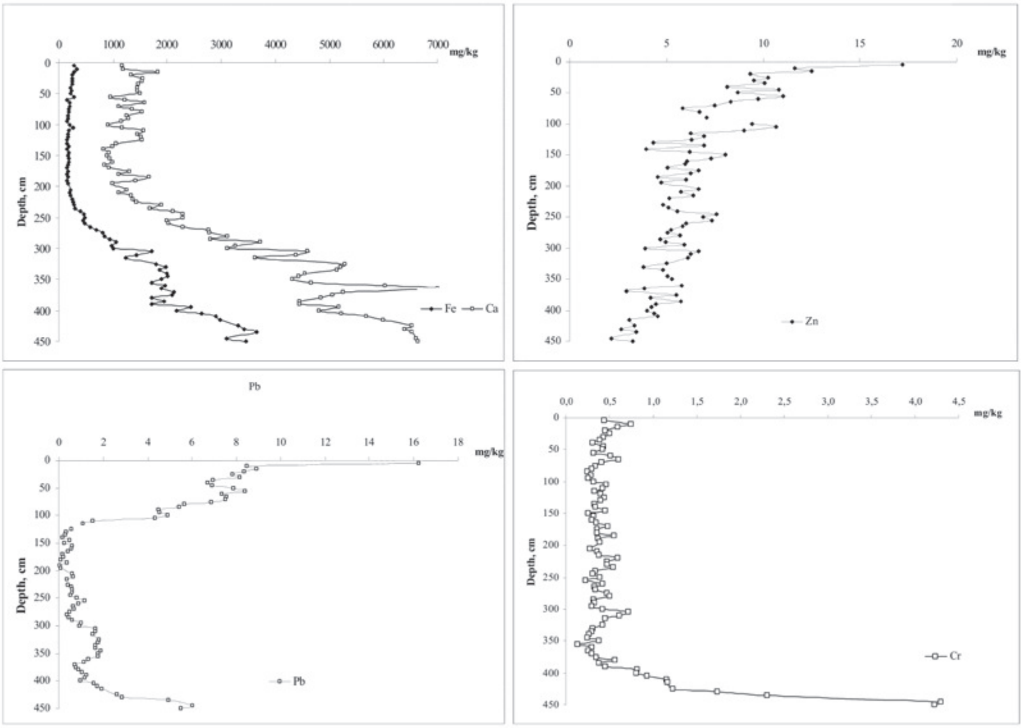

Fig. 9. Fe, Ca, Zn, Pb, Cr concentrations (mg/kg) in peat core from bog Kroņu Dzelves.

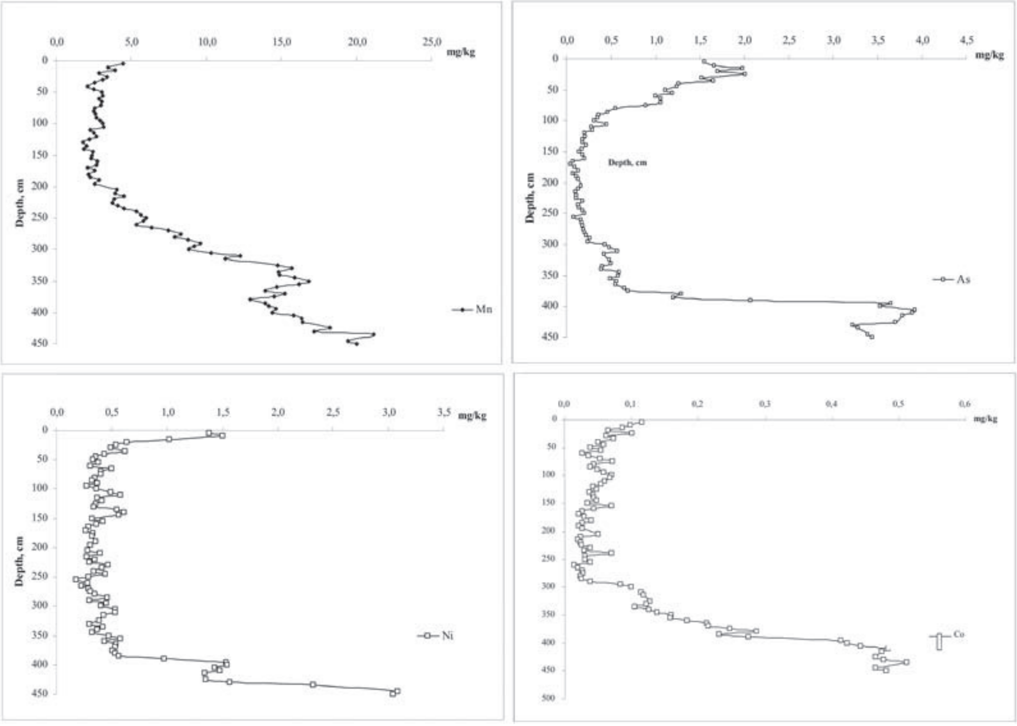

Fig. 10. Mn, Ni, As, Co concentrations (mg/kg) in peat core from bog Kroņu Dzelves.

Pb and Zn concentrations follow a similar trend at both sites: concentrations within the bulk of the peat section are stable (and they can be considered as background concentrations for corresponding elements in peat), but then steeply increases towards the surface of the bog, again slightly decreasing at approximately 10–20 cm below the surface. A subsurface maximum is also observed for As, Ni. Increase in Pb accumulation coincides with the maximum use of leaded petrol in the USSR and West European countries. It could be supposed that control of leaded petrol use in late 1970's explained the decreasing trend of this element in the peat profiles. The timing of increased lead accumulation are similar to those found in peat cores from Ireland (Coggins *et al.* 2006), Germany (Shotyk 2002) and other countries. It could be supposed that also the increased levels of studied trace elements, such as Cr, Ni, Co, As, Cu, Cd in the upper layers of the peat cores can be related to air pollution due to industrial production. Studied elements are largely immobile in the peat (Gorres & Frenzel 1997) and so they can be used as indicators of anthropogenic activity. At the same time for most of dominantly anthropogenic trace elements in the peat sections characteristic is also accumulation

Table 4. Correlation between trace elements in the peat of Kronu Dzelve Bog from depth 0–50 cm.

	Fe	Mn	Zn	Cu	Cd	Pb	Co	Cr	Ni
Mn	0.726*								
Zn	0.149	-0.088							
Cu	**0.927**	0.677*	-0.028						
Cd	0.025	0.272	-0.465	0.078					
Pb	**0.784**	0.658*	-0.148	**0.898**	-0.006				
Co	**0.899**	**0.829**	-0.185	**0.922**	0.323	**0.869**			
Cr	**0.894**	0.743*	0.046	**0.947**	0.240	**0.846**	**0.934**		
Ni	**0.938**	0.758*	0.015	**0.962**	0.209	**0.789**	**0.934**	**0.969**	
As	**0.840**	0.706*	-0.253	**0.874**	0.301	**0.863**	**0.962**	**0.867**	**0.855**

* - Correlation is significant at the 0.05 level (2-tailed); **Bold** - Correlation is significant at the 0.01 level (2-tailed).

Table 5. Correlation between trace elements in the peat of Kronu Dzelve Bog from depth 100–200 cm.

	Fe	Mn	Zn	Cu	Cd	Pb	Co	Cr	Ni
Mn	0.440								
Zn	-0.085	0.526*							
Cu	-0.476*	0.378	**0.645**						
Cd	-0.379	0.159	0.296	0.413					
Pb	-0.123	0.531*	0.530*	0.462*	**0.565**				
Co	0.000	**0.623**	0.478*	0.356	0.334	**0.834**			
Cr	-0.332	0.120	0.167	0.330	0.056	0.158	0.142		
Ni	-0.464*	0.101	0.170	0.469*	0.197	0.225	0.237	**0.938**	
As	0.104	**0.609**	**0.570**	0.302	0.474*	**0.938**	**0.851**	0.127	0.143

* - Correlation is significant at the 0.05 level (2-tailed); **Bold -** Correlation is significant at the 0.01 level (2-tailed).

in deeper layers of bog, possibly due to the feeding pattern with the groundwater. The pattern of element concentration changes in the peat sections in the studied bogs indicates that the major source of this element is weathering processes at the bottom layer of the bogs (Kalnina *et al.* 2003).

Comparatively increased values of As concentration are found in the upper 50 cm of the peat core (Fig. 8, 10). Arsenic concentrations decreases with depth, reaching lowest levels and significantly increases in the lowest part of the peat section. As suggested Shotyk (1996) also trend of As concentration changes in a peat column can reflect increased anthropogenic load, for example, increased use of As containing pesticides, use of P fertilizers as well as coal burning. Arsenic behaviour could be also influenced by redox conditions.

Also the character of correlations between metals depending on the sampling depth (Tables 4, 5) reflect the processes affecting trace element concentrations in the peat. In the upper layers (0–50 cm) of the Kronu Dzelves Bog peat the strongest correlations were amongst the element pairs of evidently anthropogenic origin, for example, Pb-Cu, Cu-Co, Cr-Cu, Ni-Cu, As-Cu, Pb-Co, Pb-Cr, Ni-Pb, As-Pb. Also the element

Table 6. Correlation matrix of parameters describing peat properties, sorption capacity and found Cu amounts in peat of Kronu Dzelves and Eipurs Bog.

Cu	0.323							
H	0.004	0.067						
N	-0.133	**0.664**	-0.142					
O	-0.346	**-0.582**	**-0.454**	**-0.617**				
C	0.448	**0.439**	**0.477**	**0.423**	**-0.963**			
O/C	-0.384	**-0.534**	-0.394*	**-0.615**	**0.929**	**-0.972**		
Sorption capacity	-0.973*	-0.299	-0.210	-0.431	**0.767**	**-0.835**	**0.832**	
HA/FA	0.848	**0.660**	0.293	0.649*	**-0.840**	**0.736**	**-0.805**	-0.688*
	Decom-position	Cu	H	N	O	C	O/C	Sorption capacity

* – correlation is significant at the 0.05 level (2-tailed); **bold** – correlation is significant at the 0.01 level (2-tailed).

pairs Cu-Fe, Pb-Fe, Co-Fe, Cr-Fe, Ni-Fe, As-Fe were all significantly correlated, thus indicating that the industrial activity and long-range transport of pollutants associated with particulate matter with high Fe concentration might be a major source of trace metals. At the same time the character of correlations between major and trace elements in peat in deeper peat layers (100–200 cm) formed before intensive human impacts (the age of peat from these horizons is from 700–2500 years after ^{14}C dating) (Table 5) very much differs as far as the strongest correlations were amongst the element pairs of possibly natural origin: Mn-Zn, Mn-Co, Mn-As, Cu-Zn, As-Zn, Pb-Co, Pb-As, Cr-Ni.

In studies of metal accumulation in peat not much attention has been paid to variability of the peat botanical composition and decomposition degree on metal accumulation in peat which may account for some variation in concentrations observed. In our study we have selected two bogs with contrasting lithology (se Figs. 3, 4) and thus also peat composition as indicated by elemental composition (Table 3; Fig. 5). Furthermore the metal sorption capacity on an example of copper sorption and its correlation with the peat properties has been tested - elemental composition, as indicated by the C, H, N, O concentration and peat decomposition indicators, such as humic and fulvic acid ratio (HA/FA), decomposition degree (expressed in %) and element ration O/C illustrating changes of oxygen containing functional groups (-COOH, -OH) in the peat (Table 6).

This study proved that testing the metal sorption capacity on example of copper (II), it becomes evident that sorption capacity of the peat depended on the concentration of oxygen containing functional groups in the peat, considering significant and positive correlation with the O concentration and O/C element ration and that it is growing with an increasing degree of decomposition and HA/FA ratio of the peat humic matter (Table 6). However the peat seems to be largely unsaturated with respect to metal ions, since sorption capacity statistically significantly can not be correlated to trace element concentration, as it can be seen on the example of copper. The actual metal concentration can rather be related to the presence of nitrogen containing ligands and humic/fulvic acid ratios.

CONCLUSIONS

The degree of trace element concentrations in bogs of Latvia can be considered as low (especially in comparison with regions where intensive anthropogenic activity has influenced trace element accumulations in upper peat layers). The element distribution within peat layers clearly shows the correspondence between element concentrations and the respective histories of local and regional environmental pollution.

At the same time, local geochemical processes may influence significant trace element accumulations in peat mass (for example that of arsenic in the deepest layers of peat, possibly influencing the use of peat for industrial purposes. Trace element concentrations in peat profiles support the concept with respect to the possibility of using element concentration records to track the regional and global environmental pollution problems with trace elements.

Trace element sorption capacity onto peat is influenced by peat properties and depends on the concentration of oxygen containing functional groups in peat and is growing with an increasing HA/FA ratio of the peat humic matter but decreasing with growing degree of decomposition of the peat. However, the peat seems to be largely unsaturated with respect to metal ions, but the peat sorption capacity can be correlated to the presence of nitrogen containing ligands and humic/fulvic acid ratios.

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