

Major and Trace Element Accumulation in Fen Peat from Elki and Viki Mires in Western Latvia

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Abstract. The purpose of this paper is to study the characteristics of the major and trace element accumulation in fen peat of two minerotrophic mires located in depressions of the Austrumkursa Highland. Concentration of the 13 elements and their occurrence in fen peat was determined by using atomic absorption spectrometry. These elements reflect the processes during mire development, impact of botanical composition, moisture and peat decomposition degree. The upper layers of the peat profile show predominantly anthropogenic impacts and precipitation effects, while characteristics of the lower layers indicate groundwater flow/saturation effects. It is important to find out how changes in fen peat characteristics in the upper peat layers depend on element accumulation, which can be affected by human activities and how they are different in comparison to the characteristics of lower peat layers excluded from anthropogenic impact.

Keywords: fen peat, trace and major elements, accumulation rate, atomic absorption spectrometry, anthropogenic impact.

I. INTRODUCTION

Worldwide, mires are formed by 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 [1].

Fen peat is formed from partly decomposed eutrophic plants, based on mineral-rich groundwater feeding during their life cycle.

The developed surface area and large number of acidic functional groups common to peat, determine the ability to bind trace elements included in the remains of the living organic matter, either both as a sedimentary, deposited, particulate matter and as sorbed or complex metal ions [2].

Major and trace elements in fen peat are very important indicators of past and current conditions. They indicate anthropogenic and natural traces of historical changes in nature, for example, in atmospheric contaminant fluxes or in climate. Mires work as geochemical archives, because of peat, which is an effective trap.

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, the affinity of metals can be arranged in the sequence: Hg>Cu>Pb>Ni>Zn>Co>Cd>Mn [3].

Other factors influencing trace metal accumulation in peat can be identified as pH in the mire waters, the presence of low molecular weight complex substances (for example,

carboxylic acids), as well as a number of other dissolved substances (for example, sulphate ions or hydrogen sulphite) [4]. 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 growing anthropogenic pollution, as far as peat forming plants are concerned and peat serves as an effective trap for trace elements brought in with atmospheric precipitations or wastewaters from local sources in the adjacent areas [5], [6] and [7].

It has been stated that peat can serve as a good indicator of recent and as well as historical changes in the pollution loading [8]. At the same time, the metal accumulations in peat are highly regional with regard to their distance from pollution forming source. Another reason why analysis of trace metals 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 trace metal biogeochemical cycling.

Metal accumulations in peat have been studied in the west European countries quite widely [5], [6], [7], [8], [9], [10] and [11], as well as in various territories in the vicinity of pollution sources including those in Latvia's neighbor country – Estonia [12] and [13]. In Latvia, the area of peatlands covers 10.7% of the entire territory and raised bogs occupy 41.7% of the whole area covered by peatlands [14].

II. MATERIALS AND METHODS

Site location

Peat sampling was carried out in two specific minerotrophic mires in western Latvia, both of them located in Austrumkursa Highland (Fig. 1). The Viki and Elki Mires both are located in Lielaucē Hillcock. They are of similar origin, but of a very different lithology and botanical composition, which point at different mire development conditions. Both mires have developed due to lake depression fill-in.

Nowadays Elki Mire is under transitional mire stage conditions, therefore fen peat is relatively non-affected by modern human activities or air pollution. Viki Mire is still in fen stage and there are possible anthropogenic impacts in upper peat layers. There are also insufficient attentions to metal accumulation studies in fens given [15].

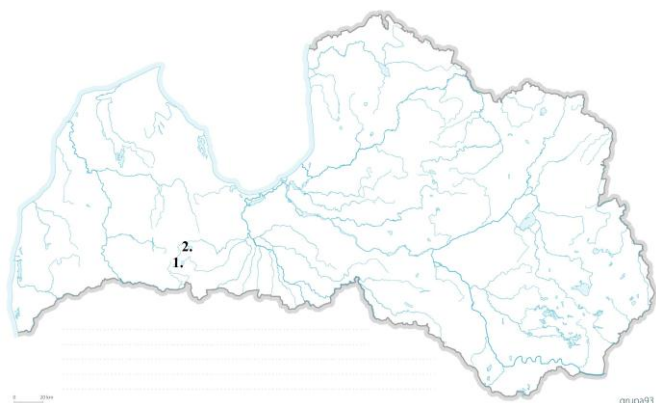


Fig.1. Site locations (1 – Elki Mire, 2 – Viki Mire)

Sampling

Sampling at Elki Mire was accomplished at coordinates: 56°37'22"N; 22°59'16"E. Sampling at Viki Mire was accomplished at coordinates: 56°30'58"N; 22°54'32"E.

Coring, sounding and sampling was accomplished in the central areas of both mires, where the most complete geological section was present, and which was also less affected by the processes in the adjacent areas [6]. The 0.5 m long peat monolithic samples were put in special plastic cartridges and wrapped in polyethylene film to preserve natural moisture and other parameters.

Samples were brought to the lab and sliced into 0.05 m sections using stainless steel knife. The outside edges of each sample were discarded, because of probable contamination during sampling.

Peat sample preparation and analysis of physical and chemical properties

From each 0.05 m peat sample piece of 5.0000 g mass were taken for loss on ignition analysis. The ash content, expressed as percentage of initial dry weight, was determined by combustion at two different temperatures: 550°C for 4 h and 950°C for 2 h [16]. The organic and carbonate content, also expressed as percentage, was determined by combustion at the same temperatures – all samples were oven-dried, non-grounded.

Some pieces were earmarked for botanical composition, decomposition analysis and ¹⁴C analysis. The remainders of each sample were used for major and trace element analysis; samples were oven-dried in Teflon bowls at 105°C and grounded in pestle. The major and trace element concentration was determined by atomic absorption spectrometry. Element (Na, Mg, K, Mn, Fe, Cu and Zn) concentrations were measured by acetylene-air flame and Ca concentration was measured by acetylene-N₂O flame. To measure Cd, Co, Cr and Pb concentration – graphite furnace atomic absorption with background correction was used.

For AAS analysis each sample was specially prepared. 1.0000 g of oven-dried grounded fen peat sample was transferred into the beaker. 25 ml 50% HNO₃ and 5 ml 30% H₂O₂ were added to the sample, mixed and left for 24 h. The samples were boiled at 150°C until half of the liquid evaporated, the another 25 ml of HNO₃ were added and boiled

until first vibrate. Samples were filtered and diluted with Millipore water to 50 ml total volume and transferred into tubes.

Peat decomposition analysis

The influence of organic matter degradation on major and trace elements in fen peat is highly important. Peat decomposition degree was estimated according to standard GOST 10650-72. The method is as follows: in aquatic conditions remove the coagulative humus from fiber by sieve analysis, put samples in centrifuge, and determine decomposition degree by specific schedules.

Peat botanical composition

Peat botanical composition has a substantial effect on a lot of other peat properties, it also shows plant-feeding conditions and mire characteristics. This parameter is one of the most important in major and trace element accumulation in fen peat. Determination of peat botanical composition assists in finding fossil plant macro-remain percentages and determining the type of peat. Peat type mostly is characterised by the formation conditions. Peat botanical composition is also used to predict mire vegetation dynamics within certain time periods. To determine micro-fossil plant residues microscope with magnification of 100 and 400 times is in use. The way to establish peat types are quantitative relationships between plants determination.

Data treatment

Statistical analysis was performed by using Microsoft Excel 2007 software with math add-ons. Relationships and dependence between the elements were assessed and the correlation was established by using Pearson Product-Moment correlation coefficient. In all cases 3 different coefficient grades were used: coefficient less than 0.2 describes very weak correlation between the elements, 0.2 – 0.4 weak, 0.4 – 0.7 average strong, more than 0.7 shows strong correlation between the elements (all coefficients are two-tailed). For the parameters, such as carbonate content and moisture, mathematical equations were used involving values from Loss on ignition analysis suggested by Heiri [16].

III. RESULTS AND DISCUSSION

Insight in the history of origin

Since the fifties of the previous century ¹⁴C dating method (radiocarbon dating) has become an important part in quaternary research [17]. According to ¹⁴C analysis The Elki Mire started to form about 8 000 yr BP, when gyttja sediments became covered by fen peat and the lake started to overgrow, as indicated by freshwater fossil finds – *Bithynia tentaculata*, *Valvata macrostoma* and *Radix labiata*. Similar conditions were also to the Viki Mire 7 600 yr BP. The Elki Mire (Fig. 2) over time developed into a transitional mire, while Viki Mire (Fig. 3) has remained as Fen.

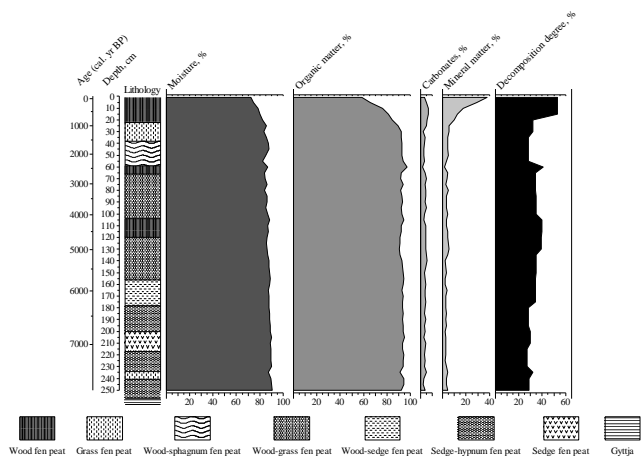


Fig.2. Changes of peat characteristics at Viki the Mire

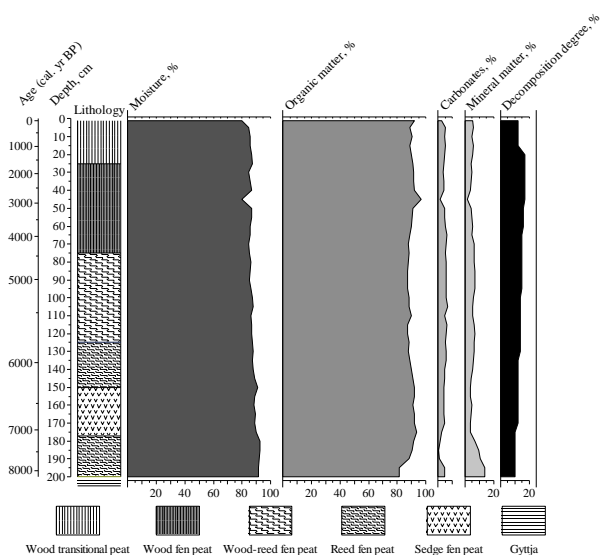


Fig.3. Changes of peat characteristics at the Elki Mire

Botanical composition

There is only one peat type in both mires similar – wood fen peat, but even this type has some unique botanical component which is specific to particular place.

Botanical composition of Viki fen peat (Fig. 3) is more complicated, than Elki fen peat (Fig. 2). There (Viki) fen peat is excreted in 15 layers with different botanical composition, while in Elki fen peat is released only in the eight.

The dominant peat types at Viki and Elki Mires are combined wood fen peats. At Elki Mire: wood fen peat (0.25 – 0.75 m), wood-reed fen peat (0.75 - 1.25 m). At Viki Mire: wood fen peat (0.00 – 0.25 m), wood-sphagnum fen peat (0.40 – 0.60 m), wood-grass fen peat (0.60 – 0.65 m, 1.05 – 1.20 m), wood-sedge fen peat (1.55 – 1.75 m).

The divisional transitional wood peat at Elki Mire is almost similar to that below, only in wood fen peat at 0.25 – 0.50 m are of different percentage values (*Pinus*, *Sph. magellanicum*, *Erioph. vaginatum*, *Phragmites*, *Equisetum*) and hypnum moss appears for the first time (the stalks), also *Carex lasiocarpa* is not observed.

In comparison to Viki Mire where the first centimetres are also formed of wood fen peat (only without any divisional layers), there are sand content and hardwood residues observed, which are not found at Elki Mire within the first centimetres of wood fen peat. One more difference is that in wood fen peat (0.00 – 0.20 m) at Viki Mire there are *Scriptus* residues.

Moisture and decomposition degree

Due to different botanical composition the researched mires have own characteristics in moisture and decomposition degree. However peat decomposition analysis shows, that in both mires in the lower peat layers disintegration degree is lower than in the upper layers and there is strong correlation between decomposition and moisture. The correlation shows also strong connection between peat decomposition and botanical composition.

At Elki Mire in fen peat the moisture value (> 85%) increases with depth, however at 0.45 m depth there is a significant drop (79,8%) in wood fen peat observed, the age corresponds to 2 800 yr BP.

At Viki Mire in fen peat moisture (> 80%) also increases with depth and without any significant fluctuations, however wood fen and grass fen peat in the first 0.30 m (last 1 400 years) is a bit dryer (< 80%).

Decomposition degree is inversely related to moisture and decreases with depth. The 0.45 m depth in wood fen peat of Elki Mire is also marked by degree of decomposition, at this level it increases with depth. In fen peat of Viki Mire fluctuations in decomposition degree are observed and it is clear, because of complicated botanical composition.

In both mires the highest decomposition degree is present at the combined wood fen peats and the lowest at sphagnum and grass fen peats – it points at the fact that decomposition degree depends on peat particle size and density.

Carbonate content

Mires are one of the largest terrestrial carbon reservoirs [18]. Carbon accumulation in mires is a function of the balance between production of living plants at the top surface aerobic layer and decomposition in both the acrotelm and catotelm (underlying anaerobic layer) [19]. As peat in the acrotelm is exposed to oxygen and varying water levels, it is subject to a higher decay rate. Once in the catotelm, the decay rate declines sharply and becomes independent of minor climatic fluctuations. The rate of peat transfer from acrotelm to catotelm, or the acrotelm residence time, therefore largely determines net peat accumulation [18].

The 0.45 m depth in Elki Mire showed a marked decline in natural moisture value followed by reduced carbonate content, this depth, as mentioned, corresponds to the period before about 2 800 years, that is significant also in some other mire sediments of Latvia. At that time there were some extreme conditions in nature, a possible drought. An increase is observed at 1.70 – 2.00 m, where reed fen and sedge fen is with gytja represented, it corresponds to 8 000 – 7 000 yr BP.

The 0.70 m depth (wood-sphagnum fen peat) in Viki Mire corresponds to 2 800 yr BP age, yet there were no specific

changes in moisture values observed, however there is a decreased carbonate content. At Viki Mire increased carbonate content is observed at the first 0.30 m in wood fen and grass fen peat, where the lowest moisture values are also represented.

Major and trace element concentrations in fen peat of study areas

According to their concentration the dominant major elements are calcium, magnesium and iron (Fig. 4 and 5), however fen peat is usually observed in slightly higher concentrations of some elements than moss peat, because of its origin and botanical composition [20].

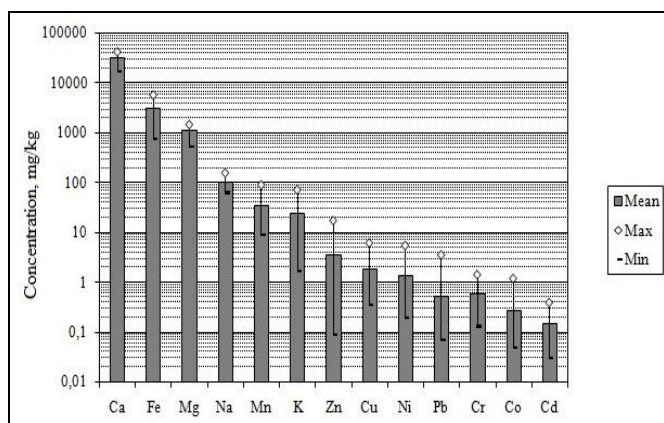


Fig.4. Major and Trace Element Concentration Values at the Viki Mire

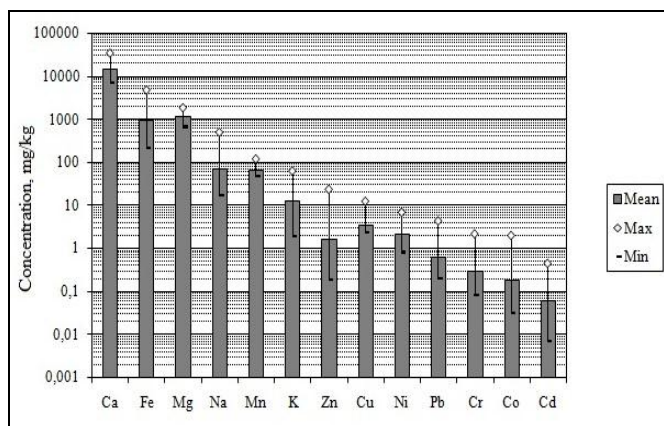


Fig.5. Major and Trace Element Concentration Values at the Elki Mire

Major and trace element accumulation is dependent on various conditions, but overall, both mires have higher mean Mg, Ca, Fe, Mn and Co concentrations and lower K, Cd, Cu, Zn and Pb concentrations (with some exceptions) than other shown mires. In some aspects fen peat is more similar to Norway's peat, than moss peat of Latvia (Tab. 1).

The absolute values – min., mean, max., of element concentration in fen peat and their intervals are a bit different to concentrations of major and trace elements in peat from other mires in Latvia [21]. This difference is also observed between the research sites. The element spreading sequence in both mires is almost identical; however there are changes between potassium and copper places in the sequence and

mean concentrations of some trace elements are lower at Viki Mire.

In the correlation matrix of fen peat from Elki Mire 13 elements are calculated (Tab. 2). A strong positive correlation ($r > 0,7$) between several major and trace elements is observed: Cu-Zn, Co-Zn, Cr-Zn, Ni-Zn, Co-Cu, Cr-Cu, Ni-Cu, Na-Cu, Cr-Co, Ni-Co, K-Co, Ni-Cr, K-Cr, K-Ni, K-Zn.

It is reasonable to assume, that these element pairs more or less are of natural origin, because fen peat is covered by 0.25 m thick layer and there are no high trace element concentrations observed at the upper fen peat layers. According to ^{14}C analysis the surface of fen peat is about 1 500 years old, when no significant anthropogenic influence was yet possible.

TABLE 1

MAJOR AND TRACE ELEMENT MEAN CONCENTRATIONS (MG/KG) IN FEN PEAT FROM STUDY AREAS WITH COMPARISON TO OTHER MIRES

	Elki Mire	Viki Mire	Eipurs Bog [21]	Peat, Norway [43]
Na	101.99	66.35	101	698
Mg	1105.13	1156.40	569	2210
K	24.08	69.02	65	1465
Ca	31316.48	15059.18	4784	3830
Cr	0.57	0.30	1.17	12.5
Mn	35.44	13.12	14.47	75.4
Fe	3021.32	963.95	1062	2050
Co	0.27	0.18	0.14	0.93
Ni	1.34	0.63	1.38	4.30
Cu	1.87	2.10	2.19	5.00
Zn	3.61	3.43	10.6	48
Cd	0.15	0.06	0.14	n.d.
Pb	0.51	1.63	4.47	n.d.

In the correlation matrix of fen peat from Viki Mire the 13 elements were also calculated, which show strong positive correlation between: Mn-Fe, Zn-Fe, Cu-Fe, Pb-Fe, Co-Fe, Cr-Fe, Ni-Fe, Zn-Mn, Cu-Mn, Pb-Mn, Co-Mn, Cr-Mn, Pb-Zn, Co-Zn, Cr-Zn, Ni-Zn, Ca-Cu, Pb-Cu, Co-Cu, Cr-Cu, Ni-Cu, Co-Pb, Cr-Pb, Ni-Pb, Ni-Cr (Tab. 3).

The strongest correlations are between the elements of natural origin; obviously, some local processes may affect element concentrations in the peat mass; however it is necessary to divide fen peat according to botanical composition, which has a significant effect on the accumulation of elements.

In wood fen peat at Viki Mire, which is divided into different layers at various depths there are very evident correlations with Fe, Mn, Zn, Cu, Cd and Pb (this element is more common in the upper layers of wood fen peat at a 0.00-0.25 m interval), meanwhile in wood fen peat at Elki Mire, generally no actual strong correlations occur, only as well as at Viki Mire, these are the correlations: Mn-Fe and Ca-Fe, also Ca-Mn is present, which is not at Viki Mire.

Wood fen peat at Elki Mire differs from that in Viki Mire by one more condition – there are some average strong negative correlations between the elements observed, but these are not in the wood fen peat at Viki Mire.

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C. Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are cadmium 8.65; iron 7.9; lead 11.34 [22]. The concentrations of heavy metals (cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc) in the “close-to” surface peat layers reflect the current urban status of the sites. Heavy metals can become incorporated into the peat either directly, wherever peat is exposed at the surface, or indirectly, via vegetation cover which later decays [23].

Leaf surfaces can act as points of uptake for heavy metals, both by stomatal and cuticle pathways. Stomates allow passage of gaseous heavy metals, whereas cuticle intake is applicable to ionic forms of heavy metals. High relative humidity promotes cuticle intake, since those conditions create a swollen cuticle, subject to easiest penetration. There is a pronounced difference on cuticular uptake rate for different heavy metals. For example, copper, zinc and cadmium are found to be taken up at high rates by cuticles of many plants, whereas lead is transmitted in very low quantities. As in the case of root tissue, leaves also have a reverse process of efflux. A more common manifestation of this reverse or efflux process is the expulsion of heavy metal ions through the cuticle. The phenomenon is particularly important when acid rain is deposited on leaf surfaces. Then, due to high hydron concentrations, there can be significant cation exchange with a result of expulsion of considerable amounts of heavy metals onto leaf surfaces, and eventual washing of the leaves by the precipitation itself [24].

Accumulation and distribution of metals in fen peat at research sites

Features of element concentration and distribution are more appropriate to describe in descending order, starting with more common major elements and end with less common trace elements. In both mires there is almost similar element distribution system (chain).

In comparison with the Elki Mire where the system consists of $Ca > Fe > Mg > Na > Mn > K > Zn > Cu > Ni > Pb > Cr > Co > Cd$, at the Viki Mire only potassium (K) and lead (Pb) has changed their place in the system. At the Viki Mire their occurrence is more common – potassium is collocating between magnesium (Mg) and sodium (Na), but lead between manganese (Mn) and zinc (Zn).

Calcium

The calcium is most common metal in fen peat at both research sites. At the Viki Mire calcium (Fig. 6) is more common at first centimetres of fen peat. Maximum concentration (33.96 g/kg) is at 0.10 m observed where the

wood fen peat with decomposition degree of 53% is represented. According to ^{14}C dating it corresponds to 400 years before present. By depth calcium distribution significantly decreases, however there are fluctuations observed.

At the Elki Mire calcium distribution is a bit different (Fig. 7). From 0.35 to 0.50 m, where wood fen peat is represented, there is decrease in concentration observed (2 000 – 3 000 years BP). The second decrease (maximum decrease) is in the wood-reed fen peat at depth of 1.75 m observed (7 000 – 7 500 yr BP). Directly above decrease starting point at 1.50 m, where reed fen peat is lying is maximum concentration (40.76 g/kg) observed. Although lithology of the Elki Mire is simpler, than the Viki Mire, there is more mean calcium concentration observed.

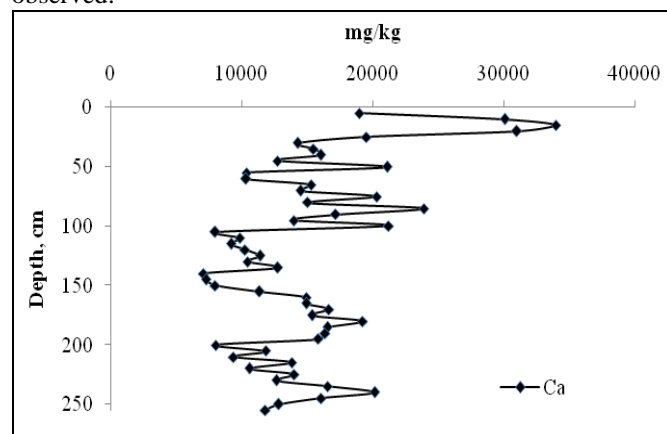


Fig.6. Ca distribution at Viki Mire

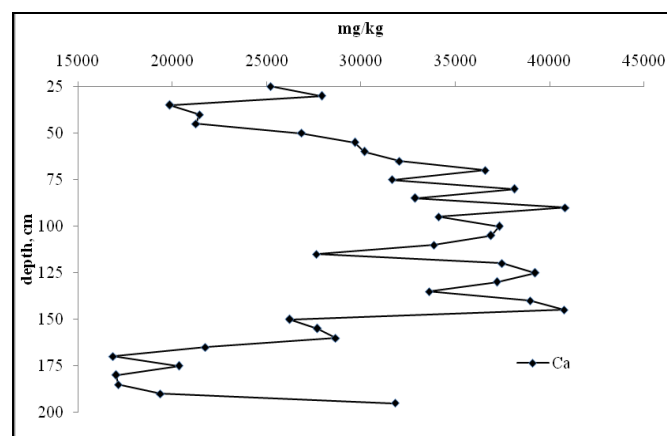


Fig.7. Ca distribution at Elki Mire

Differences in calcium distribution between both research sites may be the result of different conditions in mires. Calcium most commonly accumulates at surface when plants die-off and start to disintegrate. This condition can be observed at the Viki Mire, but not at the Elki Mire, because of divisional transitional wood peat layer. Calcium concentrations decreases with depth by the effect of water flow – calcium has washed out, however intensity of this effect depends on botanical composition, which together with divisional mass provides density.

In both mires calcium distribution can be linked to carbonate content distribution, both this parameters have similar fluctuations at both research sites.

Iron

Although in both mires iron is the second common major element and distribution of this metal is similar to calcium (it accumulates after plant die-off, it also depends on decomposition degree), at the Elki Mire mean concentration is higher. At the Viki Mire the highest concentrations are observed near the surface. Maximum concentration (4.73 g/kg) is observed at 0.10 m (similar like calcium) were wood fen peat with sand content is represented.

It is reasonable to believe that increased iron concentration is from admixture of sand. After significant increase in iron concentration (0.86 g/kg) at depth of 0.25 m a 1 000 years old grass fen peat is present, increasing with and reaching its maximum (1.7 g/kg) at 2.40 m where the 7 500 year old grass fen peat is found.

At the Elki Mire (Fig. 8) an increase starts with the first centimetres of fen peat and reaches the highest values from 1.60 m. Maximum concentration (5.59 g/kg) at the depth of 1.65 m in sedge fen peat is observed, which corresponds to 6 500 years before present; the second maximum (5.61 g/kg) is observed at gyttja contact, which corresponds to approximately 8 000 years before present.

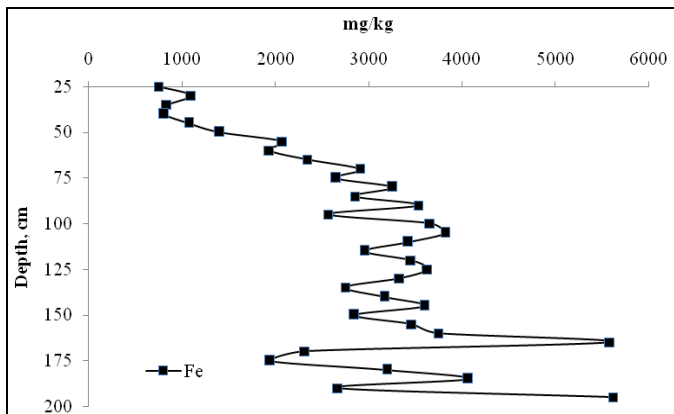


Fig.8. Fe distribution at Elki Mire

Magnesium

Distribution (and conditions of it) of this element is largely similar to calcium and iron. At the Viki Mire (Fig. 9) near surface (first 0.30 m) high concentration of magnesium is observed, (maximum 1.5 g/kg at 0.20 m), but it is not the highest. The maximum concentration (1.8 g/kg) at 0.85 m is observed where wood-grass fen peat is represented. At the Elki Mire the concentration of magnesium increases without any significant fluctuations, the maximum concentration being observed at 0.30 m (1.4 g/kg) in wood fen peat layer.

Sodium

Sodium is generally opposed to any new changes and is a good indicator of salinity. Usually, an increase in salinity increases the concentration of Na. Salinity increases during

evapotranspiration in the root zone at the surface and/or in some cases from lateral flow of a saline groundwater [25]. Increase of Na also can be induced by weathering. At Viki Mire the highest concentrations are observed at the first 0.50 m, where wood fen, grass fen and wood-sphagnum fen peat is present. Maximum concentrations (107 mg/kg) are at 0.20 m where grass fen peat layer underlying below wood fen peat layer (at connection) is located. At Elki Mire highest concentrations are at lower layers, concentration increase with depth.

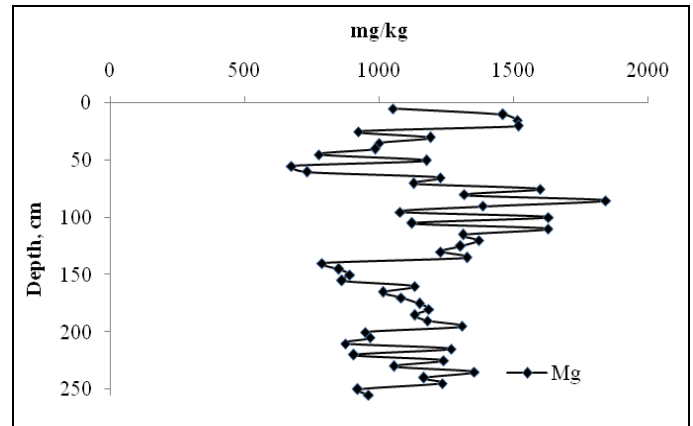


Fig.9. Mg distribution at Viki Mire

Manganese

At Viki Mire the highest concentrations of manganese are near the surface. Maximum concentration (62.6 mg/kg is observed at depth of 0.05 m. After that a significant decrease down to 0.50 m is observed. At 0.50 m an concentration starts to increase and at 2.40 m reaches its maximum 27 mg/kg in the sedge-hypnum fen peat. Similar situation is observed at Elki Mire – the concentration is increasing down to 0.95 m when it reaches its maximum of 55.7 mg/kg (wood-reed fen peat), after that it decreases again. At depth of 1.40 m in reed fen peat it reaches the second maximum (54.8 mg/kg). In the presence of oxygen Mn forms quaternary oxides, which can be important reservoirs for trace elements, especially for Co, Zn and Cr [26]. Interesting relationship is formed between Mn and Co at Elki Mire. In most cases among them there is negative correlation, but in the wood-reed fen peat in the range of 0.75 – 1.25 m, there is a strong positive correlation. It is important that this interval coincides with the peak prevalence of Mn. At this range there is also the strongest positive correlation with Zn. Without presence of oxygen or in suboxidable conditions Mn quaternary oxides reductively dissolve, releasing dissolved bivalent Mn [27]. Mn is a lithophile trace element and typically is not found in association with organic matter [28]. Concentrations of manganese in fen peat of Elki Mire are antipodal to organic matter as at Viki Mire.

TABLE 2
CORRELATION COEFFICIENT MATRIX OF ANALYSES OF MAJOR AND TRACE ELEMENTS IN FEN PEAT OF ELKI MIRE

Mn	0.45												
Zn	0.45	-0.02											
Cu	0.45	-0.11	0.83										
Mg	-0.39	-0.02	-0.45	-0.49									
Ca	0.33	0.50	-0.42	-0.42	0.62								
Cd	0.59	0.17	0.28	0.23	-0.12	0.19							
Pb	-0.12	0.61	0.18	0.05	0.13	0.02	-0.10						
Co	0.47	-0.13	0.89	0.93	-0.62	-0.55	0.30	-0.01					
Cr	0.21	-0.18	0.72	0.86	-0.27	-0.41	0.14	0.18	0.77				
Ni	0.52	-0.12	0.84	0.96	-0.45	-0.35	0.28	-0.01	0.93	0.83			
Na	0.09	0.01	0.35	0.82	-0.40	-0.32	-0.07	0.16	0.37	0.47	0.40		
K	0.20	0.08	0.70	-0.49	-0.46	-0.49	-0.01	0.40	0.74	0.79	0.75	0.52	
	Fe	Mn	Zn	Cu	Mg	Ca	Cd	Pb	Co	Cr	Ni	Na	

TABLE 3
CORRELATION COEFFICIENT MATRIX OF ANALYSES OF MAJOR AND TRACE ELEMENTS IN FEN PEAT OF VIKI MIRE

Mn	0.85												
Zn	0.75	0.79											
Cu	0.82	0.79	0.69										
Mg	0.24	0.17	0.02	0.41									
Ca	0.54	0.50	0.41	0.73	0.58								
Cd	0.49	0.53	0.55	0.43	0.03	0.40							
Pb	0.79	0.83	0.84	0.82	0.16	0.55	0.54						
Co	0.86	0.82	0.89	0.84	0.14	0.46	0.52	0.96					
Cr	0.94	0.73	0.80	0.87	0.18	0.45	0.47	0.82	0.91				
Ni	0.92	0.63	0.71	0.87	0.19	0.44	0.39	0.73	0.83	0.98			
Na	0.32	0.07	0.15	0.31	0.13	0.25	-0.08	0.11	0.16	0.34	0.40		
K	0.21	0.09	0.13	0.17	0.29	-0.19	-0.02	0.24	0.28	0.31	0.30	0.14	
	Fe	Mn	Zn	Cu	Mg	Ca	Cd	Pb	Co	Cr	Ni	Na	

Potassium

K is produced by organic matter decay; however it may be taken up by plant roots [25]. K compounds can't be leached from peat by water fluctuations; K also migrates upwards in the living plant cells. Potassium has a greater concentration in the "live" peat layers, it belongs to the elements, which in the process of plant decomposition are disposing and has been washed out from the peat layers by waters [29]. K maximum concentration (300 mg/kg) at Viki Mire is at depth of 1.05 m where the wood-grass fen peat is present, which corresponds to 4 500 years BP. Potassium concentration at Elki Mire is increasing with depth, the maximum concentration is reached at depth of 1.60-2.00 m (71.9 mg/kg).

Zinc

At Viki Mire the highest concentrations are the near surface, the maximum concentration of 12.4 mg/kg is reached at depth of 0.05 m in wood fen peat, which corresponds to last the 800 years. At Elki Mire the highest concentrations with fluctuations are deep below the surface – at depth of 1.60 to 2.00 m, where reed fen peat and sedge fen peat with gyttja are present, it correspond to 6 500 – 8 100 years BP, it may have been caused by lake overflow in early days. Maximum concentrations (17.36 mg/kg) are at depth of 1.85 m.

Copper

At Viki Mire the highest concentrations are near the surface, maximum (6.9 mg/kg) at the depth of 0.10 m in wood

fen peat. At Elki Mire the highest concentration starts at the depth of 1.60 m. Maximum of 30.9 mg/kg is reached at the depth of 1.65 m. Copper is often found in association with organic matter, it has an affinity to it, forms very strong complexes [30]. Cu is chalcophile element and form discrete sulfide minerals [31].

Nickel

At Viki Mire the highest concentrations are near the surface, and similar to copper maximum concentration (3.25 mg/kg) are found at the depth of 0.10 m, with depth concentration significantly decreases. At Elki Mire in the first centimetres of fen peat concentration is also slightly higher than average, but the highest concentrations start at 1.60 m. Maximum concentration (4.8 mg/kg) is reached at the depth of 1.85 m.

Lead

Lead concentration in both mires is relatively low, especially in comparison with other mentioned mires in Latvia or in other countries (Tab. 1). The fen peat of Elki and Viki Mires is characterised by non-elevated pollution with lead. There are differences in Pb concentrations between Elki and Viki Mires, an explanation for this situation is that fen peat of Elki Mire starts at 0.25 m and is covered with transitional peat, whereas fen peat of Viki Mire is revealed in the surface, consequently, it is exposed to pollution, precipitation, anthropogenic impact, e.g. Historically both mires have been always at isolated location. At Viki Mire lead mean concentration (Fig. 10) is less than 1 mg/kg, however there is peak concentration (23.5 mg/kg) in wood fen peat and a bit lesser in grass fen peat below (> 20 mg/kg) near surface observed (last 0.35 m – last 1 500 years).

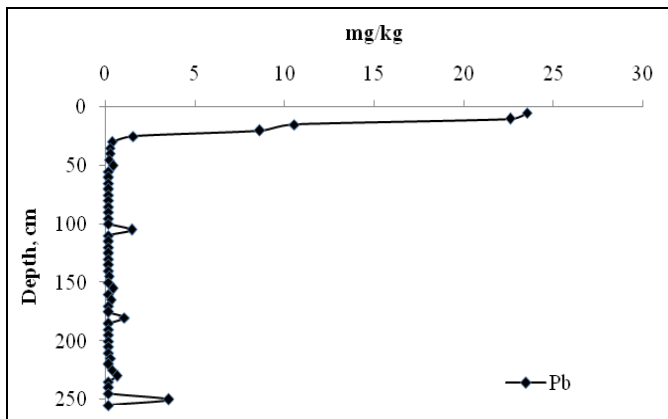


Fig.10. Pb distribution at Viki Mire

At Elki Mire (Fig. 11) Pb mean concentration is < 1mg/kg, the maximum concentration 0.8 mg/kg. Pb, Cu and Cd belong to the serious hazardous heavy metals [32]. Pb is chalcophile element and under anoxic conditions form distinct sulfide phases [33], also it associates with organic matter [34].

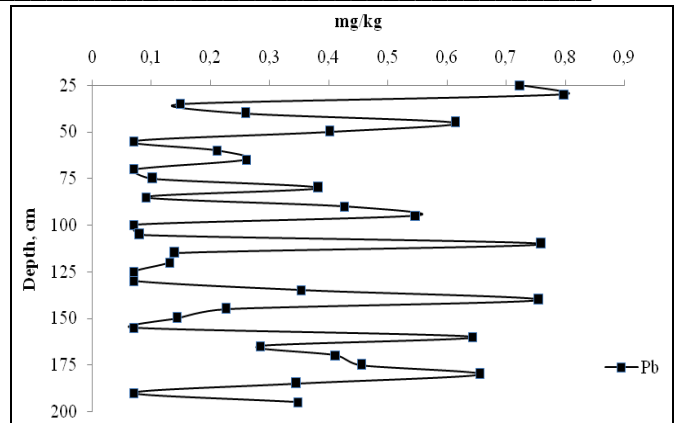


Fig.11. Pb distribution at Elki Mire

Freeze-drying can shift lead from oxidisable fraction to the exchangeable, carbonate or reducible fractions [35]. Freeze-drying is the same sublimation drying [36]. Comparison of Pb and Zn distributions in different species and plant organs in the surface vegetation shows that in non-bryophyte samples Zn is in higher concentration in the younger, actively-growing organs than in other parts of the plants. Lead, however, is more concentrated in the older living parts of the plants and in the peat and decomposing plant litter.

There are several possible explanations for the predominance of lead in the older plant parts. The observed higher concentration could be an intrinsic property of plant organs themselves. Lead may be accumulated in the older organs as a heavy metal resistance mechanism, so preventing it from entering the more sensitive younger tissues; alternatively, accumulation of lead in the older parts could be passive process, and simply a reflection of their longer exposure to environmental lead [23]. Higher concentration of lead may be the result of selective loss of organic matter by decay [37]. Lead and zinc, and to a lesser extent copper, are heavy metals which are associated not only with specific heavy industries, but also with activities connected with urban or industrial areas of appreciable size. The metals are released during the burning and recycling of scrap metals, manufacture of car batteries [38], and combustion of petrol additives in motor vehicles [23].

Chromium

Chromium is also in highest concentrations in the wood fen peat layers near the surface at Viki Mire, with depth it decreases in concentration. The maximum concentration is 2.1 mg/kg, which is observed in wood fen peat mixed with sand. At Elki Mire (Fig. 12) Cr concentration fluctuates, however the highest concentrations in the upper layers are observed. The maximum concentration of 1.31 mg/kg is present at 0.25 m. The second maximum 1.43 mg/kg is found at connection with gyttya at the depth of 2.00 m where sedge fen peat and reed fen peat are mixed with gyttya (similar to Zn concentration). Cr often is found in association with Mn oxides [39]. Actually strong correlation between Cr and Mn is observed at Viki Mire ($r = 0.73$), but at Elki Mire this correlation is negative and also irrelevant.

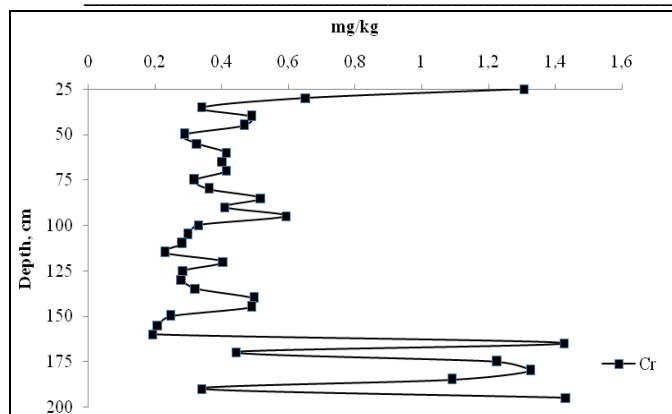


Fig.12. Cr distribution at Elki Mire

At Elki Mire chromium concentration significantly reduces, when the degree of decomposition is increasing, however there are no correlations between these parameters at Viki Mire. Changes in Cr concentrations indicate changes in dust composition, usually chromium concentration and distribution is controlled by plant feeding conditions and absorption onto organic ligands in slightly decomposed organic matter [40].

It is believed, that Cr distribution is controlled by botanical composition in full section, and also by atmospheric impact at upper layers. Chromium is lithophile element and is generally not associated with sulfides [31]. In anoxic conditions it is associated with organic matter [41]. In suboxic or oxic condition Cr is sorbed to flavin – containing monooxygenase [30].

Cobalt

At Viki Mire the highest concentration is observed at the first centimetres in wood fen peat near the surface – the maximum concentration 2 mg/kg. At Elki Mire cobalt is more common in lower peat layers, starting with depth of 1.60 m. Maximum concentration at depth of 1.85 m – 1.2 mg/kg in reed fen peat. Cobalt is a siderophile element, frequently found in association with Fe [42]. Distribution of this element is similar to copper in both mires.

Cadmium

Highest concentrations of cadmium are observed near surface at Viki Mire, in the first 0.25 m of wood fen peat, which corresponds to the last 1000 years. Maximum concentration is at the depth of 0.05 m – 0.26 mg/kg. At Elki Mire in first centimetres of fen peat cadmium concentration is low. Maximum concentration at the depth of 1.65 m is reached (0.40 mg/kg) in sedge fen peat aged approximately 6600 years. Raised concentration of the cadmium in the peat layers probably is related to the migration upwards from the mineral soils under peat layers above-mentioned element [29].

IV. CONCLUSIONS

The period before 2800 years marks different conditions of vegetation development that might have been characterised by a drought.

Due to the fact that in Elki Mire lead concentration in fen peat is lower than in transitional peat, it has not migrated (was unable to migrate) down through divisional layers, and anthropogenic impact around 1500 yr BP (the Medieval Times) was minor.

In the upper fen peat layers at Viki Mire, which is covered only by contemporary mire vegetation, higher trace element concentration appears. It confirms the fact that some elements do not tend to migrate lower into the peat layers.

Calcium is the most common metal in the fen peat; its concentration and distribution are linked to carbonate content in peat.

High Fe concentration in peat may be caused by sand supply from the nearest areas.

It is believed, that Cr distribution is controlled by botanical composition in full section, and also by atmospheric impact at the upper layers.

Fluctuations in sodium concentration (possibly caused by weathering) at Elki Mire in comparison with Viki Mire mark changes in salinity in the ambient environment.

Although both mires are located relatively close to each other, the accumulation of major and trace elements is different because of different botanical composition and decomposition degree in each of the fen peats.

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Jānis Krūmiņš, Eliza Kuške, Māris Kļaviņš. Makroelementu un mikroelementu akumulācija zemā tipa kūdrā Elku un Viķu purvos Rietumlatvijā
Pētījumā analizētas divu atšķirīgu mineratīvu purvu makroelementu un mikroelementu akumulācijas īpatnības zemā tipa kūdrā. Atomu absorbcijas spektrometrijas analizē noskaidrotas 13 dažādu elementu (Ca, Fe, Mg, K, Mn, Na, Zn, Ni, Cu, Cr, Co, Cd, Pb) koncentrācijas vērtības Elku un Viķu purvu nogulumos. *Loss on Ignition* analizē apzinātas organiskās vielas, karbonātiskā materiāla un minerālo daļiņu procentuālās attiecības; noteikts kūdras botāniskais sastāvs un sadalīšanās pakāpe, kā arī absolūtais vecums.

Vīķu purvs veidojies pirms apmēram 7 600 gadiem atlantiskā laika sākumā. Elku purvs veidojies pirms aptuveni 8 000 gadu boreālā laika beigās. Abi purvi veidojušies līdzīgos apstākļos – aizaugot ūdenstilpnēm, tomēr vides procesi veidošanās sākumposmā ir bijuši krasi atšķirīgi.

Elku purva griezumā elementu maksimālās koncentrācijas vērojamas lielākoties griezuma apakšdaļā intervālā 1.60 – 2.00 m grīšļu un niedru kūdrās (piemēram, Fe, Cu, Na, Zn, Ni, K). Šī griezuma daļa atbilst laika periodam aptuveni no 8 000 līdz 6 500 gadiem. Šajā laikā visticamāk valdījuši pārmitri apstākļi, iespējams norisinājusies ūdenstilpnes pārplūšana, kas radījusi intensīvu metālisko elementu uzkrāšanos. Par pārmitriem apstākļiem liecina arī samazinātais kalcija saturs un minimāla sadalīšanās pakāpe. Vīķu purvā šāda parādība nav novērojama, un lai arī botāniskais sastāvs ir daudz komplicētāks, tomēr šeit metālu akumulācija norisinājusies samērā vienmērīgi.

Abu purvu zemā tipa kūdrā novērojamas minimālas antropogēnās ietekmes pazīmes. Antropogēnās izcelsmes elementu paaugstināta koncentrācija vērojama kūdras augšējās slāņos. Visniecīgākās antropogēnās ietekmes izpausmes konstatētas Elku purva zemā tipa kūdrā, kur to pārsedz līdz 1 500 gadus veca pārejas tipa koku kūdra.

Янис Круминьш, Елиза Кушке, Марис Клявиньш. Накопление макроэлементов и микроэлементов в болотах Элки и Вики в Западной Латвии

В этом исследовании были проанализированы накопления различных элементов природы в низинный тип торфа из двух разных минеротрофных болот.

Атомно-абсорбционный спектрометрический анализ выявил значения концентрации 13 различных элементов (Ca, Fe, Mg, K, Mn, Na, Zn, Ni, Cu, Cr, Co, Cd, Pb) в отложениях болот Элки и Вики.

При анализе потерь при прокаливании определены проценты органического вещества, карбонатного материала и минеральных частиц. Болото Вики формируется примерно 7 600 лет, с начала атлантического периода. Болота Элки были сформированы около 8 000 лет назад в конце бореального периода. Оба болота образовались в аналогичных обстоятельствах - органическое зарастание воды, однако на ранних стадиях формирования претерпели множество изменений. В болотах Элки при разделе элементов максимальная концентрация наблюдается в большом пласте нижней части разреза в диапазоне 1,60 - 2,00 м (например, Fe, Cu, Na, Zn, Ni, K), и соответствует периоду 8 000 – 6 500 года. За это время, скорее всего, развитие происходило в водно-болотных условиях, возможно были наводнения, которые вызвали интенсивное накопление металлических элементов, на эти обстоятельства указывают пониженное содержание кальция и минимальная степень разложения. В болотах Вики такого явления не наблюдается, хотя ботанический состав является более сложным, но накопления металлов происходили довольно гладко. Оба болота подвергались низкому антропогенному воздействию, в верхних слоях наблюдается низкая экспрессия, повышенные концентрации свинца, хрома и др. В болото Elki антропогенные воздействия являются самыми низкими.