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FEN PEAT PROPERTIES AND METAL ACCUMULATION IN IT

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SUMMARY

There are a few publications about fen peat composition and properties, thus it is important to develop studies on fen peat to find out and to expand the application possibilities of this type of peat. Fen peat is formed from decomposed plant remains - development of these plants mostly was based on nutrient supply from mineral-rich groundwater. In general fen peat is built up from sedges, reeds, grasses, shrubs or wood under waterlogged conditions. The developed surface area and large number of acidic functional groups common to peat, determine the ability to bind trace elements including remains of living organic matter, either both as sedimentary, deposited, particulate matter or as sorbed or complexed metal ions. The main goal of this study was to explore and analyze the distribution and accumulation patterns of major and trace elements in fen peat under differing environmental conditions in Latvia. In this study we found that concentrations of some major elements significantly change depending on their location in the peat profile. In general, there were concentrations of the thirteen chemical elements, Ca, Mg, Fe, Mn, Zn, Cu, Na, K, Cd, Co, Cr, Ni and Pb; however in several peat profiles, for instance, in the *Svētupes* peat profile, concentrations of some elements (i.e. Cd and Co) were below the detection limit and could not be determined

Keywords: trace elements; fen peat, accumulation

INTRODUCTION

Chemical composition of peat changes according to its position in the vertical and horizontal level, water table and peat forming plant composition and their decomposition characteristics (Damman, 1978). The increase of anthropogenic impact causes changes in the natural accumulation pattern, for instance - drainage and peat use in agriculture or forestry significantly affect metallic element cycles. Fen plants are fed predominantly by groundwater and that is why fen peat is rich with lithogenic metallic elements. Weathering of sedimentary rocks and mineral deposits are another important source of metal ions that migrate upward into peat by diffusion, especially in fen ecosystems (Shotyk and Steinmann, 1994). Due to the weathering metal ions are released into groundwater and supplied to peat. Metal ion supply, either by diffusion or by groundwater, as well as the intensity of both these processes depends on basal deposits and mires that are formed on calcareous sedimentary rocks are chemically more affected by ion uptake diffusion than those formed on metamorphic rocks (Givelet *et al.*, 2004).

The developed surface area and large number of acidic functional groups common to peat determine the ability to bind metallic elements included in remains of the plant organic matter, either as sedimentary, deposited, particulate matter, or as sorbed or complexed metal ions (Brown *et al.*, 2000). The ability of peat to accumulate metallic elements depends not only on the element capacity to bind with functional groups, but also on the pH reaction, on the presence of low molecular weight compounds (carboxylic acids, polyphenols) and other dissociating compounds, for instance, sulphate or hydrogen carbonate ions (Tipping *et al.*, 2003). Source of metallic elements in peat mass can be attributed to atmospheric precipitation, to metallic elements present in peat-forming plants, as well as to supply with groundwater and surface runoff. Another important source of metallic elements in peat are sedimentary rocks in the base of mire, as due to the weathering metal ions migrate upward by diffusion into the peat layer (Shotyk and Steinmann, 1994).

All studied metallic elements in peat were divided into groups with similar chemical characteristics, respectively, - alkaline earth metals (Ca and Mg), alkali metals (K and Na), transition metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn) and post-transition metals (Pb). Many studies (Coggins *et al.*, 2006; Ukonmaanaho *et al.*, 2004; Shotyk *et al.*, 2002; Martinez-Cortizas *et al.*, 2002; Shotyk *et al.*, 2001) have shown a gradual increase of heavy metals in peat mass during the last hundred years as a result of anthropogenic pollution.

The goal of this study was to explore and analyze distribution and accumulation pattern of major and trace elements in fen peat under differing environmental conditions in Latvia.

MATERIALS AND METHODS

To characterize the influence of peat composition on metallic element accumulation, four fens in the territory of Latvia were chosen, those were Elku and Viķu mire. These fens were chosen as the study subject due to their similar origin, but with significant differences in peat botanical composition and variable Quaternary deposit character in mire catchment area. Field studies were carried out during the period from 2009 to 2015.

Fen peat was studied using standardized methods (Tan, 2005). Peat profiles from each study site were separated into 5 cm thick layers and the metallic element content was determined by acid digestion using atomic absorption spectroscopy (Krachler *et al.*, 2003). Acid digestion was carried out using 25 ml 50% HNO₃ and 5 ml 30% H₂O₂ on 1 g of oven-dried peat sample. Each sample was mixed with the acid solution and left for 24 h; mixtures were then boiled at 150°C until half of the liquid evaporated and then another 25 ml of 50% HNO₃ were added and the mixture boiled until vibrating started. Digested samples were filtered and diluted with Millipore water up to 50 ml of the total volume and transferred into tubes and further used in atomic absorption spectroscopy. Metallic element concentration was normalized against Ti content in peat samples. Sample dating was performed using the conventional liquid scintillation counting technique, but as the scintillation solvent benzene was used. Botanical composition and decomposition degree. The analysis of peat decomposition degree was followed by the centrifugation method according to the GOCT 10650-72 standard, and peat decomposition degree was expressed as percentage of the total peat sample mass (Malterer *et al.*, 1992). Peat botanical composition was determined using a binocular microscope at 56 to 140 x magnification according to the GOCT 28245-89 standard. The content of organic matter, carbonate matter and mineral matter was determined and values calculated using the Loss on Ignition method (Heiri *et al.*, 2001). Samples were dried in an oven at 105°C for 24 h, heated in a muffle furnace at 550°C for 4 h and at 950°C for 2 h. Elemental composition (C, H, N and S) was determined using a Carlo Erba Elemental Analyzer EA-1108 with PC based data system. All values were normalized against the ash content. The oxygen content was measured as the residual (100% minus the content of C, H, N and S). T

RESULTS AND DISCUSSION

Study sites are of similar origin, but of varied botanical composition, which points on different conditions of mire development. However, in general, the studied mires were formed in similar conditions and characterize environmental conditions in Latvian fens. This situation was assumed as one of the main criteria for selection of particular study area. Relatively simple environmental conditions, similar origin, but differences in further development suggest also a variability in peat properties.

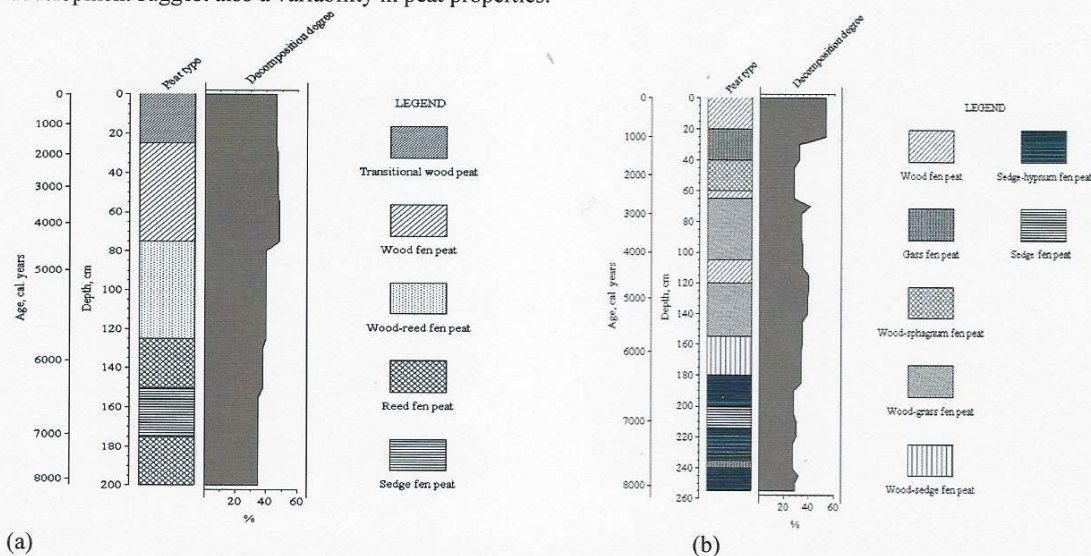


Figure 1: The botanical composition and decomposition degree of Elku Mire (a) and Viķu Mire (b) peat

Elku Mire: Nowadays Elku Mire is considered to be transitional mire and is covered by a 0.25 m thick layer of transitional wood peat. The studied Elku Mire peat profile consists of 5 different peat layers with a total depth of 2

m (Fig. 1); the age of the mire is 8000 years. The superficial peat layer (0.00-0.25 m) is composed of transitional wood peat, but the rest of the mire profile consists of various fen peat types (wood, wood-reed, reed and sedge peat). Peat decomposition degree is in the range between 35 and 48% and can be considered as high. Peat botanical composition studies show that Elku Mire has been formed due to a lake overgrow and this fact can also be confirmed by the findings of thick and continuous sapropel layer below mire deposits.

Vīķu Mire: The superficial peat layer in Vīķu Mire is similar to that of Elku Mire and consists of wood peat. However, although - this mire is still in the stage of fen and its peat is more affected by anthropogenic activity than the fen peat in Elku Mire. Vīķu Mire peat profile (Fig. 1) consists of 7 peat types (wood, grass, wood-*sphagnum*, wood-grass, wood-sedge, sedge-*hypnum* and sedge peat) with a total peat layer of 2.5 m in depth; the age of the mire is 8000 years. Peat decomposition degree in the studied section varies from 27 to 41%.

Five base elements in fen peat elemental composition are C, H, N, O and S. The most part of peat elemental composition is built up of C, being the base element in the organic world, second in line is O, then H and finally N. The content of all elements was normalized against the ash content in peat.

The concentration of C in the studied peat is in range of 27.6 to 48.9%, but the exact value depends on the peat botanical composition, thus this element has no particular accumulation pattern. C content in Elku Mire peat is in the range of 41.2 to 48.9% and it seems to gradually increase with depth, although, C content is practically stable within the peat profile.

In order to obtain the most complete picture of the metallic element accumulation character, it is necessary to analyse the full peat profile and not particularly selected parts, because the location of specific peat layers can significantly affect data interpretation. Metallic elements were grouped in 4 general classes: 1) alkaline earth metals (Ca, Mg); 2) alkali metals (Na, K); 3) transition metals (Fe, Mn, Zn, Cu, Co, Cd, Cr, and Ni); 4) post-transition metals (Pb).

Alkaline earth metals: Ca and Mg are biophile elements and are closely related to mire vegetation growing conditions. Both metallic elements are main plant nutrients and belong to the most important metallic elements that are involved in fen development. Alkaline earth metals in fen peat are supplied by groundwater, but their source of supply can be both natural and anthropogenic. Amongst natural sources are sediments in mire catchment areas – these can be sapropel, sand, silt, till and others. Quaternary deposits with high carbonate mineral content. Agricultural land use may cause anthropogenic alkaline earth metal supply from mire catchment area – for instance, soil liming can lead to high Ca concentrations in upper peat layers. The highest Ca concentration in Elku Mire is located in the wood-reed fen peat layer, in the middle part of peat profile (Fig. 2), where peak concentration exceeds 40 g/kg. It can be explained by groundwater supply. At the same time, the lowest Ca content is in the bottom part of peat profile, where peat contains 16.8 g/kg Ca. The distribution of Mg is similar (with slight differences) to the Ca accumulation pattern (Fig. 2) and it can be explained by common source of supply – dolomite minerals in Quaternary deposits of mire catchment area. However, Mg concentration is significantly lower than Ca content. Peak concentration is 1.5 g/kg, but minimum amount of Mg in Elku Mire peat profile is 0.5 g/kg. The concentration of both metallic elements is decreasing by the depth, although there is also a relation to the peat botanical composition and decomposition degree.

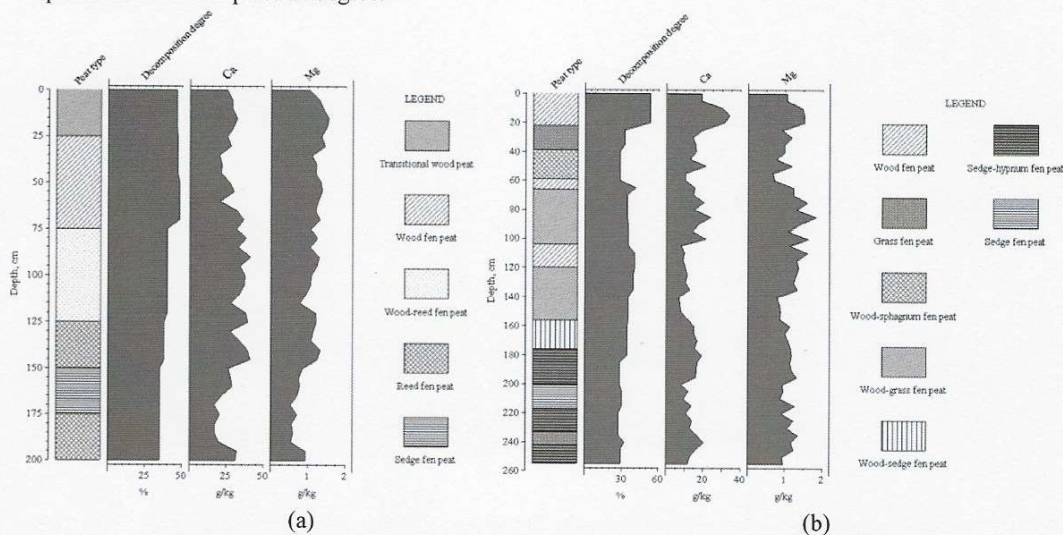


Figure 2: The accumulation pattern of alkaline earth metals in Elku (a) and Vīķu (b) Mire peat profile

Alkali metals: K is a biophile element and closely related to the growing conditions of mire vegetation, while Na content can also be associated with atmospheric deposition. Alkali metals in fen peat are supplied by groundwater from deposits in mire catchment area, but their supply source can be also of anthropogenic origin. Amongst natural sources is till, which contains K and Na feldspar minerals, but one of the most significant anthropogenic sources might be fertilizers used in agriculture.

The highest K concentration in Elku Mire is located in transitional wood peat, in the upper part of the peat profile (Fig. 3), where peat contains 269 mg/kg K. The location of the mire and the K content in the upper peat layer allows the assumption that K has a natural supply source. The lowest K content is in reed fen peat, in the middle part of the peat profile, where peat contains 1.6 mg/kg K. The highest Na concentration in Elku Mire is located in the transitional wood peat layer (177 mg/kg), where also the least Na content was identified (39 mg/kg). While K concentration seems to be variable throughout the peat profile, because of K high mobility, Na content is rather stable; this can be explained by different sources of supply.

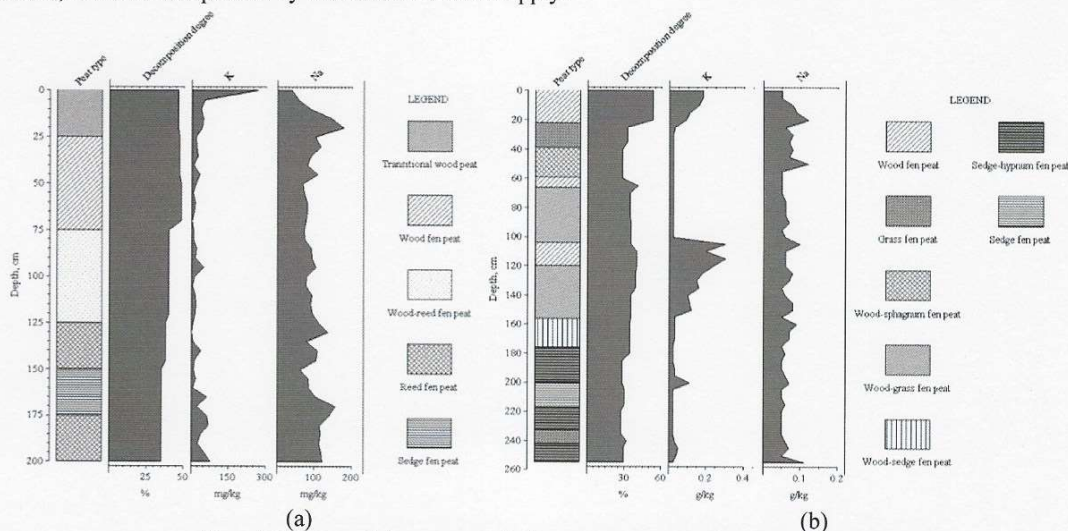


Figure 3: The accumulation pattern of alkali metals in Elku (a) and Viķu (b) Mire peat profile

Transition metals: Transition metal accumulation in peat can be explained by both natural and anthropogenic causes. Metallic elements can be supplied with groundwater from deposits in mire catchment areas and with atmospheric precipitation, but agricultural land use can also be of possible consideration. All transition metals in reasonable amounts are essential plant micronutrients, however if their concentration in soil is high, they must be seen as heavy metals and a potential threat. Fe, Mn, Ni and Co are siderophile elements and have no affinity for oxygen (except Fe and Mn), thus they tend to migrate down the peat profile. Moreover, all siderophile elements form strong chemical bonds with carbon and sulphur. Zn, Cu and Cd are chalcophile elements and generally remain in the upper part of peat profile, where they form chemical compounds which do not tend to migrate downwards.

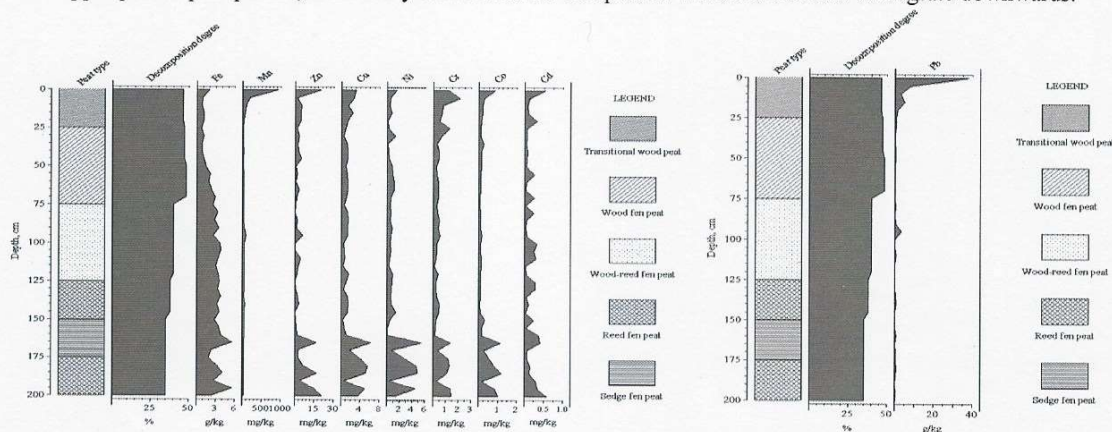


Figure 4: The accumulation pattern of transition metals and lead in Elku Mire peat profile

According to the results (Fig. 4) Zn, Cu, Cr, Ni, Co and Cd have similar accumulation characteristics – these metallic elements have high concentrations in the upper and bottom peat layers, while in the middle layers their content is low and rather stable. This can be explained by groundwater level changes that caused transition metal migration in the bottom part of peat profile, while metallic element content in upper part of peat profile is affected by atmospheric precipitation.

The highest Fe concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile (Fig. 4), where peat contains 4.7 g/kg Fe. The lowest Fe content is in wood-*sphagnum* peat, in the middle part of the peat profile where peat contains 216 mg/kg Fe. The highest Mn concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile, where peat contains 63 mg/kg Mn. The lowest Mn content is in wood-*Sphagnum* peat, in the middle part of peat profile, where peat contains 1.9 mg/kg Mn. The highest Ni concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile (Fig. 4), where peat contains 3.2 mg/kg Ni. The highest Co concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile (Fig. 4), where peat contains 2 mg/kg Co. The highest Zn concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile (Fig. 4), where peat contains 12.4 mg/kg Zn. The lowest Zn content is in the middle part of peat profile, where peat contains 2.3 mg/kg Zn. The highest Cu concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile, where peat contains 6.9 mg/kg Cu. Pb has no known biological functions and can be considered as heavy metal. Pb is chalcophile element, has low affinity for oxygen and under anaerobic conditions forms distinct sulphide phases. Moreover, at its highest concentration, Pb remains close to the surface. Pb solubility in water is pH function and depends on water hardness, salinity and the presence of humic substances. Pb is the most soluble in soft, acidic water; it means that weak acidic fen peat environment limits Pb solubility. The highest Pb concentration in Elku Mire is located in transitional wood peat, in the upper part of peat profile (Fig. 4), where peat contains 38 mg/kg and it can be considered as Pb pollution. The lowest Pb content is below 0.5 mg/kg and the concentration remains low throughout the full peat profile. The highest Pb concentration in Viķu Mire is located in wood fen peat, in the upper part of peat profile, where peat contains 23.5 mg/kg Pb, but in the rest of the peat profile Pb content remains low (below 0.5 mg/kg).

CONCLUSIONS

Elevated Pb concentration in upper peat layer is related to environmental pollution due to anthropogenic activities. Pb has no tendency to migrate downwards, thus in bottom peat layers its content remains low. Overall, Pb content in studied peat is negligible and does not demonstrate any relations with peat characteristics. However, high Pb concentration in upper peat layers has negative impact on mire vegetation and thus on peat accumulation. Elevated transition metal concentration in upper peat layers is related to their accumulation with precipitation and can be related to atmospheric pollution and modern anthropogenic activities itself. However, it can be also associated with natural processes such as - biomass production and supply from mire catchment areas. An elevated metallic element concentration in bottom layers can be explained by significant groundwater level changes that cause migration of a particular metallic element.

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