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Impact of the physico-chemical properties of fen peat on the metal accumulation patterns in mires of Latvia

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Abstract The article presents a study of the physico-chemical properties of fen peat and their influence on the metal accumulation patterns in three Latvian fens: Svētupes Mire, Elku Mire and Vīķu Mire. Full peat profiles were obtained at all study sites and analysed with a multi-proxy approach. The content of metals in fen peat was determined using the atomic absorption spectroscopy (AAS) and normalised to the concentration of Ti in the studied peat profiles. Both the character of deposits and agricultural land use in the mire catchment areas were taken into account and the possible natural and anthropogenic metal supply sources were evaluated. The content of metals in the studied fen peat significantly varied due to the heterogeneity of fen environment; however, noticeable similarities were also traced throughout all study sites. The results indicate an increased amount of transition metals and Pb in the upper peat layer. This can be explained by a direct impact from anthropogenic sources (agricultural land use, pollution, etc.). Metal binding in fen peat profiles is directly related to the alkali and alkaline earth metal content in peat, as Ca, Mg, Na and K ions are replaced by more tightly bound metal ions. In raised bogs, in turn, metal binding is associated with the acidic functional groups common to peat.

Keywords • *fen peat* • *metals* • *peat physico-chemical properties*

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INTRODUCTION

Mires provide essential ecosystem services; they are important for regulation of hydrological regime and biogeochemical cycling of elements (metals, carbon, nitrogen, etc.). 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 and trees under waterlogged conditions (Coccozza *et al.* 2003). The developed specific surface area and large number of acidic functional groups common to peat determine its ability to bind metals. The major sources of metals in the peat mass can be attributed to atmospheric precipitations, metals present in the

peat-forming plants as well as groundwater supply (Brown *et al.* 2000).

There are numerous studies on metal accumulation in raised bogs (Shotyk *et al.* 2001; Martinez-Cortizas *et al.* 2002; Shotyk *et al.* 2002; Ukonmaana-ho *et al.* 2004; Coggins *et al.* 2006; Klavins *et al.* 2009; Silamiķele 2010; Pujāte 2015; Stankevica *et al.* 2015). Notably, it has been demonstrated that the significant increase of metal accumulation in ombrotrophic bog peat is due to increasing anthropogenic pollution (Shotyk *et al.* 2001; Martinez-Cortizas *et al.* 2002; Coggins *et al.* 2006). Moreover, peat can serve as a good indicator of recent and as well as historical changes in pollution loading (Shotyk *et al.* 2002). At the same time, the pattern of metal accumulation

in fens has not been widely studied; therefore, factors affecting the cycling of metals in fen peat are not fully known. However, there is a reason to believe that the metal accumulation mechanism in fens is different from that in raised bogs, and this is related to differences in the amounts of functional compounds, pH, peat decomposition degree, peat botanical composition and other properties, which in fen peat are significantly different from those in bog peat.

Fen environment significantly differs from raised bogs, and not only biologically but also in terms of chemical composition, which is understudied in Latvia. Numerous authigenic minerals (carbonates, sulphides, phosphates, etc.) have been formed in fen peat and have a significant impact on the metal accumulation pattern. Moreover, while bogs predominantly have only one basic source of metal supply (atmospheric precipitation), fens have a variety of potential sources of supply, which are highly site-related (Silamiņe 2010; Krumins *et al.* 2011). At present, approximately 10% of Latvia is covered by raised bogs, fens and transitional peatlands, which are irregularly distributed throughout the country (Lacis, 2010). Fens are an important type of peatlands, occupying significant areas – up to 52% of the whole area covered by mires (Pakalne, Kalnina 2005).

The main aim of this study was to investigate the relation between fen peat physico-chemical properties on metal accumulation and also to identify the potential sources of metal supply in fen peat. In order to achieve this aim, the following tasks were set: (1) to describe the geological conditions of mire catchment area; (2) to describe the physico-chemical properties of fen peat; (3) to determine the content metal in fen peat; (3) to evaluate the impact of fen peat properties on metal content.

DESCRIPTION OF STUDY SITES

In this study three typical fens (Fig. 1) in Latvia were selected (Svētupes Mire, Elku Mire and Vīķu Mire). The criteria of this selection were based on the

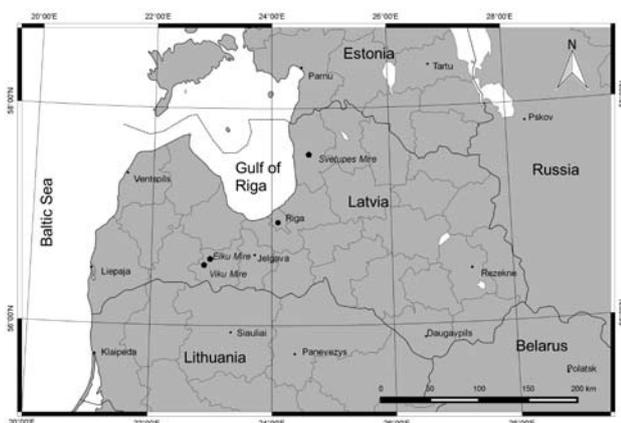


Fig. 1 Location of the study area: 1) Svētupes Mire, 2) Elku Mire, 3) Vīķu Mire. Compiled by J. Krūmiņš, 2015

representativeness of these fens and variety of available data on the properties of fen peat. Differences in mire formation timing, development conditions and interaction with environment influence differences in the botanical composition of peat. All study sites are of similar origins (basin overgrowth) but have very different botanical compositions. Relatively similar physico-geographical conditions and similar origins on the one hand and noticeable differences in further development of the mires on the other hand suggest high variability in peat properties and their impact on metal accumulation in peat.

Svētupes Mire

Svētupes Mire is located in Idumeja Upland, 71 m above sea level, at coordinates: 57°32'49"N : 24°41'48"E. The nearest populated areas is Ozolaine (3 km to the south), Katvari (5 km to the east) and Viļķene (8 km to the north), and they are not related to the significant recent pollution sources. The total area of Svētupes Mire is 917 ha, and now it is mostly covered by forest (640 ha). The average depth of the peat profile is 1.2 m, with the maximum known depth of 3.0 m.

Elku Mire

Elku Mire is located in Lielaucē Hillcock, 86 m above sea level, at coordinates: 56°37'22"N : 22°59'16"E. The nearest populated areas are Zebreņe (7 km to the southwest) and Kaķenīki (7 km to the northeast). The total area of Elku Mire is 285 ha, 188 ha of which is covered by typical fen. The average depth of the peat profile is 1.1 m, with the maximum known depth of 3.5 m.

Vīķu Mire

Vīķu Mire is located in Lielaucē Hillcock, 100 m above sea level, at coordinates: 56°30'58"N : 22°54'32"E. The nearest populated area is Lielaucē (1 km to the east). Vīķu Mire completely surrounds Lake Lielaucē, and the total area of the mire is 875 ha, 397 ha of which is fen. The average thickness of the fen peat layer is 2.0 m, with the maximum known depth of 4.5 m.

METHODOLOGY

The sites for peat sampling were carefully selected in line with the aim and tasks of the study (Givelet *et al.* 2004). Peat samples were taken with a stainless steel 'Russian' type corer. Constraints of usage of the corers of this type were taken into account following Zacccone *et al.* (2012). A semi-cylindrical corer with a shutter was penetrated into peat deposits, twisted and recovered to display a full and undisturbed peat profile (Jowsey 1966; de Vleeschouwer *et al.* 2007). For the survey, a model with a 0.50 m long sample chamber with the inner diameter of 0.07 m was used. The coring, probing and sampling were performed in the central areas of the mires, where the most complete

geological sections can be found (Shotyk *et al.* 2001; Coggins *et al.* 2006). The 0.5 m long, monolithic peat samples were put in special plastic cartridges and wrapped in polyethylene film to preserve the natural moisture and other parameters. The peat monoliths were divided into 0.05 m samples, and the outside edges of each 0.05 m sample were discarded because of possible contamination during the sampling. Fen peat was studied using standardised laboratory methods (Tan 2005), and all analyses were performed on 5 cm thick peat profile samples.

The metal content was determined in acid-digested samples of fen peat, using atomic absorption spectroscopy (AAS), and in peat ashes, using the total reflection X-ray fluorescence (TXRF) method (Potts 1987; Bish *et al.* 1989; Krachler *et al.* 2003). Acid digestion was carried out using 25 ml 50% HNO₃ and 5 ml 30% H₂O₂ per 1 g of oven-dried peat samples. Each sample was mixed with the acid solution and left for 24 h. The mixtures were then boiled at 150°C until half of the liquid evaporated, and then 25 ml of 50% HNO₃ were added one more time. The digested samples were filtered and diluted with Millipore water up to a total volume of 50 ml for further use in atomic absorption spectroscopy. To obtain more accurate and comparable results, the metal concentration was normalised against Ti content in the peat samples, which was determined as described in Bish *et al.* (1989). TXRF measurements (metal and non-metal content in peat mineral matter) were performed on peat ash using a PANalytical X'Pert PRO X-ray diffractometer.

In order to obtain data on the physico-chemical properties of fen peat, a variety of analytical techniques were used. Dating of the bulk samples of peat was performed using the conventional liquid scintillation counting technique (Tamers 2010; Piotrowska *et al.* 2011) at the Institute of Geology, Tallinn University of Technology (Tln), Estonia. The absolute age was calculated using 'Clam' v. 1.0.2 add-on for 'R' v. 2.11.0 software. To calibrate the obtained data, the authors used the calibration curve IntCal09.14C (Reimer *et al.* 2009). The decomposition degree of peat was determined by the centrifugation method according to GOST 10650-72 standard and expressed as percentage of the total peat sample mass (Malterer *et al.* 1992). The botanical composition of peat was determined with a binocular microscope at 56 x to 140 x magnification according to GOST 28245-89 standard (Kac *et al.* 1977; Lamacraft 1979). The humification index was determined by means of the spectro-photometric method (Blackford, Chambers 1993; Borgmark 2005). 1.00 g of peat with 25 ml of 8% NaOH added were heated for 1.5 h at 95°C in water bath. After the heating, the samples were filtered and half of the solution was diluted with deionised water to a volume of 100 ml. The humification index

was evaluated as the peat extract absorption value at 540 nm. Although D₅₄₀ is a simplistic measurement, it is a reliable and informative indicator describing the transformation process of living matter, and it can be also considered as a K-value (Hughes *et al.* 2012). The content of organic matter, carbonate matter and mineral matter was determined and the values were calculated using the loss-on-ignition method (Heiri *et al.* 2001). The samples were dried in an oven at 105°C for 24 h and heated in the oven at 550°C for 4 h and at 950°C for 2 h. The elemental composition (C, H, N and S) was determined using a Carlo Erba Elemental Analyzer EA-1108 with a PC-based data system. All values were normalised against the ash content, because of the high and site dependent mineral matter content in fen peat. The oxygen content was measured as the residue (100% minus the content of C, H, N and S). The elemental composition was further used to calculate the oxidation index (ω) and hydrogen deficiency (ϕ) (Fong *et al.* 2007).

The presence of functional compounds in peat, such as alcohols, aliphatic hydrocarbons and polysaccharides was determined by the method of Fourier-transform infrared spectroscopy. 250 mg of KBr salt were mixed up with 25 mg of air-dried and powdered peat sample, and then the substance was manually compressed into a pellet and irradiated with infrared radiation. Infrared spectra were recorded in the wavelength range from 4000-450 cm⁻¹ with resolution of 4 cm⁻¹ and demonstrate the functional composition of fen peat (Stuart 2004).

The obtained data were statistically processed using the principal component and correlation analyses. The principal component analysis was performed using MATLAB R2014a v. 5.3.0.532 and PCORD 5 software. Additional statistical and graphical post-processing of data was carried out using Microsoft Office Excel 2007, Tilia 1.7.16 and SPSS 17 software. The Pearson correlation analysis was carried out between the concentrations of particular metals and the properties of peat. Each measured metal was subject to the determination of metrological parameters, the method detection limit and the quantitative limit.

RESULTS

Composition of the peat profile of Svētupes Mire

The peat profile of Svētupes Mire (Fig. 2) has been formed by three different fen peat types (wood-grass, wood-sedge and sedge fen peat) since 9000 cal yr BP. The peat samples for radiocarbon dating were taken from 3 specific locations in the profile: 1) Tln-3376, 0.50–0.70 m, 5775±55 ¹⁴C yr BP; 2) Tln-3377, 1.30–1.50 m, 7289±60 ¹⁴C yr BP and 3) Tln-3378, 2.20–2.40 m, 8190±60 ¹⁴C yr BP. The age scale of the profile (Fig. 2) was calculated as described in the methodology section. The peat decomposition degrees

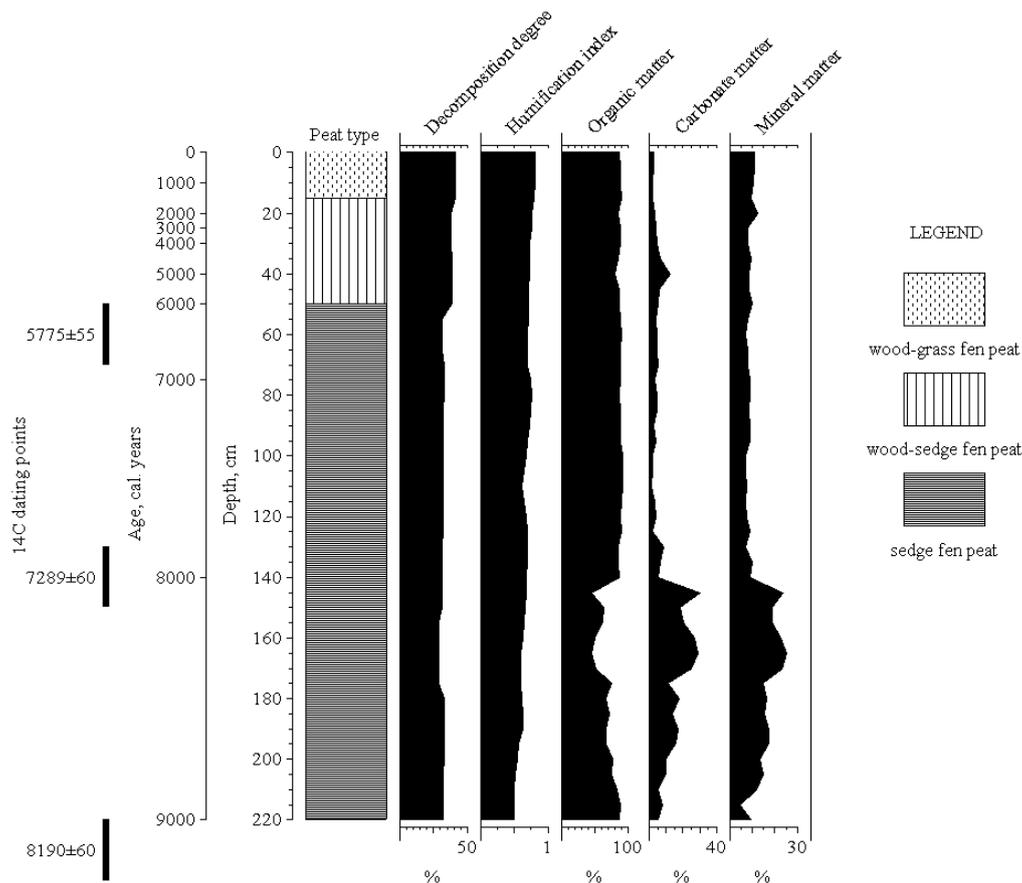


Fig. 2 Changes of properties in the peat profile composition of Svētupes Mire (N=44). Compiled by J. Krūmiņš, 2015

varied from 29 to 41%, with the highest value in the upper wood-grass fen peat layer. The peat humification index varied from 0.49 to 0.81. The organic matter content was from 51.9 to 91.2%, the carbonate matter content – from 1.21 to 24.84%, and the mineral matter – from 6.9 to 23.24% of the fen peat composition.

The elemental composition of fen peat from Svētupes Mire was: C – 27.6–39.2%, H – 1.0–4.7%, N – 0.5–2.7%, and O – 51.1–67.9%; the amount of S was less than 0.5% throughout the full peat profile.

Composition of the peat profile of Elku Mire

The peat profile of Elku Mire (Fig. 3) consists of 1 transitional peat type and 4 different fen peat types (wood transitional, wood fen, wood-reed fen, and reed fen and sedge fen peat) with the absolute age 8 000 cal yr. The peat samples for radiocarbon dating were taken from 3 specific locations in the profile: 1) Tln-3239, 0.90–1.00 m, 4900±55 ¹⁴C yr BP; 2) Tln-3240, 1.50–1.60 m, 5150±55 ¹⁴C yr BP and 3) Tln-3241, 1.82–1.92 m, 6360±100 ¹⁴C yr BP. The age scale of the profile (Fig. 3) was calculated as described in the methodology section. The peat decomposition degrees varied from 35 to 46%, with the highest value in the upper peat layer and the lowest value in the bottom peat layer. The peat humification index varied from 0.28 to 0.68. The organic matter content was from 79 to 90%, with the high-

est value in the upper peat layer. The carbonate matter content, in turn, varied from 3 to 6.51%, and the mineral matter content – from 3 to 13.92%.

The elemental composition of peat from Elku Mire was: C – 41.2–48.9%, H – 3.9–5.2%, N – 0.8–2.5%, and O – 43.62–53.5%; the amount of S was less than 0.5% throughout the full peat profile.

Composition of the peat profile of Viķu Mire

The peat profile of Viķu Mire consists of 7 different fen peat types (wood, wood-grass, grass, wood-*sphagnum*, wood-sedge, sedge-*hypnum* and sedge fen peat) with the absolute age of 8.000 cal yr (Fig. 4). The peat samples for radiocarbon dating were taken from 2 specific locations in the profile: 1) Tln-3213, 1.50–1.60 m, 5060±60 ¹⁴C yr BP and 2) Tln-3216, 2.70–2.80 m, 7205±105 ¹⁴C yr BP (underlying sapropel deposits). The age scale of the profile (Fig. 4) was calculated as described in the methodology section. The peat decomposition degrees varied from 27 to 53%, with the highest value in the upper peat layer and the lowest – in the bottom peat layer. The peat humification index varied from 0.21 to 0.81, and this parameter does not seem to correlate with the peat decomposition degree. The organic matter content in peat was rather stable (~90%) throughout the full peat profile, while the carbonate and mineral matter was subject of change. The carbonate

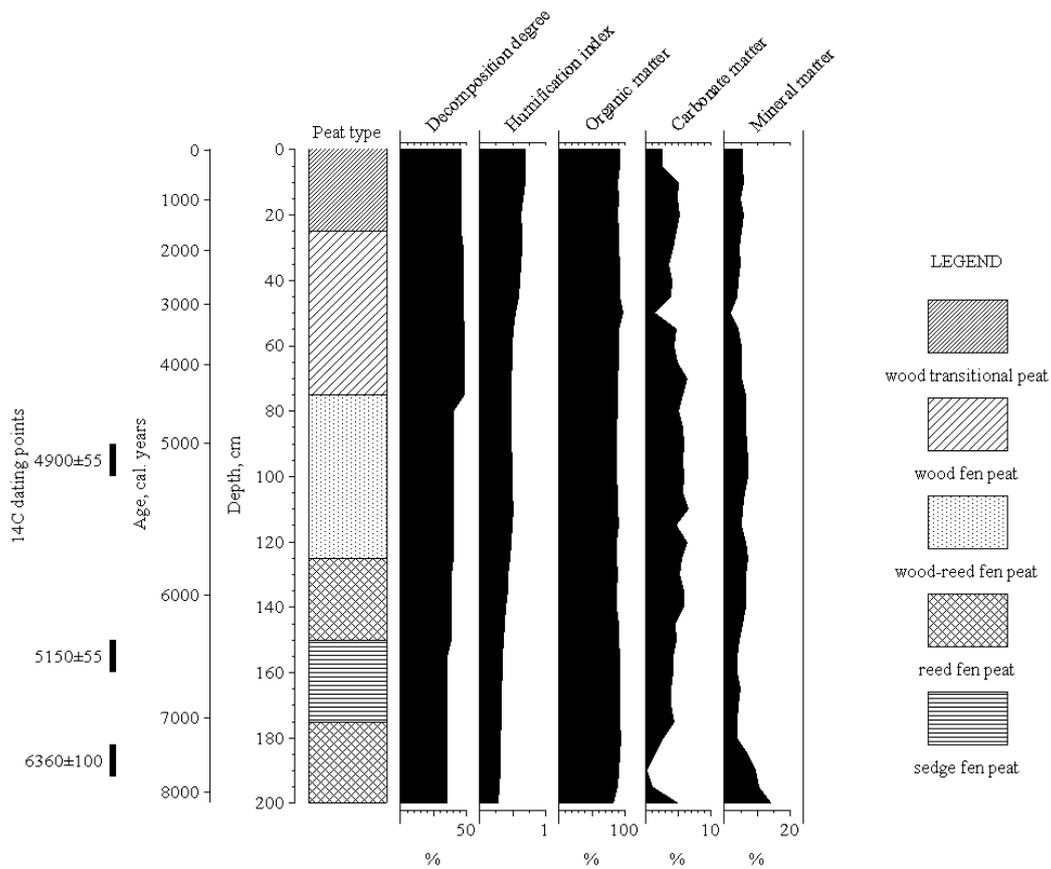


Fig. 3 Changes of properties in the peat profile composition of Elku Mire (N=40). Compiled by J. Krūmiņš, 2015

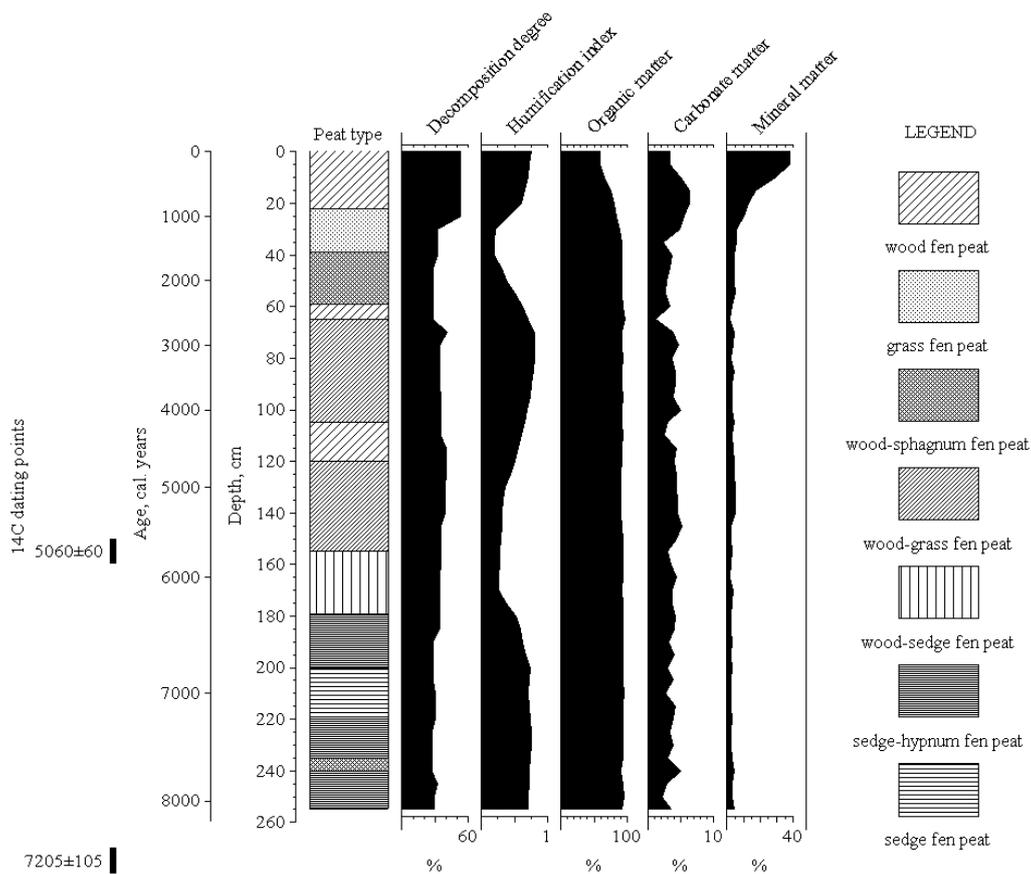


Fig. 4 Changes of properties in the peat profile composition of Viķu Mire (N=50). Compiled by J. Krūmiņš, 2015

matter content in the fen peat profile varied from 1.27 to 6.38% and the mineral matter – from 2.23 to 38.09%.

The elemental composition of peat from Vīķu Mire was: C – 28.7–42.2%, H – 3–4.77%, N – 1.5–2.9%, and O – 50.13–66.8%; the amount of S was less than 0.5% throughout the full peat profile.

Alkali and alkaline earth metals in fen peat

The highest concentration of K (202 mg/kg) in peat from Svētupes Mire was found in the upper part of the peat profile, and the lowest (8 mg/kg) – in the middle part (Fig. 5). The highest concentration of Na (132.1 mg/kg) was in the upper part of the peat profile, and the lowest (25 mg/kg) – in the middle part. The highest content of Ca (> 171 g/kg) in peat from Svētupes Mire was found in the middle part of the peat profile, in sedge fen peat; the lowest (4.6 g/kg) – in the upper part. The distribution of Mg in the peat profile from Svētupes Mire was different from the accumulation pattern of Ca. The peak Mg concentration (3.1 g/kg) occurred in the upper part of the peat pro-

file, in wood-sedge fen peat; the lowest (0.5 g/kg) – in the bottom part.

The highest concentration of K (269 mg/kg) in the peat profile from Elku Mire (Fig. 6) was in the upper part of the profile, in transitional wood peat; the lowest (1.6 mg/kg) – in the middle part of the profile, in reed fen peat. The highest content of Na (177 mg/kg) in peat from Elku Mire was in transitional wood peat, where the least concentration (39 mg/kg) was also identified. The highest content of Ca (> 40 g/kg) in peat from Elku Mire was detected in the middle part of the profile, in wood-reed fen peat; the lowest (16.8 g/kg) – in the bottom part. The distribution of Mg, with slight differences, was similar to the accumulation pattern of Ca. However, the concentration of Mg was significantly lower – only 1.5 g/kg at the highest and 0.5 g/kg at the lowest.

The highest concentration of K (498 mg/kg) in peat from Vīķu Mire (Fig. 7) was found in the middle part of the peat profile; the lowest (not exceeding 17 mg/kg) – in the upper part. The highest concentration

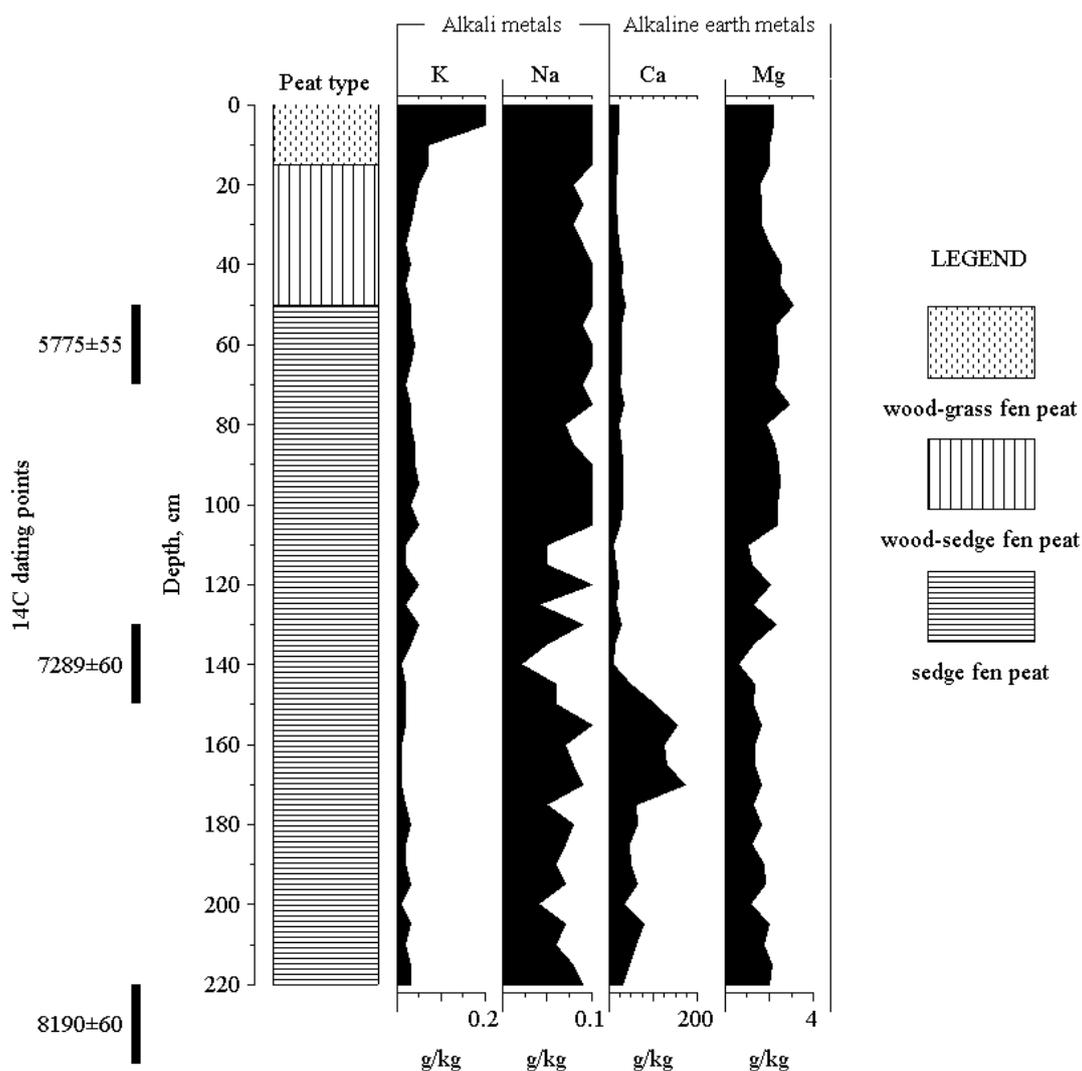


Fig. 5 Alkali and alkaline earth metal distribution in the peat profile from Svētupes Mire (N=44). Compiled by J. Krūmiņš, 2015

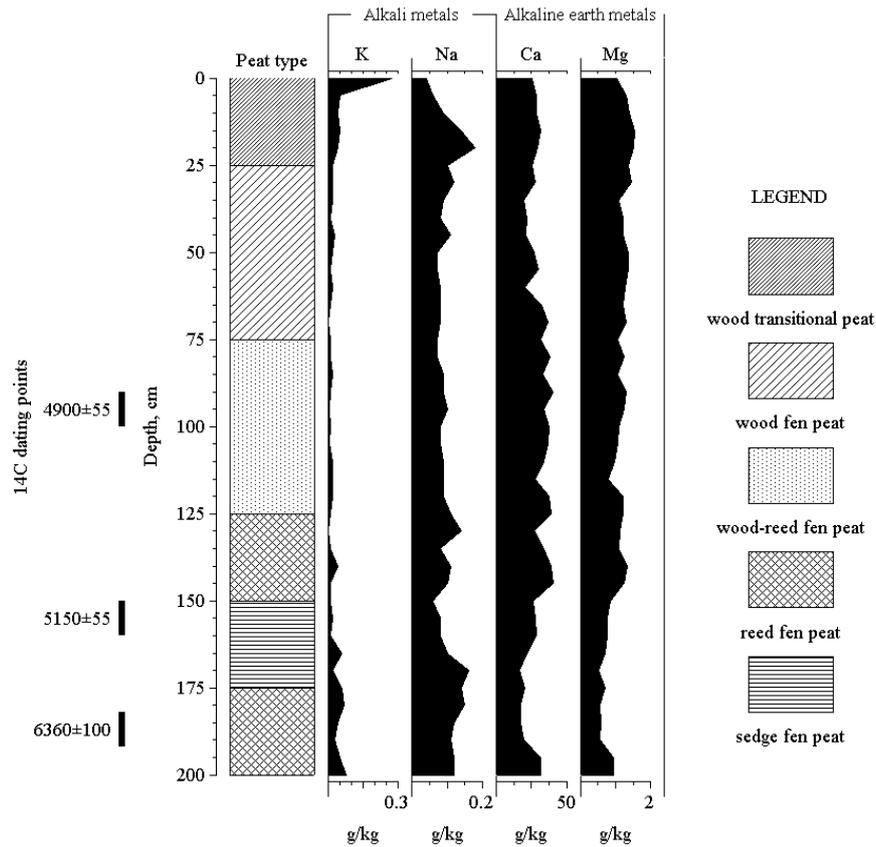


Fig. 6 Alkali and alkaline earth metal distribution in the peat profile from Elku Mire (N=40). Compiled by J. Krūmiņš, 2015

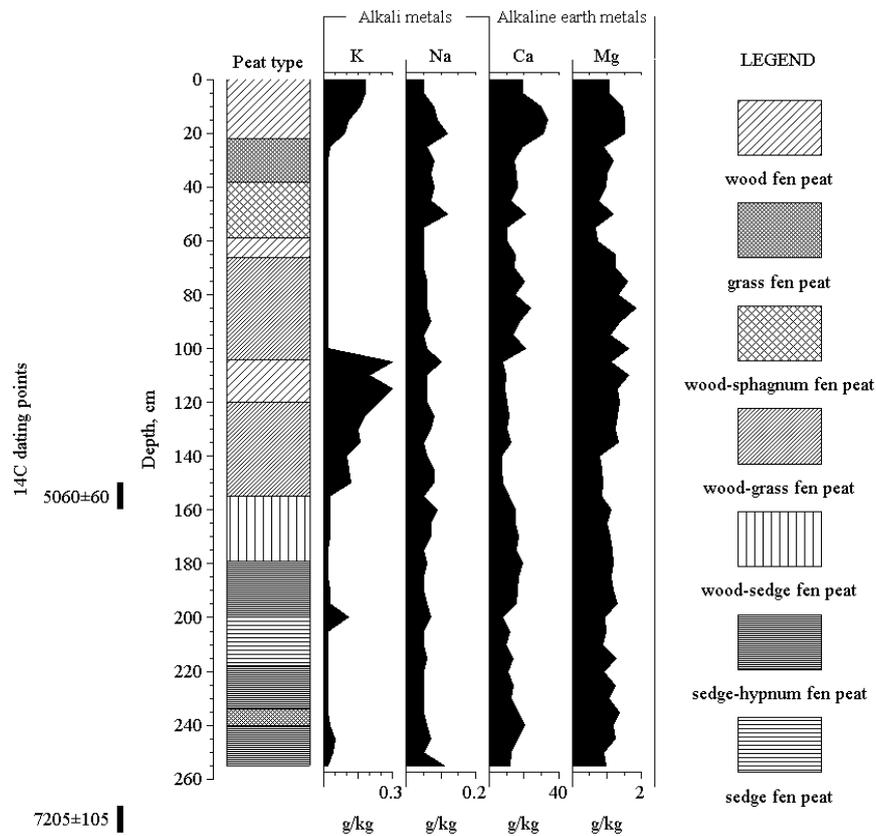


Fig. 7 Alkali and alkaline earth metal distribution in the peat profile of Vīķu Mire (N=50). Compiled by J. Krūmiņš, 2015

of Na (119 mg/kg) in peat from Viķu Mire was in the upper part of the peat profile, in wood-*sphagnum* fen peat; the lowest (47 mg/kg) – in wood-grass fen peat. The highest content of Ca (> 33.9 g/kg) in peat from Viķu Mire was in the upper part of the profile, in wood fen peat; the lowest (7.1 g/kg) – in the middle part, in wood-grass fen peat. The distribution of Mg was similar to the accumulation pattern of Ca. The highest amount of Mg (1.8 g/kg) was observed in the middle part of the peat profile, represented by wood-grass fen peat; the lowest (0.7 g/kg) – in the upper part, in wood-*sphagnum* peat.

Transition metals and lead in fen peat

The highest concentration of Fe (6.43 g/kg) in peat from Svētupes Mire (Fig. 8) was identified in the bottom part of the peat profile; the lowest (0.52 g/kg) – in the upper part, in wood-sedge fen peat. The highest concentration of Mn (95 mg/kg) in peat from Svētupes Mire was in the bottom part of the peat profile; the lowest (10 mg/kg) – in the upper part. The highest concentration of Ni (1.5 mg/kg) was in the upper part of the peat profile, in wood-grass fen peat; the lowest (0.16 mg/kg) – in the bottom part. The highest concentration of Co (1.2 mg/kg) in peat from Svētupes Mire was

determined in the middle part of the peat profile, while the low concentration (0.12 mg/kg) could be traced throughout the profile. The highest concentration of Zn (32 mg/kg) was in the upper part of the peat profile, in wood-grass fen peat; the lowest (0.2 mg/kg) – in the middle part. The highest concentration of Cu (7 mg/kg) in peat from Svētupes Mire was in the upper part of the peat profile, in wood-grass fen peat; the lowest (0.1 mg/kg) – in the middle part. The highest concentration of Cd (0.8 mg/kg) was in the upper part of the peat profile, in wood-grass fen peat; the lowest (0.04 mg/kg) – in the middle part. The concentration of Cr throughout the peat profile from Svētupes Mire was below the AAS detection level, so it can be considered as very low. The highest concentration of Pb (44 mg/kg) in peat from Svētupes Mire was in the upper part of the peat profile, in wood-grass fen peat, while in the rest of the peat profile the Pb content did not exceed 0.5 mg/kg.

The highest concentration of Fe (5.6 g/kg) in peat from Elku Mire (Fig. 9) was in the bottom part of the profile, in sedge fen peat; the lowest (0.75 g/kg) – in the upper part, in wood fen peat. The highest concentration of Mn (0.92 g/kg) in peat from Elku Mire was in transitional wood peat; the

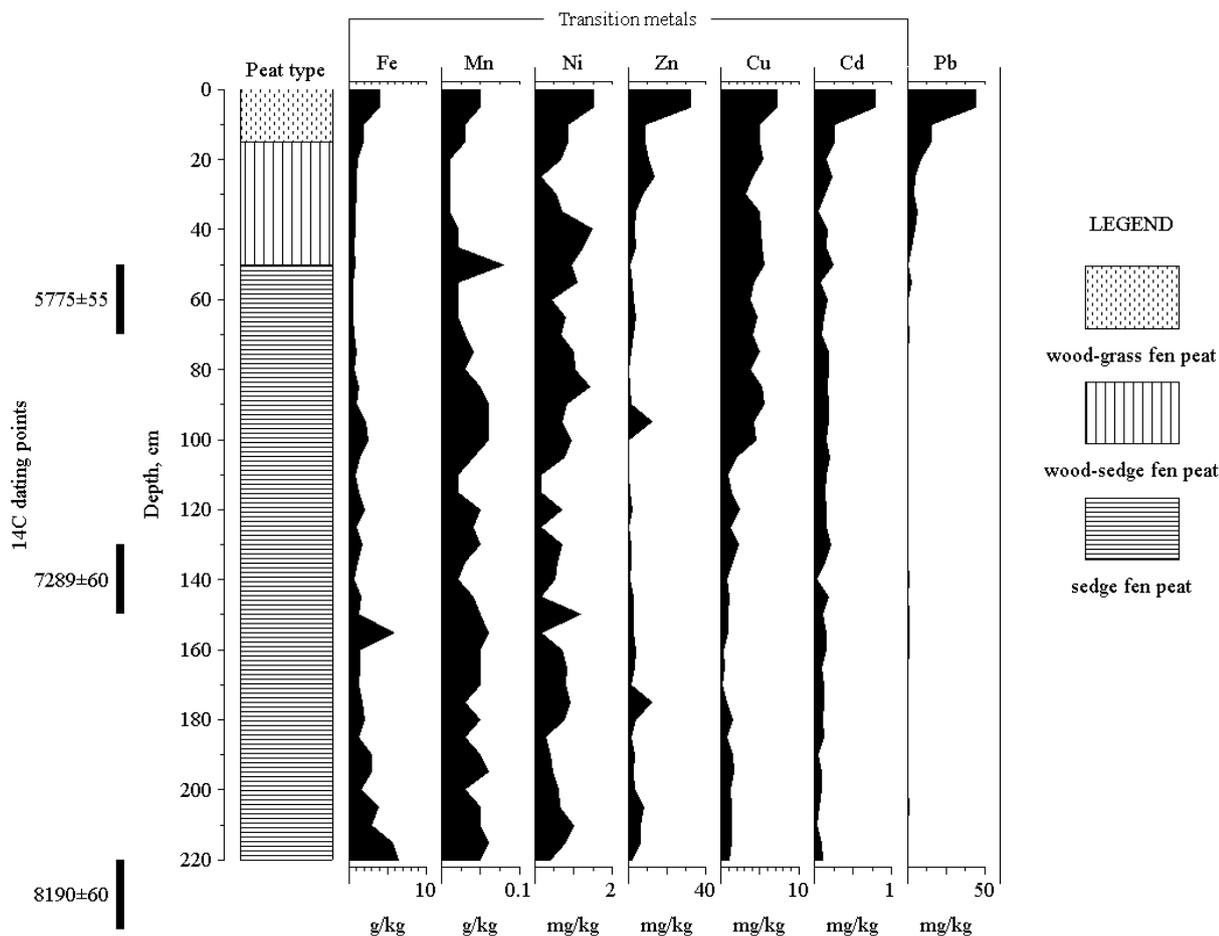


Fig. 8 Transition metal and Pb distribution in the peat profile from Svētupes Mire (N=44). Compiled by J. Krūmiņš, 2015

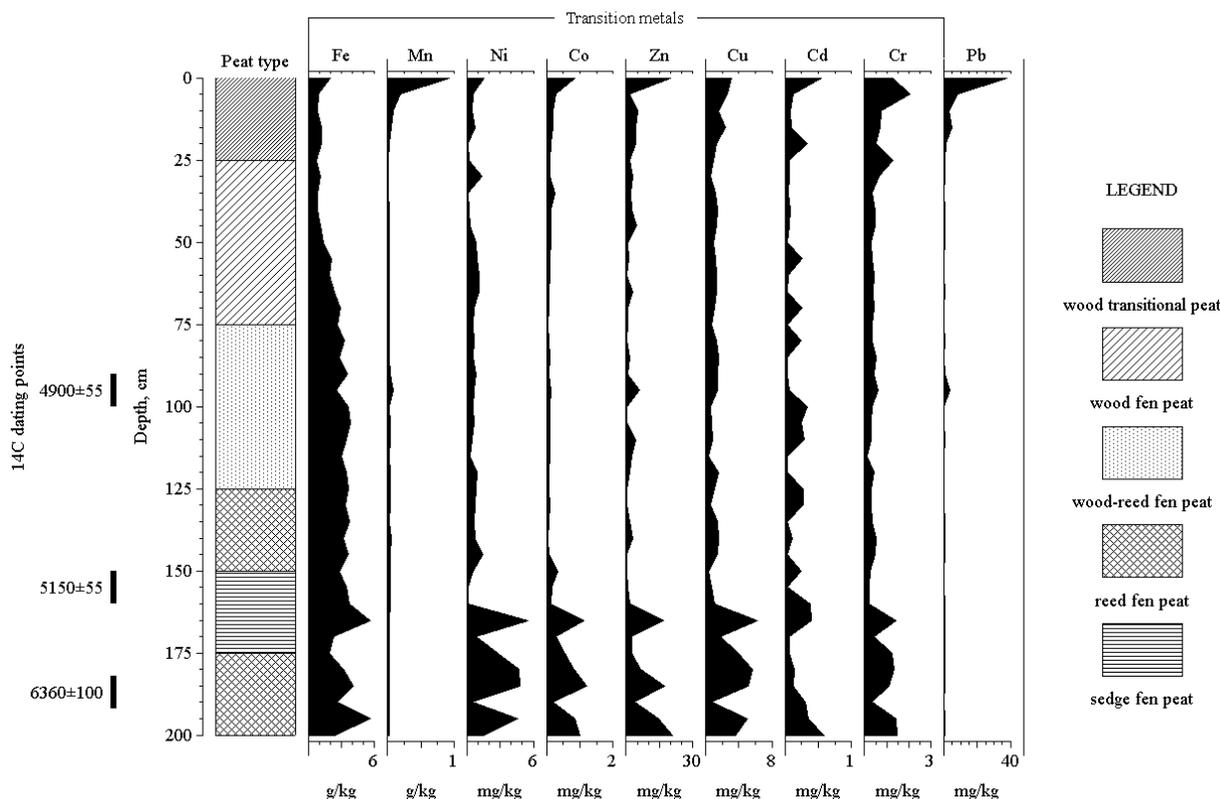


Fig. 9 Transition metal and Pb distribution in the peat profile of Elku Mire (N=40). Compiled by J. Krūmiņš, 2015

lowest (8.8 mg/kg) – in the upper part, in wood fen peat. The highest concentration of Ni (5.47 mg/kg) was in the bottom part of the peat profile, in sedge fen peat; the lowest (0.2 mg/kg) – in the upper part, in wood fen peat. The highest concentration of Co (1.2 mg/kg) in peat from Elku Mire was in the bottom part of the peat profile, in reed fen peat; the lowest (0.03 mg/kg) – in the middle part, in wood-reed fen peat. The highest concentration of Zn (20 mg/kg) was in transitional wood peat; the lowest (0.2 mg/kg) – in the middle part, in reed fen peat. The highest concentration of Cu (6 mg/kg) in peat from Elku Mire was in the bottom part of the peat profile, in sedge fen peat; the lowest (0.4 mg/kg) – in the middle part, in reed fen peat. The highest concentration of Cd (0.54 mg/kg) was in transitional wood peat; the lowest (0.03 mg/kg) – in the middle part, in wood-reed fen peat. The highest content of Cr (2 mg/kg) was in transitional wood peat; the lowest (0.13 mg/kg) – in wood-reed fen peat in the middle part of the peat profile. The highest concentration of Pb (38 mg/kg) in peat from Elku Mire was in transitional wood peat, while the rest of the peat profile contained low Pb concentrations (< 0.5 mg/kg).

The highest concentration of Fe (4.7 g/kg) in peat from Viķu Mire (Fig. 10) was detected in the upper part of the peat profile, in wood fen peat; the lowest (216 mg/kg) – in the middle part, in wood-*sphagnum* fen peat. The highest concentration of Mn (63 mg/kg) in peat from Viķu Mire was in the upper part of the peat

profile, in wood fen peat; the lowest (1.9 mg/kg) – in the middle part, in wood-*sphagnum* fen peat. The highest concentration of Ni (3.2 mg/kg) was in the upper part of the peat profile, in wood fen peat. The highest concentration of Co (2 mg/kg) in peat from Viķu Mire was found in wood fen peat in the upper part of the peat profile. The highest concentration of Zn (12.4 mg/kg) was in the upper part of the peat profile; the lowest (2.3 mg/kg) – in the middle part. The highest concentration of Cu (6.9 mg/kg) in peat from Viķu Mire was determined in wood fen peat in the upper part of the peat profile; the lowest (0.8 mg/kg) – in the bottom part, in sedge-*hypnum* peat. The highest concentration of Cd (0.26 mg/kg) was in the upper part of the peat profile, while the low Cd content (0.01 mg/kg) was traced throughout the peat profile.

The highest concentration of Cr (1.9 mg/kg) was in the upper part of the peat profile, in wood fen peat. The highest concentration of Pb (23.5 mg/kg) in the peat profile of Viķu Mire was in the upper part, in wood fen peat contains, while in the rest of the profile the Pb content remained low (did not exceed 0.5 mg/kg).

DISCUSSION

Mire catchment area

It is a well known fact that groundwater plays the major role in metal accumulation in fens (Tjuremnov 1976). Therefore, it is essential to describe the mire catchment area to identify the deposits through which

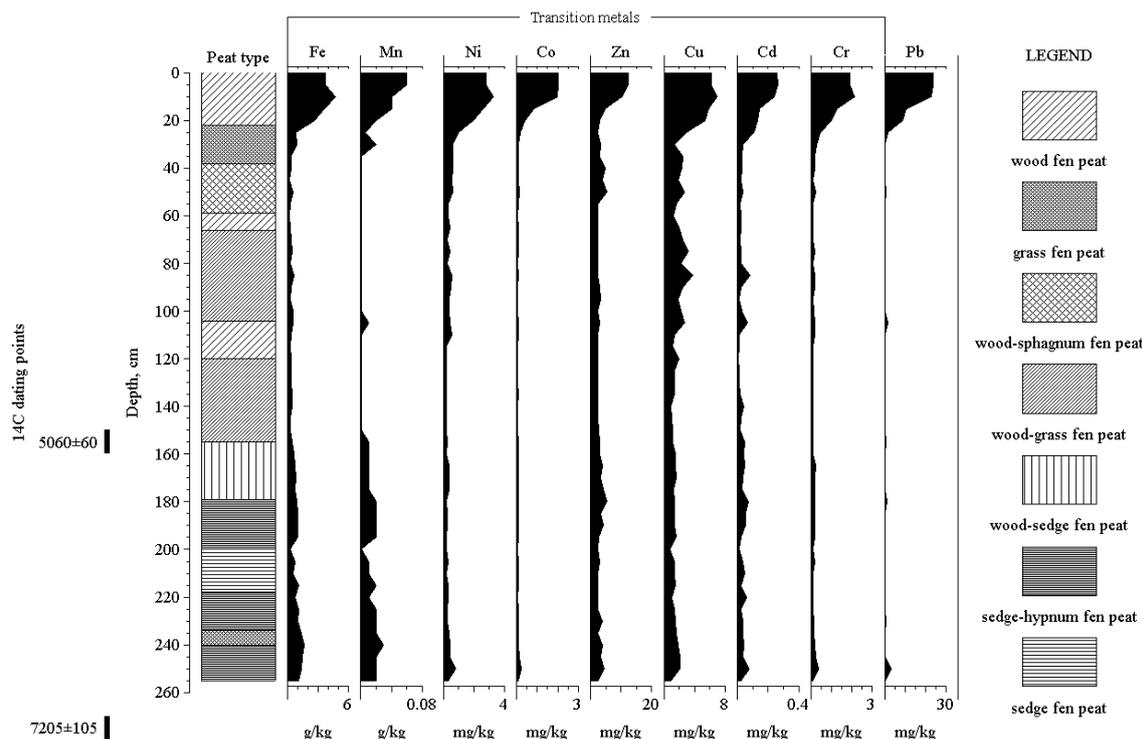


Fig. 10 Transition metal and Pb distribution in the peat profile of Viķu Mire (N=50). Compiled by J. Krūmiņš, 2015

Table 1 Lithology of Quaternary deposits of mire catchment areas

Deposits Mire	Mire (bQ ₄)	Glaciofluvial (fQ ₃ <i>ltv</i>)	Glaciolacustrine (lgQ ₃ <i>ltv</i>)	Glacigenic (gQ ₃ <i>ltv</i>)	Alluvial (aQ ₄)
Svētupes Mire	Peat, sapropel	Sand, gravel, pebble	Clayey silt	Till	Sand, gravel, pebble, silt
Elku Mire	Peat, sapropel	Sand, gravel, pebble	Sand, clayey silt	Till	-
Viķu Mire	Peat, sapropel	Sand, gravel, pebble	Sand	Till	-

the groundwater flows. Also, a noteworthy aspect is the presence of geochemical barriers (biochemical, mechanical, physico-chemical, etc.), which, fundamentally, are changes in the environmental settings and may lead to an increased amount of metals in peat (Orru, Orru 2006). In this study, to mark the boundaries of mire catchment areas, we have conducted a detailed analysis of the cartographical material, including topography, geomorphology, hydrological networks, watersheds, hydrogeological conditions and other aspects.

Quaternary geology and agricultural land use of the mire catchment area

Metals in superficial deposits in mire catchment areas are essential to the accumulation and concentration of metals in fens (Syrovėtnik *et al.* 2004). Due to deposit weathering, metal ions are released into the groundwater and delivered to the mire. The Quaternary surface of the catchment area of Svėtupes Mire is composed of till, clayey silt and sand (Table 1). The bot-

tom part of the peat profile contains a high amount of mineral matter (Fig. 2), which can be explained by the groundwater flow through the glacigenic and glaciolacustrine deposits. In the base of the mire lies carbonate-rich sapropel. However, the metal accumulation character does not suggest the presence of a geochemical barrier. The land surface of the catchment areas of Elku Mire and Viķu Mire (Table 1) are composed of clayey silt, sand, gravel, pebble and, to a lesser extent, also of till. In the base of Elku Mire lies sandy and carbonate-rich sapropel, which hypothetically can be evaluated as a geochemical barrier and can cause an elevated metal concentration in peat. Viķu Mire is surrounded by sandy deposits of varying coarseness, which explains the high mineral matter content in the upper peat layer (Fig. 4). In the base of the mire lies carbonate-rich sapropel. However, the metal accumulation in peat seemingly is not affected by this factor.

Agricultural land use in mire catchment areas is one of the major factors with a direct contribution to the accumulation of metals in fens because of soil

liming and conditioning, pesticide and fertiliser use and other anthropogenic impacts (van der Warf, Petit 2002). High amounts of Ca, Na, K and other metals get into the groundwater and then are delivered to the mire. The catchment area of Svētupes Mire is mostly covered by forests, and there is no agricultural land. Deposits of the land surface in the catchment areas of Elku Mire and Vīķu Mire are similar: in both areas there are both forests and agricultural lands lying on the sandy deposits. Thus, the soil improvers used for agricultural lands have impact on the metal content in fen peat (Figs. 3, 4, 6, 7, 9, 10).

Relation between the physico-chemical properties of fen peat

Data analysis indicated that each study site has an individual set of statistically significant correlations ($p < 0.05$) between the physico-chemical properties of fen peat (Fig. 11), pointing to the heterogeneous nature of fen peat due to differences in geomorphological, geological, hydrological and hydrogeological conditions in the mire catchment areas.

The results obtained in the study showed that interactions among the physico-chemical properties of peat were specific for each study site. Thus, it can be concluded that all relations among the properties of peat are highly site-dependent. However, despite distinct interactions among the properties of peat, the quantities of organic matter and mineral matter, elemental composition, botanical composition, decomposition degree, depth, age and groundwater impact are all of great importance for the variability of fen peat properties.

Relations among the metal content and fen peat properties

The results show a direct relation between the ash content and metal concentration in peat (Fig. 12). Although figure 12 demonstrates relations between peat characteristics and metal content in Vīķu Mire; however same pattern can be observed also in peat profiles from Elku and Svētupes Mire, This can be explained by the high importance of groundwater

flow for the composition of fen peat. Respectively, metals are supplied with groundwater from the mire catchment area, and their concentrations in peat are highly dependent on the character of deposits through which the groundwater flows.

Factors determining metal accumulation in fen peat

The principal component analysis (PCA) can be successfully used to characterise possible metal sources and primary peat-forming factors, which cannot be observed directly and/or are not correlated to one another, but describe the mire origin and

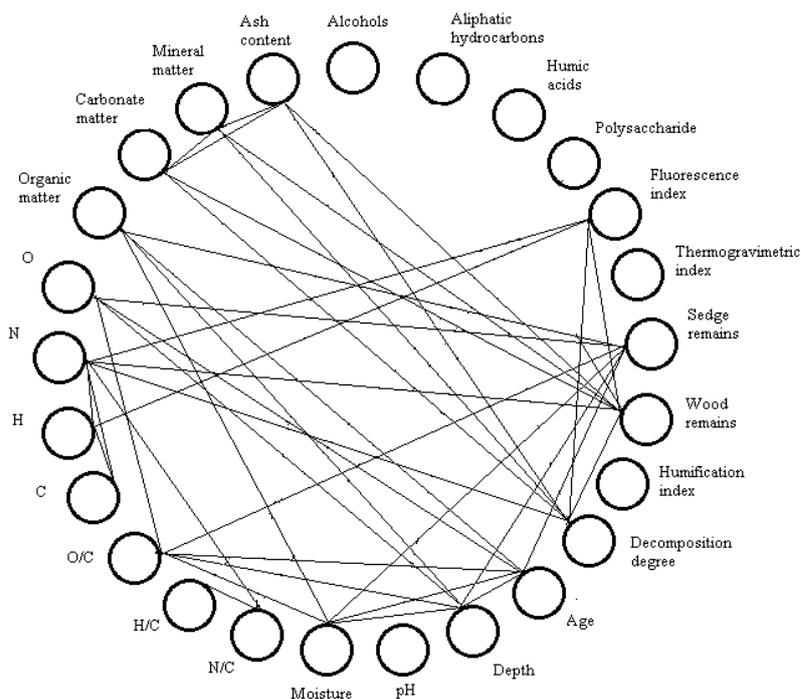


Fig. 11 Interactions among the physico-chemical properties of fen peat from Vīķu Mire ($P < 0.05$; $N = 50$). Compiled by J. Krūmiņš, 2015

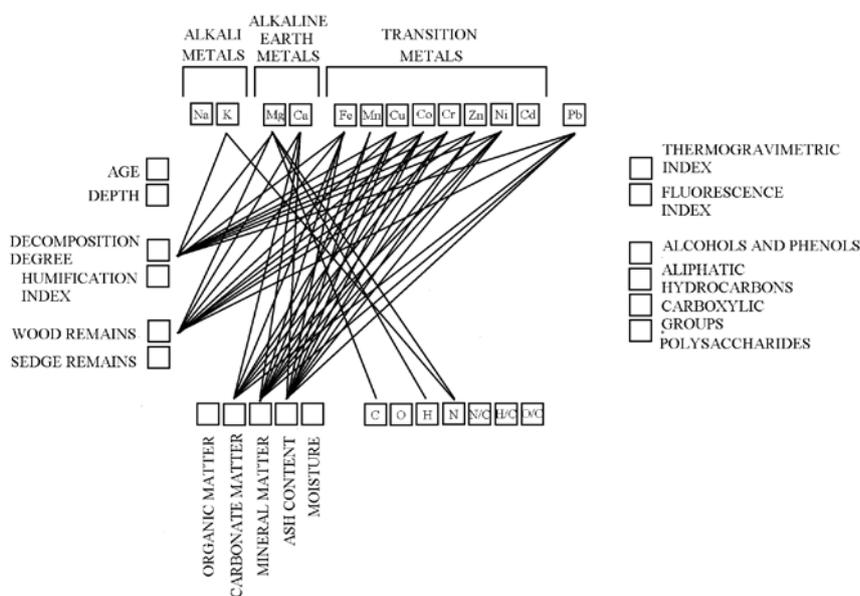


Fig. 12 Relations among metals and the physico-chemical properties of Vīķu fen peat ($P < 0.05$; $N = 50$). Compiled by J. Krūmiņš, 2015

peat accumulation characteristics. The PCA results are described as statistically significant correlations ($r > 0.50$) between the principal components and characteristic parameters of peat. The absolute values of metal content and distribution patterns are affected by a combination of several major factors. Geographical location and spatial characteristics, mire formation conditions and variability of metal supply sources play the key role among the metal accumulation determining factors in a fen peat profile. The PCA matrices created by taking into account several variables allow determining what kind of processes – natural or anthropogenic – has had an impact on the metal accumulation in peat. Although the parameters of the studied fen peat are heterogeneous in nature, the PCA results delineate three separate segments with distinct elemental compositions, metal accumulation and its determining factors.

The PCA results for the peat profile of Vīķu Mire (Fig. 13) and the rest of studied peat profiles demonstrate that the carbonate matter and mineral matter content, peat decomposition degree and elemental composition are of major importance for the metal accumulation in fen peat. Furthermore, the accumulation characters of Mn, Co, Ni, Cr, Zn, Fe, Cu and Ca (Figs 7 and 10) have a strong resemblance. The distribution of such parameters as peat decomposition degree, elemental composition, organic matter and mineral matter content and metal concentration on the coordinate plane is statistically significant for axis 1 (p-value: 0.001) and axis 2 (p-value: 0.002), which explains the 65.17% of the total data dispersion. For axis 1, which explains 44.72% from the total dispersion, statistically significant ($r > 0.50$) positive correlations were found with the decomposition degree ($r = 0.84$), humification index ($r = 0.48$), carbonate matter content ($r = 0.70$) and mineral matter content ($r = 0.98$), N ($r = 0.57$), H ($r = 0.54$), Fe ($r = 0.88$), Mn ($r = 0.75$), Zn ($r = 0.87$), Cu ($r = 0.94$), Mg ($r = 0.55$), Ca ($r = 0.73$), Co ($r = 0.80$), Cr ($r = 0.93$), Ni ($r = 0.87$) and Pb ($r = 0.95$). Axis 1, in turn, has a statistically significant but negative correlation between depth ($r = -0.56$) and organic matter content ($r = -0.96$). Axis 2 explains 20.45% of the dispersion of characteristic peat parameters. In this case, there were positive correlations with the humification index ($r = 0.48$), C ($r = 0.77$), N ($r = 0.49$), H ($r = 0.71$), Mg ($r = 0.55$), K ($r = 0.50$) and H-deficient ($r = 0.77$), while the correlations with the depth ($r = -0.47$), O ($r = -0.78$), Cd ($r = -0.56$) and the oxidation index ($r = -0.56$) were negative. Both axes have a statistically significant correlation with H content, and this is indicative of the dependence of metal concentration on the content of this element.

In sector 1 (see Fig. 13), there are peat parameters grouped, which are characteristic of peat composition and its variability, including peat decomposition de-

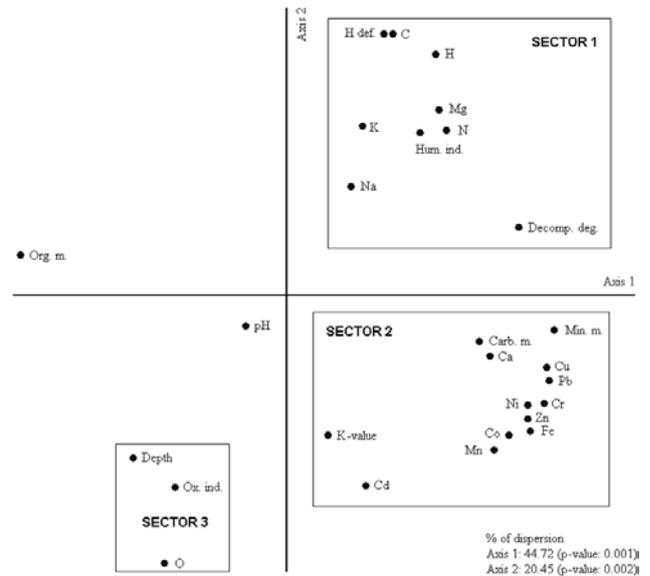


Fig. 13 PCA results of the peat properties and metal content in Vīķu Mire ($P < 0.01$; $N = 50$). Compiled by J. Krūmiņš, 2015

gree, humification index, elemental composition and alkali and alkaline earth metal content (see Figs 4 and 7). All of these parameters are the determining factors for metal binding and accumulation in fen peat. In sector 2, various metal concentrations are distributed, including carbonate matter and mineral matter content as the source of these elements. Furthermore, a variety of metals of a natural origin is distributed in this sector, for instance, Ca and Fe, and also a variety of metals of an anthropogenic origin – Ni, Cu and Pb. However, the variety of metals in sector 2 is generally related to the parameter variability in sector 3, which is the peat depth range and oxygen content in peat.

The PCA results of the peat profile from Svētupes Mire demonstrate a wide variability in the interdependence among fen peat parameters, although there is also a clear similarity with the PCA results of Vīķu Mire peat. The inorganic matter content, peat decomposition degree and elemental composition are also the determinant factors for metal accumulation in the peat profile of Svētupes Mire. Moreover, the Mn, Co, Ni, Zn and Cu distribution patterns have strong a resemblance to those in the peat profile of Vīķu Mire.

The dispersion of data concerning the physico-chemical parameters and variability of metal concentration in peat from Elku Mire is highly heterogeneous. Only axis 1 is statistically significant, and it explains 38.21% of the total data dispersion (p-value: 0.001). Although the data dispersion is high, it is possible to identify similarities with the PCA results for peat from Vīķu Mire and Svētupes Mire. The results delineate three separate segments with distinct peat elemental compositions, organic/inorganic matter ratios and metal accumulation in the studied fen peat.

The obtained data (see Figs 11 and 12) show the

heterogeneity of relations between the metal content and peat properties. So, the sets of peat properties with an impact on the metal concentration are individual. However, similarities can also be identified. The data demonstrate that the content of alkaline earth and alkali metals in peat generally depends on the peat elemental composition, botanical composition and decomposition degree, while the content of transition metals is significantly affected by the peat inorganic matter and groundwater (see Fig. 12).

The metal content in mires – irrespective of whether it is bog (Silamiķele 2010) or fen peat – has natural and anthropogenic sources of supply. Among the natural sources are deposits in the mire catchment area, while the anthropogenic sources can be site-related (agricultural land use, etc.) or pollution-related (wastewater, motor vehicle exhaust emissions, etc.). Metals in bog peat are generally supplied by atmospheric precipitation (Silamiķele 2010), while groundwater is the main supply agent in fens (Tjuremnov 1976). Nevertheless, the atmospheric pollution is also of high importance in describing the metal content in the upper fen peat layer.

CONCLUSIONS

The character of metal accumulation in fen peat profiles is site-dependent due to its heterogeneous nature (variable botanical composition and physico-chemical properties) and hydrological and hydrogeological conditions in the mire catchment area (including the character of deposits). Links among the fen peat properties and metal content depend on the origin of particular metals. The alkaline earth and alkali metal content is linked to the botanical composition and elemental composition of peat, while the transition metal content depends on the character of mineral matter. The upper peat layers in the studied mires contain an increased amount of heavy metals, which can be explained by modern anthropogenic impact. The results of this study also demonstrate that the concentrations of the analysed metals in vertical peat profiles are rather stable and can be used as high-quality data in the reconstruction of past environmental conditions.

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REFERENCES

Bish, D.L., Post, J.E., 1989. Modern powder diffraction. *Reviews in Mineralogy* 20, 101–144.

- Blackford, J.J., Chambers, F.M., 1993. Determining the degree of peat decomposition for peat-based palaeoclimatic studies. *International Peat Journal* 5, 7–24.
- Borgmark, A., 2005. Holocene climate variability and periodicities in south-central Sweden, as interpreted from peat humification analysis. *Holocene* 15, 387–395.
- Brown, P.A., Gill, S.A., Allen, S.J., 2000. Metal removal from wastewater using peat. *Water Resources* 34, 3907–3916.
- Cocozza, C., D’Orazio, D., Miano, T. M., Shotyky, W., 2003. Characterization of solid and aqueous phases of peat bog profile using molecular fluorescence spectroscopy, ESR, and FT-IR. *Organic Geochemistry* 34, 49–60.
- Coggins, A.M., Jennings, S.G., Ebinghaus, R., 2006. Accumulation rates of the heavy metals lead, mercury and cadmium in ombrotrophic peatlands in the west of Ireland. *Atmospheric Environment* 40, 260–278.
- de Vleeschouwer, F., Gerard, L., Goormaghtigh, C., Mattielli, N., le Roux, G., Fagel, N., 2007. Atmospheric lead and heavy metal pollution records from a Belgian peat bog spanning the last two millennia: human impact on a regional to global scale. *Science of Total Environment* 377, 282–295.
- Fong, S.S., Seng, L., Mat, H.B., 2007. Re-use of nitric acid in the oxidative pre-treatment step for preparation of humic acids from low rank coal of Mukah, Sarawak. *Journal of the Brazilian Chemical Society* 18, 41–46.
- Givelet, N., Le Roux, G., Cheburkin, A., Chen, B., Frank, J., Goodsite, M., Kempter, H., Krachler M., Noernberg, T., Rausch, N., Rheinberger, S., Roos-Barraclough, F., Sapkota, A., Scholz, C., Shotyky, W., 2004. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. *Journal of Environmental Monitoring* 6, 481–492.
- Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in deposits: reproducibility and comparability of results. *Journal of Paleolimnology* 25, 101–110.
- Hughes, P.M.D., Mallon, G., Essex, H.J., Amesbury, M.J., Charman, D.J., Blundell, A., Chambers, F.M., Daley, T.J., Mauquoy, D., 2012. The use of k-values to examine plant “species signals” in a peat humification record from Newfoundland. *Quaternary International* 268, 156–165.
- Jowsey, P.C., 1966. An improved peat sampler. *New Phytologist* 65, 245–248.
- Kac, N. J., Kac, S.V., Skobejeva, E. I., 1997. Atlas rastitel-nich ostankov v torfach. Moskva, Nedra. [In Russian]. [Atlas of plant remains in peats].
- Klavins, M., Silamikele, I., Nikodemus, O., Kalnina, L., Kuske, E., Rodinov, V., Purmalis, O., 2009. Peat properties, major and trace element accumulation in bog peat in Latvia. *Baltica*, 22 (1), 37–49.
- Krachler, M., Mohl, C., Emons, H., Shotyky, W., 2003. Two thousand years of atmospheric rare elements (REE) deposition as revealed by ombrotrophic peat bog profile,

- Jura Mountains, Switzerland. *Journal of Environmental Monitoring* 5, 111–121.
- Krumins, J., Kuske, E., Klavins, M., 2011. Major and Trace Element Accumulation in Fen Peat from Elki and Viki Mires in Western Latvia. *Materiālzinātne un lietišķā ķīmija* 24, 71–81.
- Lacis, A., 2010. Mire identification and studies in Latvia, methods applied and obtained results. *Scientific Papers of University of Latvia. Earth and Environmental Sciences, Vol. 752*, LU Riga, 106–115. [In Latvian].
- Lamacraft, R.R., 1979. A method of displaying differences in botanical composition. *Australian Journal of Ecology* 4, 407–409.
- Malterer, T.J., Verry, E.S., Erjaves, J., 1992. Fiber content and degree of decomposition in peats: review of natural methods. *Soil Science Society of America Journal* 56, 1200–1211.
- Martinez-Cortizas, A., Garcia-Rodeja, E., Pontevedra-Pombal, Z., Novoa-Munoz, J.Z., Weiss, D., Cheburkin, A., 2002. Atmospheric Pb deposition in Spain during the last 4600 years recorded by two ombrotrophic peat bogs and implications for the use of peat as archive. *Science of Total Environment* 292, 33–44.
- Orru, M., Orru, H., 2006. Sources and distribution of trace elements in Estonian peat. *Global and Planetary Change* 53, 249–258.
- Pakalne, M., Kalnina, L., 2005. Mire ecosystems in Latvia. In G. M. Steiner (Ed.), “*Moore – von Sibirien bis Feuerland / Mires – from Siberia to Tierra del Fuego*”, 147–174.
- Piotrowska, D.G., Cieslak, M., Królewska, K., Wróblewski, A.E., 2011. Design, synthesis and cytotoxicity of a new series of isoxazolidines derived from substituted chalcones. *European Journal of Medicinal Chemistry* 46, 1382–1389.
- Potts, P.J., 1987. *A handbook of silicate rock analysis*. 2nd ed. Blackie, 622 pp.
- Pujāte, A., 2015. Traces of environmental change and human impact in the sediments of lakes along the coast of the Gulf of Riga. *Doctoral thesis*, University of Latvia. [In Latvian].
- Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk-Ramsey, C., Buck, C.E., Burr, G.S., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Hajdas, I., Heaton, T.J., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., McCormac, F.G., Manning, S.W., Reimer, R.W., Richards, D.A., Southon, J.R., Talamo, S., Turney, C.S.M., van der Plicht, J., Weyhenmeyer, C.E., 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. *Radiocarbon* 51 (4), 1111–1150.
- Shotyk, W., Krachler, M., Martinez-Cortizas, A., Cheburkin, A.K., Emons, H., 2002. A peat bog record of natural, pre-anthropogenic enrichment of trace elements in atmospheric aerosols since 12 370 ¹⁴C yr BP, and their variation with Holocene climate change. *Earth Planetary Science Letters* 199, 21–37.
- Shotyk, W., Weiss, D., Kramer, J.D., Frei, R., Cheburkin, A.K., Gloor, M., Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruere, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12 370 ¹⁴C yr BP. *Geochimica et Cosmochimica Acta* 65 (14), 2337–2360.
- Silamikele, I., 2010. The Character of Humification and Accumulation of Chemical Elements in Raised-Bog Peat Depending on Its Composition and Formation. *Doctoral thesis*. University of Latvia [In Latvian].
- Stankevica, K., Pujate, A., Kalnina, L., Klavins, M., Cerina, A., Drucka, A., 2015. Records of the anthropogenic influence on different origin small lake sediments of Latvia. *Baltica* 28 (2), 135–150.
- Stuart, B.H., 2004. *Infrared Spectroscopy: Fundamentals and Applications*. John Wiley & Sons, Ltd., 244 pp.
- Syrovetnik, K., Neretnieks, I., Malmström, M.E., 2004. Accumulation of heavy metals in the Oostriku peat bog, Estonia: Determination of binding processes by means of sequential leaching. *Environmental Pollution* 147 (1), 291–300.
- Tamers, M.A., 2010. Carbon-14 dating with the liquid scintillation counter: total synthesis of the benzene solvent. *Science* 132, 668–669.
- Tan, K.H., 2005. *Soil sampling, preparation and analysis*. 2nd ed. Taylor & Francis Group, 680 pp.
- Tjuremnov, S.N., 1976. *Peat deposits and their exploration*. Moskva: Nedra. [In Russian].
- Ukonmaanaho, L., Nieminen, T.T., Rausch, N., Shotyk, W., 2004. Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland. *Water Air Soil Pollution* 158 (1), 277–294.
- van der Warf, H., Petit, J., 2002. Evaluation of the environmental impact of agriculture at the farm level: a comparison and analysis of 12 indicator-based methods. *Agriculture, Ecosystems and Environment* 93 (1-3), 131–145.
- Zaccone, C., Miano, T.M., Shotyk, W., 2012. Interpreting the ash trend within ombrotrophic bog profiles: atmospheric dust deposition vs. mineralization processes. The Etang de la Gruere case study. *Plant and Soil* 353, 1–9.