UNIVERSITY OF LATVIA
FACULTY OF GEOGRAPHY AND EARTH SCIENCES
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THE INFLUENCE OF PEAT COMPOSITION ON METALLIC ELEMENT ACCUMULATION IN FENS

KŪDRAS SASTĀVA IETEKME UZ METĀLISKO ELEMENTU AKUMULĀCIJU ZEMAJOS PURVOS

DOCTORAL THESIS
Submitted for the Doctoral Degree in Geography and Environmental Science
Subfield of Environmental Protection

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SATURS

ABBREVIATIONS USED IN THIS WORK

^{13}C MNR	carbon 13 nuclear magnetic resonance
AAS	atomic absorption spectrometry
AC	ash content
asl	above the sea level
CM	carbonate matter
DOM	dissolved organic matter
DTA	differential thermal analysis
DTG	derivative thermogravimetry
EEM	excitation-emission matrix
EF	enrichment factor
Em	emission
Ex	excitation
FA	fulvic acids
FI	fluorescence index
FT-IR	Fourier-transform infrared
GFAAS	graphite furnace atomic absorption spectrometry
GI	geo-accumulation index
GIC	geo-accumulation class
HA	humic acids
HI	humification index
HS	humic substances
IR	infrared
LOI	Loss on Ignition
Me	metallic elements
MM	mineral matter
NMR	nuclear magnetic resonance
OM	organic matter
PARAFAC	parallel component analysis
PCA	principal component analysis
PI	pollution index
SEM	scanning electron microscopy
TG	thermogravimetry
TGI	thermogravimetric index
TLS	total luminescence spectroscopy
TXRF	total reflection X-ray fluorescence
UV/Vis	ultraviolet/visible light

ANNOTATION

In the PhD thesis fen peat from four different fens (Elku, Salas, Svētupes, and Vīķu) has been studied and work gives a detailed description of fen peat botanical and physico-chemical characteristics. A detailed characterization of metallic element accumulation and fen peat composition were carried out to evaluate changes over time, within the depth and in different peat layers. Identification and verification of metallic element interaction with peat composition and particular fen peat characteristics have also been given. In the evaluation of metallic element concentration and its relation to a variety of peat botanical and physico-chemical characteristics, wide range of physico-chemical analysis methods, such as – atomic absorption spectroscopy, Fourier-transform infrared spectroscopy, 3D fluorescence spectroscopy, C-13 nuclear magnetic resonance spectrometry, differential thermal analysis etc. methods were used. Results show on differences amongst metallic element accumulation for each study site. Even though, the dependence of peat composition and other peat characteristics on metallic element accumulation are unquestionable, there is no particular accumulation pattern, which can be attributed to all fen systems, because the diversity of fen peat characteristics, even within borders of mire, and variability of geological conditions make it impossible. Fen peat formation and metallic element accumulation pattern are both sensitive to changes in environmental conditions, which are site dependent.

Keywords: fen peat, peat characteristics, metallic element sorption, metallic element accumulation, humification

INTRODUCTION

Topicality

Mire ecosystems carry important ecosystem service functions with high instrumental value in respect to material life and non-material life support, thus mire research is high on agenda (Joosten and Clarke, 2002). Mires are topical for various science branches: geology, biology, environmental science, archaeology etc. So far, the main focus has been made on bog peat, while studies of fens are considerably in smaller number. Existing studies, regarded to fen ecosystems, are mostly based on the biological investigation, but not so much on mire formation, development or peat physico-chemical characteristics. In recent decades, due to the improvement of analytical method applications, the mire research methodology has been significantly developed. Current physico-chemical investigation, remote sensing and other methods allow gathering more information on peat composition and its characteristics with a high detail level.

The accumulation of metallic elements in fens has not been widely studied, thus factors affecting their cycling in fen peat are not fully known. The accumulation of metallic elements in fen peat in Latvia is partially addressed in *Dr. geogr.* Agnese Pujāte's PhD thesis "Traces of environmental change and human impact in the sediments of lakes along the coast of the gulf of Riga", where studies on metallic element concentration in lake deposits and overlying fen peat deposits are described (Pujāte, 2015).

It is reason to believe that metallic element accumulation and cycling mechanisms are different from the ones in bogs, because of the amount of functional compounds in fen peat, differences in environmental pH and decomposition rates and fen peat botanical composition itself is different from bog peat composition (Krumins et al., 2011; Silamiķele, 2010).

Chemical elements in peat have either natural or anthropogenic sources. A great deal of research of metallic element content in peat was and is focused on trace metal deposition historical records in bog peat. An extensive study of trace metal concentration in bog peat in Latvia has been conducted in Ķemeri Mire by team of researchers under the leadership of prof. *Dr. geogr.* Oļģerts Nikodemus (Kalnina et al., 2003), while to studies on metallic element concentrations in Latvian fens there is not yet paid detailed scientific attention. One of the reasons is that fens are considered as unwieldy for such study, because early diagenesis can significantly remobilise metals within peat profile and the variety of input sources prevails over other impact factors (Norton, 2007; Gambrell, 1994). Further chemical element remobilisation depends on local factors of particular site, such as hydrological and hydrogeological conditions, geomorphology, climate, flora and wild animals (Knorr et al., 2009; Koretsky et al., 2006), considering these facts studies on element cycling in fens are considerably less.

The main source of metallic elements accumulated in bogs is atmospheric precipitation and mire vegetation. At the same time, in fens, surface runoff and groundwater

is also of high importance (Orru and Orru, 2006). The formation of number of authigenic minerals is also characteristic to fen peat profiles, including variety of carbonates, sulphides and phosphates. Fens accumulate a variety of chemical elements and reflect a typical terrestrial metallic element supply from surrounding environment (Shotyk, 1996).

Aim

Aim of this work is to ascertain properties and composition of fen peat in Latvia using multi-proxy analysis methods in regard to evaluate the influence of peat composition on metallic element accumulation in fens.

Main tasks

Main tasks to achieve the aim of this PhD thesis were to:
1. to describe physico-chemical properties of fen peat;
2. to describe peat humification in fens under weak acidic/alkaline environment;
3. to study relations and interactions between fen peat characteristics;
4. to characterize metallic element accumulation patterns and mechanisms in fen peat profile;
5. to study interactions between metallic element concentration and fen peat characteristics.

The novelty of doctoral thesis

The novelty of this work is associated with a detailed study on fen peat characteristics and metallic element concentration in fens in the region (Latvia) and study object (fens) that has previously been studied very rare, but at the same time has been formed under unique natural conditions and has low heavy metal pollution levels. Moreover, such a comprehensive study to date has not been carried out. Another novel aspect is use of new and advanced methods in the characterization of fen peat. For the first time in fen peat analysis 3D fluorescence spectroscopy has been used and it gives the opportunity to describe peat organic matter in more detailed scale. The novelty of this work is also associated with the extension of fen peat research methodology, which is an invaluable aid in evaluation of peat physico-chemical characteristics, characterization of humification in fens under weak acidic/alkaline environment, fen peat characteristics as bio-sorbent with high added value, and the metallic element accumulation pattern and mechanism in fens.

Thesis for defence

1. Peat composition has a direct influence on metallic element accumulation pattern in fens;
2. Heavy metal mean concentration in fen peat in Latvian fens is low and fens can be considered as unpolluted ecosystems.

Hypothesis

Metallic element accumulation in fen peat differs from metallic element accumulation pattern in bog peat and includes the replacement of calcium and magnesium ions by other more tightly bound metal ions.

The theoretical and practical significance of results

The theoretical and practical importance of this work is associated with the study of metallic element accumulation and concentration in fens in the territory of Latvia, fen peat humification process, and the research of complex interrelations amongst various peat components. The quality of peat and range of its applications largely have a direct dependence upon concentration of metallic elements present in peat. The ability of peat to accumulate chemical elements also depends on the ability of ions to bind with particular functional groups. This PhD thesis gives a description of fen peat physico-chemical character and, accordingly, provides the information, which is significant to directions of fen peat potential use. The results of this PhD thesis have been used in the preparation of patent in regard to fen peat use in organic farming (Klavins et al., 2015).

Approbation of the results

The data of this research have been published in 8 scientific articles and 1 monograph, submitted to 2 scientific journals, discussed in 9 international and 5 local scientific conferences; the obtained data have been used in the preparation of 1 patent. On the basis of research work, obtained data have been used for the development of the following projects: 1) National Research program: "Peat and sapropel as high-quality raw materials for new technologies and products with high added value" (Kūdra un sapropelis kā augstvērtīgas izejvielas jaunām tehnoloģijām un produktiem ar augstu pievienoto vērtību); 2) "The assesment of Latvian clay suitability for the production of new products and technologies" (Latvijas mālu piemērotības novērtēšana jaunu produktu un to ražošanas tehnoloģiju izstrādei); and 3) "Interdisciplinary team of young scientists for research of bog resources, sustainable use and protection in Latvia (PuReST)" (Starpdisciplināra jauno zinātnieku grupa Latvijas purvu un to resursu izpētei, ilgtspējīgai izmantošanai un aizsardzībai).

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Publicity of the results

1. **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.
2. **Krumins, J.**, Klavins, M., Seglins, V. 2012. Accumulation of the major and trace elements in fens (Latvia). Peatlands in balance: Proceedings of the 14th International Peat congress, 2012, Stockholm, Sweden. 145 p.
3. **Krumins, J.**, Klavins, M., Seglins, V., Kaup, E. 2012. Comparative Study of Peat Composition by using FT-IR Spectroscopy. Materiālzinātne un lietišķā ķīmija 26, 106-114.
4. **Krumins, J.**, Kuske, E. 2012. The distribution regularities of calcium and magnesium in fen peat profile. pp. 42-55. In: Scientific papers of University of Latvia, Earth and environmental sciences 785. (Ed.) V. Zelcs. University of Latvia, Riga.
5. Kļaviņš, M., Robalds, A., Dūdare, D., Ansone, L., **Krūmiņš, J.**, Poršņovs, D. 2013. Kūdras īpašības un tās izmantošanas iespējas sorbcijas procesos un humusvielu iegūšanai. pp. 40-42. In: Sustainable Use of Local Resources (Entrails of the Earth, Forest, Food and Transport) – New Products and Technologies (NatRes). Issued by the Latvian State Institute of Wood Chemistry, Riga.
6. **Krūmiņš, J.**, Robalds, A., Purmalis, O., Ansone, L., Poršņovs, D., Kļaviņš, M., Segliņš V. 2013. Kūdras resursi un to izmantošanas iespējas. Materiālzinātne un lietišķā ķīmija 29, 82-94.
7. **Krumins, J.**, Klavins, M., Seglins, V., Kuske, E. 2013. Use of differential thermal analysis and thermogravimetry in the characterization of fen peat profile. pp. 28-31. In: Bog and lake research in Latvia. (eds. Klavins, M. and Kalnina, L.). The University of Latvia Press, Riga.
8. **Krumins, J.**, Robalds, A. 2014. Biosorption of Metallic Elements onto Fen Peat. Environmental and Climate Technologies 14, 12-17.
9. **Krūmiņš, J.**, Kļaviņš, M., Segliņš, V. 2015. Smago metālu ģeoakumulācijas raksturs zemā tipa kūdrā. Latvijas Zinātņu Akadēmijas Vēstis, "B" daļa. Iesniegts.
10. **Krumins, J.**, Klavins, M., Segliņš, V. 2015. Metallic elements in fen peat and their relation to peat physico-chemical characteristics. Baltica. Submitted.

Monographs

1. **Krumins, J.**, Klavins, M., Silamikele, I. 2015. Peat, its characteristics and wise use: peat studies in Latvia. LAP Lambert Academic Publishing. 240 p.

Patents

1. Klavins, M., **Krumins, J.**, Bunere, S. 2015. Soil substrate for use in organic farming and method of producing thereof. No. LV15013. Applicant: Latvijas Universitāte. Classification: international (C05D9/00; C05F11/02), cooperative. Application number: LV20150000025 20140305.

Reports in local conferences

1. **Krūmiņš, J.**, Kuške, E. 2011. Zemā tipa kūdras fizikālo un ķīmisko īpašību izmaiņas purva attīstības gaitā. Latvijas Universitātes 69. zinātniskā konference, Rīga, Latvija.
2. **Krūmiņš, J.**, Kļaviņš, M., Segliņš, V., Kuške, E. 2013. Diferenciālās termālās analīzes/termogravimetrijas pielietojums zemā tipa kūdras profilu raksturošanā. Latvijas Universitātes 71. zinātniskā konference, Rīga, Latvija.
3. **Krūmiņš, J.** 2014. Zemā tipa kūdras izmantošanas perspektīvas. Latvijas Universitātes 72. zinātniskā konference, Rīga, Latvija.
4. **Krūmiņš, J.**, Kļaviņš, M., Segliņš, V. 2015. Zemā tipa kūdras sadalīšanās procesu raksturošana, izmantojot 3D fluorescences metodi. Latvijas Universitātes 73. zinātniskā konference, Rīga, Latvija.
5. **Krūmiņš, J.**, Kļaviņš, M., Segliņš, V. 2015. Purvu un kūdras pilnvērtīgas izmantošanas risinājumi. Latvijas Universitātes 73. zinātniskā konference, Rīga, Latvija.

Reports in international conferences

1. Kuške, E., Strautnieks, I., Kalniņa, L., **Krūmiņš, J.** 2010. Paleoveģetācijas sastāva izmaiņu pētījumi Vīķu purva attīstības gaitā. Daugavpils Universitātes 52. starptautiskā zinātniskā konference, Daugavpils, Latvija.
2. **Krumins, J.**, Klavins, M., Seglins, V. 2012. Accumulation of the major and trace elements in fens (Latvia). Peatlands in balance: 14th International Peat congress, Stockholm, Sweden.
3. **Krūmiņš, J.**, Kuške, E., Kļaviņš, M., Segliņš, V. 2013. Diferenciālās termālās analīzes pielietojums Svētupes un Vīķu purva kūdras raksturošanā. Latvijas Universitātes 71. zinātniskā konference, Rīga, Latvija.
4. **Krumins, J.**, Klavins, M., Kuske, E., Seglins, V., Kaup, E. 2013. The Comparative Study of Element Accumulation in Wood Fen Peat (Latvia). 10th EGU General Assembly, European Geosciences Union, Vienna, Austria.
5. **Krūmiņš, J.**, Kļaviņš, M., Segliņš, V. 2013. Comparative study of differential thermogravimetry of peat and its fractions. International Workshop "Peat and humic substances and their application", Riga, Latvia.
6. **Krūmiņš, J.**, Kļaviņš, M., Segliņš, V. 2013. Perspectives of fen peat as natural resource in Latvia – a review. International Workshop "Peat and humic substances and their application", Riga, Latvia.
7. Klavins, M., **Krumins, J.**, Silamikele, I. 2014. Accumulation of the major and trace elements in bogs and fens (Latvia). Biogeomon 2014, Bayreuth, Germany.
8. **Krumins, J.**, Silamikele, I. 2014. Accumulation of metallic elements in peat: raised bogs vs. fens. 19th International Scientific conference "Ecobalt 2014" Riga, Latvia.
9. Silamikele, I., **Krumins, J.**, Klavins, M. 2015. Variability of peat soil characteristics in boreo-nemoral environment (Latvia). ISMOM 2015, Montreal, Canada.

The author's contribution

The author of PhD thesis did the field work in all study sites including peat sampling and collection, has characterized full peat profiles from four Latvian fens – for the purpose of analysis each profile was divided in 0.05 m thick layers with diverse botanical composition and decomposition degree. The concentration of 13 different metallic elements has been determined, normalised and the character of their accumulation in peat profiles given. The author has also determined the content of organic compounds and functional groups in fen peat samples, humification degree, Loss on Ignition parameters, performed bio-sorption tests and other experiments. The determination of metallic element content in fen peat has been performed in the University of Latvia, Faculty of Geography and Earth Sciences, Laboratory of Environmental Monitoring. Variety of separate analyses of peat structural composition and characteristics were performed in faculties of Biology and Chemistry, Institute of Wood Chemistry, Tallinn Technical University, and Riga Technical University. The author has given an interview to national-wide newspaper "Neatkarīgā Rīta Avīze" and regional TV channel TV24 about the research work associated with PhD thesis. In 2013 the author has participated in the preparation of an informative report about subsoil use in Latvia, and in 2015 in the preparation of patent "Soil substrate for use in organic farming and method of producing thereof".

1 LITERATURE REVIEW

1.1 Mires, their diversity and characteristics

Although the importance of mires is axiomatic on a global scale, the detail level of studies varies depending on particular mire types. The major part of environmental studies focuses on the ombrotrophic systems (bogs); while the minerotrophic mires (fens) are considerably less studied, although the direction of studies depends on their objectives.

Mires cover approximately 3% of Earth surface (~ 4 million km^2) and can be considered as geological and biological formations and as a significant part of azonal habitats (Maltby and Proctor, 1996; Ellenberg, 1988). 3% is an approximate value, because it is not possible to provide accurate estimates of the worldwide areas of mires. The accuracy is highly variable, because for every country there is a definition of its own land and soil terms, but the information must be interpreted in terms of standard categories of mires (Rydin and Jeglum, 2008). Mires have been developing on Earth since wetland plants first existed. First mires on Earth appeared in Devonian period and Late Devonian coals record the evolution of the first peat-accumulating wetlands, indicating when plants had evolved the production and shedding of prolific amounts of biomass, which allowed peat to accumulate under specific chemical conditions (Greb et al., 2006). Peat from tropical mires of Upper Carboniferous (320-290 million years ago) and sub-tropical mires of Tertiary (65-3 million years ago) is also currently found as coal and lignite. The great majority of present-day mires are upland and aquatic ecosystems (Mitsch and Gosselink, 2000).

1.1.1 Mire diversity and functions

In general, three main types of mire can be classified; these are fens, transitional mires and bogs (Nomals, 1930). Each type of mire is with its own specific botanical and physico-chemical characteristics. Thus fens, transitional mires and bogs have an individual metallic element accumulation character, because of the differences in mire feeding conditions. Each of these mire types can exist as a separate ecosystem or be parts of one ecosystem. Peat layers, particular to fens or transitional mires, can also be found in bogs under bog peat layer (Pakalne and Kalniņa, 2000; Nomals, 1936).

In the most widely used definitions as the most significant characteristic of the mire is mentioned the increase of OM in comparison with the loss of organic substances (Čivić and Jones-Walters, 2010; Joosten and Clarke, 2002; Overbeck, 1975) in conditions, when the large amount of retained water (90-95%) slow down the decomposition of OM, but the low temperature and the lack of oxygen support the accumulation of plant remains. According to this definition, mires can be characterized as areas of Earth surface with an active peat formation, permanent or episodic moisture and a specific flora and fauna (Walker and Lowe, 1981). Although, we cannot select universal indicators for the classification of mires (Table 1.1), because they are systems

with gradual development and any type of mire characterizes only the phase of development at a specific moment (Borgmark, 2005).

Table 1.1

Mire classification criteria (Joosten and Clarke, 2002; Clymo, 1983)

Characteristics	Description
Peat characteristics	Botanical composition, nutrient content and structure, agriculture
Mire and peat chemical characteristics	Water chemical composition, acidity, nutrients
Mire stratigraphy	Mire vertical cross-section and peat composition
Mire hydrology	Nutrient supply sources and the flow regime
Mire morphology	Peat profile cross-section and mire geomorphology
Peat structure	The structure of dominant plant species
Mire vegetation	Composition of plants

Over the time an interaction between natural autogenic and anthropogenic processes and the accumulation of peat changes the type of mire. Thus the ecological classification indicators (feeding conditions and others) better show dynamics of the mire development than, for instance, vegetation indicators do (Clymo, 1983).

Fens are nutrient medium to nutrient rich mires and, because of the groundwater input of oxygen and dissolved mineral nutrients; fens are richer in nutrients and have a higher pH level than bogs have. Although fen communities are sharing many plant species with bog communities, they also contain species that indicates nutrient-rich environment and are specific only to fens. The degree of differences in vegetation between fens and bogs increases with the nutrient richness (Nomals, 1930). Fens, predominantly, are minerotrophic systems and are fed mainly from groundwater, resulting in high saturation of lithogenic elements (including metallic elements) in peat. However, fens constitute a complex ecological system and have an important impact from combined sources, such as precipitation, weathering, etc. The pH reaction in fens is from weak acidic to alkaline (5-7) and the environment typically is anaerobic and/or sulphide (Shotyk, 1996), but if the supplied groundwater is poor in nutrients fens are scanty (Nomals, 1930). Weak acidic to alkaline pH reaction is one of the determinant factors for differences in metallic element concentration and accumulation pattern in fens when compared to bogs.

An essential feature of mires is peat accumulation and its storage and both processes are associated with a number of other characteristics that distinguish mires from most of other ecosystem types. Mires largely consist of water, thus hydrological characteristics play the major role (Joosten and Clarke, 2002; Overbeck, 1975). The principal characteristic is that the water level, in long-term, must be near the surface of a mire to let it exist and make the accumulation of peat possible. The water level, which is too low or too high, is detrimental to the peat accumulation and, because of it, the mire development is impossible. Thus any natural or human made activity, which substantially lower or raise the water level in mires, negatively affect the capacity of peat accumulation and

all functions associated with it (Joosten and Clarke, 2002; Finlayson and van der Valk, 1995). The drainage of mires leads to the subsidence and peat oxidation, mineralisation and compaction and these processes rapidly change physical, chemical, hydraulic and biological properties of peat (Joosten and Clarke, 2002; Nomals, 1936, 1937, 1939, 1943). The precipitation water is low in nutrients and acidic. The water quality in soil changes when it is in interaction with the geosphere. This change depends on chemical properties of the catchment area, the residence time of the water, electrolyte and oxygen concentration, nutrient richness, pH, and the temperature of water (Joosten and Clarke, 2002). Mire and peat functions can be distinguished in 5 general groups (Table 1.2), each of which is with a high importance in particular fields of mire and peat use.

Table 1.2

Mire functions (Joosten and Clarke, 2002)

Function	Description
Production functions (Natural resources for sustainable development of civilization)	Peat extracted and used as/for humus and organic fertiliser in agriculture, substrate in horticulture, energy generation, raw material for chemistry, bedding material, filter and absorbent material, peat textiles, building and insulation material, balneology, therapy, medicine, and body care, flavour enhancer
	Drinking water
	Wild plants growing on mires and peatlands for/as food, raw material for industrial products, medicine
	Wild animals for food, fur, and medicine
	Peat substrate in situ for agriculture and horticulture, forestry
Carrier functions (Mires can be used as a space for....)	Water reservoirs for hydro-electricity, irrigation, drinking and cooling water, and recreation
	Fish ponds
	Urban, industrial, and infrastructure development, waste deposits/landfill, military exercises and defence, prisons, transport and herding
Regulation functions (Regulation of climate and soil conditions)	Regulation of regional and local climates
	Regulation of catchment hydrology
	Regulation of catchment hydrochemistry
	Regulation of soil conditions
Informational functions (Historical, religious and philosophical aspects)	Social-amenity and history functions
	Recreation and aesthetic functions
	Symbolism
	Spirituality, and existence functions
	Signalisation and cognition (philosophical) functions

Mires meet the most of essential human needs – food, freshwater, shelter, warmth and employment. Although, the growing understanding of mire importance in biogeochemical and ecological cycles of the planet cause the arising of many conflicting uses of mires. Moreover the content of metallic elements in peat is determining factor for most of mire functions described in the table above (Table 1.2).

1.1.2   The importance of mire studies

Mires belong to the most representative archives of past environmental conditions in large areas of the temperate zone. However, mires can be found also in both cold and tropical climate zones. Moreover, mires are archives of the human history and keep the evidence of ancient cultures and modern human activity and store about one third of the soil organic carbon in the world and contain up to 10% of the global liquid freshwater resources originated in the last 15 000 years (Čivić and Jones-Walters, 2010; Joosten and Clarke, 2002). Therefore the research of mires is an integral part of global change studies. It has been stated, that peat can serve as a good indicator of recent as well as historical changes (Shotyk et al., 2002). Fens are less studied than bogs and one of the main reasons is the complexity of factors, which can have an impact on the formation of peat. In turn bogs, due to their dome-shaped structure mainly are affected only by the atmospheric precipitation, while other external influences are small and relatively simple separable. Thus bog peat is more widely studied all over the world, while there are only few publications about fen peat composition and properties. The lack of information on fen peat makes it important to conduct studies on fen peat – to characterize the transformation of plant OM into peat in high detail and to find out and to expand the application possibilities of this type of peat.

1.2 Peat formation and characteristics

The formation of peat and its characteristics depend on environmental conditions of the area where the particular mire is located. The determinant factors are current vegetation, temperature, geological conditions, relief and water table fluctuations (Kušķe et al., 2010).

Peat is an organic deposit, which in air-dried condition consists of more than 50% of OM. During peat formation plant remains are affected by the gradual destruction of morphological and anatomical structures, as well as, by changes in the chemical composition (Orru and Orru, 2006; Black et al., 1955). Alongside with coal, peat is included in the group of caustobiolithes (combustible organic rocks). Several peat classification systems are based on peat chemical properties, but not so much on properties of peat material itself as on the properties of mire as an environment (Black et al., 1955). The distinction of peat into eutrophic (nutrient rich), mesotrophic (moderately rich) and oligotrophic (nutrient poor) organic soils applies to both – peat material and mire environment characteristics and also is adressing the accumulation of metallic elements in peat.

1.2.1   Peat formation

The formation of peat can be distinguished into two main stages: 1) the accumulation of plant OM, which is provided by the annual accession of peat forming plants; and 2) the transformation of OM into peat (Тюремнов, 1976). Knowing that organic soil layer and vegetation cover significantly affect the speed and amount of

evaporation, water amount and the composition of groundwater, it must be taken into account that the specificity of particular vegetation either slows down or speeds up both these processes.

Fen peat is formed of disintegrated, decomposed plant remains. Plants have developed mostly by feeding of a mineral-rich groundwater and surface water, while atmospheric precipitation was insignificant. Fen peat reflects the plant community of which it is made from, thus peat chemical characteristics and elemental composition strongly depend on chemical characteristics of peat forming plants, which at the same time depend on the feeding regime, geomorphological location, geological, geobotanical and microbial processes of the area (Yeloff and Mauquoy, 2006; Fortescue, 1980). In general, fen peat is built up from sedges; reeds, grasses, shrubs and/or wood remain under waterlogged conditions. Main fen peat forming plants are *Carex lasiocarpa, C. limosa, C. riparia*, and *Phragmites australis* with the addition of horsetail and wood remains (Foster and Fritz, 1987; Clymo, 1983).

The thickness of fen peat layer in mires can be relatively small, in comparison to other peat types. However, in fens that are not transformed into bogs, the fen peat layer can be as thick as peat in raised bogs. Fen peat has an increased amount of the natural moisture (> 90%) and the degree of mineralisation (6-16%); and degree of decomposition is the highest among peat types (20-50% and higher). It has also been stated that fen peat, compared to bog peat, has a higher pH levels, ash content, nitrogen and sulphate content, amino acid and amino sugar content (Borgmark, 2005). Fen peat is dense and pore volume is negligible and the groundwater table almost reaches the surface, thus oxygen-involving processes are more limited here than in bog peat (Rydin and Jeglum, 2008).

1.2.2 Composition of peat profile

Practically in all mire types it is possible to distinguish three different peat accumulation zones – acrotelm, catotelm, and the bottom layer (hedotelm) (Table 1.3) (Silamiķele, 2010). However, after the extraction of peat, acrotelm layer becomes highly degraded and loses its typical characteristics. The remaining, degraded, thin acrotelm layer is called haplotelm. Haplotelm is associated with a number of changes in relation to carbon sequestration (Lindsay, 2009).

Table 1.3

Peat accumulation zones in bogs and fens

Fens	Bogs	Bogs after peat layer removal	
Acrotelm	Acrotelm	Haplotelm	Bottom layer (hedotelm)
Catotelm	Catotelm	Catotelm	
Bottom layer (Hedotelm)	Bottom layer (Hedotelm)	Bottom layer (Hedotelm)	

To describe the upper, oxygen rich, peat layer, in which air is freely circulating and also the water circulation takes place, H. Ingram (1978) introduced the term acrotelm – it is an aerobic layer with intensive water movement and rapid OM

decomposition degree (YaVitt, 1995; Ingram, 1978). Acrotelm layer, where the most intensive peat accumulation takes place, occupies a significant part of peat profile. However, the thickness of this layer differs depending on mire type; it is several times thicker in bogs than it is in fens. The freshly formed peat is being affected by oxygen and groundwater level, thus the decomposition degree of peat in this layer is high. A typical thickness of acrotelm is in the range from 0.2-0.8 m. Aerobic decay of organic material in acrotelm results in up to 90% loss of dry mass in the peat profile before it is incorporated in catotelm, where anaerobic decay takes place (Kuhry and Vitt, 1996; Clymo, 1983).

The lower, anaerobic peat layer, – catotelm, is constantly saturated with water and is almost completely free of oxygen. This layer is characterized by low hydraulic conductivity and slow decomposition of OM in an anaerobic environment (Bragg and Tallis, 2001; Тюремнов, 1976). In catotelm layer, due to the lack of oxygen, decomposition degree significantly decreases and is independent from climatic local scale fluctuations (Yu et al., 2003). According to R. Clymo (1983) model, the loss of plant remains due to their transformation in acrotelm layer, is around 80-90% and this means that the transfer of peat mass to catotelm consists only from 10-20% of total plant remains. Thus peat in catotelm layer is decomposing slowly – approximately 0.1% of the speed of decomposition in acrotelm (Clymo, 1983).

Deepest and oldest peat layers, – hedotelm, is compressed and saturated with water, the decomposition is almost non-existent as the lack of oxygen and low temperature prevent the decomposition (Silamiķele, 2010; Williams and YaVitt, 2003; Belyea and Clymo, 2001).

Peat OM consists of variety of organic compounds, but base compounds are: carbohydrates (cellulose, hemicellulose, sugars); nitrogenous compounds (proteins, amino acids); polyphenols (lignin, HA); lipids (waxes, resins, steroids, terpenes); nucleic acids, pigments, alkaloids, vitamins; HS (HA, FA and humin), and other organic compounds (Choudhry, 1984). The quality of OM reflects numerous environmental processes, including the primary production and decomposition, redox gradients, hydrologic transport and photochemistry (Larsen et al., 2010). The composition of OM (Table 1.4) clearly depends on the environmental source (Aiken and Costaris, 1995).

Most of the natural OM in peat consists of HS (FA and HA), which are the result of degradation and polymerization of OM during microbial, chemical and photochemical reactions (Rodriguez and Núñez, 2011; Pernet-Courdier et al., 2011; Galapate et al., 1998; Langais et al., 1991).

HS is polydisperse complex mixture of high to low molecular weight species (Rodriguez and Núñez, 2011; Myllykangas et al., 2002; Cabaniss et al., 2000). Two main fractions of HS are FA and HA and they can be distinguished by their different solubility at pH 1, – the precipitated fraction is HA and the part remaining in solution is FA (Rodriguez and Núñez, 2011). Peat always contains more FA than HA and they are more soluble than HA, it can be explained by their lower average molecular weight and higher carboxylic acidity in comparison with HA. In turn, HA are often in colloidal form due to large size of their molecules and they show more aromaticity and

Table 1.4

The conceptual model of peat composition (Aiken and Costaris, 1995; Choudhry, 1984)

Peat	Water			
	Dry matter	Inorganic matter	Anions and silica	
			Metals	Heavy metals
				Fe, Al
				Na, K, P, Mg, Ca
			Metalloids	
		Organic matter	Humic substances	
			Amino acids	+ Charged (non-acidic)
				- Charged (acidic)
				Uncharged (hydrophilic)
				Non-polar (hydrophobic)
			Carbohydrates	Deoxysugars
				Pentoses
				Hexoses
			N, H, C, S, O	
			Lignin	
			Bitumen and wax	

ultraviolet absorbance and have darker colour than FA have (Rodriguez and Núñez, 2011; Andrews and Huck, 1996; Langais et al., 1991).

The MM in peat deposits is supplied by wind and water, and in many cases forms so called "brought ash", but mineral particles can also be supplied from the mineral base layer during the mire formation, also volcanic ash (tephra) can be found in peat deposits as thin MM layers. In general, though, two types of ash in peat can be distinguished – the constitutional ash (MM in fens 4-9%) and the brought ash (MM up to 70-80% of total fen peat dry mass) (Тюремнов, 1976). Accordingly, the average content of MM in fen peat is from 6.6-12% (Fuchsman, 1980).

Carbonates are salts of carbonic acid and are characterized by the presence of carbonate ion. CM consists of volatile particles and is subjected to the mass loss due to heat input. CM is the minor part of MM in peat mass. Main sources of CM are carbonate minerals and carbonate rock. Carbonate particles in peat mass are also related to plant remains and carbonated groundwater. However, because of the constant ground and/or surface water flow, a significant part of carbonate particles can leach out. The average content of CM in fen peat is ranging from 2-4%.

1.2.3   Peat characteristics

To characterize different peat layers, the selective nature of peat forming plant decomposition character, must be taken into account as various plant species and plant forming structures have a diverse decay and decomposition character (Bragazza et al., 2007; Charman, 2002). The degree of decomposition (Table 1.5) gives not only the information about palaeoecological conditions at the time of peat layer formation,

but also is related to variety of peat characteristics (such as thermal conductivity, density, durability, viscosity, etc.).

Table 1.5

Peat decomposition characteristics (Von Post and Granlund, 1926)

Index	Decomposition degree	Expressed as %	Colour	Plasticity
H1	Low	< 20	Light brown	Elastic
H2				
H3			Yellowish brown	
H4				
H5	Average	21–34	Brown	
H6				
H7	High	> 35	Dark brown	Plastic
H8				
H9			Black	
H10				

In relation to peat decomposition character, it has been found that: proteins and carbohydrates of plant cell protoplast are first exposed to decomposition; pectins, cellulose and hemicellulose of the cell membrane forming substances are exposed next, but as the last exposed to decomposition is cellulose and lignin in cell walls. Very slow decomposition rate is characteristic also to lipids, resin, wax, and spore and pollen casings (Moore and Webb, 1978).

The decomposition of peat is slow and due to the release of methane and carbon dioxide it causes the formation of HS – high molecular polycationites with high environmental durability. Depending on the HS solubility and molecular weight, they are described either as HA or FA (Kļaviņš, 1993). The decomposition degree characterizes the relation between the amount of HS and the total peat mass. The degree of decomposition depends on the proportion of peat forming plants, because, for instance, – the degradation of vascular plants is different from foliage plants or mosses (Bohlin et al., 1989). The decomposition is also affected by the presence of antiseptic substances in peat and fluctuations in natural moisture, which inhibits the oxidation or reduction process (Тюремнов, 1976; Black et al., 1955). The decomposition degree depends on peat botanical composition. The highest decomposition degree is characteristic to wood peat, the lowest to grass, sedge and reed peat. The decomposition degree is a concept that describes how decomposed peat is. A high fibre content is associated with low decomposition degree and contrariwise (Rydin and Jelgum, 2008; Malterer et al., 1992).

An important indicator of peat composition is the humification degree, what shows on the amount of HS in peat. Nitrogen compounds in the peat composition are determinant for the high importance of HS, because HS become the source of biogenic elements due to nitrogen compound transformation into biologically available forms (Klavins et al., 2008).

Botanical composition is a fundamental property for determining the nature of peat. The composition and relative proportions of main plant species in peat mass are determining the physical and chemical properties of peat (Rydin and Jelgum, 2008). Changes in the botanical composition of peat are affected by the variation in environmental conditions. Depending on climatic conditions of a particular area, a specific peat type will be formed with its own accumulation characteristics. The botanical composition of peat represents peat-forming plants and is one of the most important characteristics of peat (Тюремнов, 1976; Black et al., 1955). The botanical composition of peat is close related to plant feeding conditions, peat base layer conditions and the groundwater mineralisation degree, moisture and physico-mechanical characteristics (Тюремнов, 1976).

During peat formation and accumulation, plant remains are affected by the destruction of morphological and anatomical structures and changes in the chemical composition (Black et al., 1955). The content of peat OM characterizes past vegetation, its diversity and expansion. This characteristic depends on mire feeding conditions – OM in euthrophic fen environment will always be in a higher amount than in bogs. A proper amount of nutrients in fens provides the development of relatively rich sedge, reed and other hydrophilic grass species. Depending on the growth conditions fens can be rich or poor in terms of plant species. However, in comparison to other mire types, there is the highest diversity of plant species, especially in nutrient rich calcareous fens. During fen development, depending on the intensity of peat accumulation, the impact of groundwater is decreasing, thus the composition of vegetation is changing and plants gradually are replaced with less demanding plant communities. Individual plant species have different specialties, thus also peat characteristics are changing in the course of time.

Physical characteristics of peat depend on the peat botanical composition, mineral composition and from one another (Overbeck, 1975). Possibilities of compression and peat density depend on the size of plant remains and mineral particles in peat. A homogeneous grass peat has a relatively compact accumulation conditions naturally, but at the same time wood peat is intensively exposed to the pressure and thus this peat has also higher moisture content (Rydin and Jelgum, 2008; Okruszko, 1993). Bulk density is perhaps the most important intrinsic characteristic of peat, because many other properties are closely related to it. However, bulk density depends on the amount of peat compaction, the botanical composition of peat, decomposition degree and the content of MM and natural moisture. Some research workers also determine the specific density, which indicates the true density of solid peat material. Specific density values depend on the amount of MM present in organic material. Driessen and Rochimah (1976) quoted that peat specific density values range from 1.26 g/cm^3 to 1.80 g/cm^3. Peat fibrosity is determined by the botanical composition of peat and, in general, shows on how much of the original plant material is left un-decomposed (as peat fibre). Fibrosity can be measured in range from fibric to mesic to humic. Fibric peat is weakly decomposed peat with clearly identifiable plant remains; mesic peat is moderately decomposed peat with high humus content;

but hemic peat (also known as sapric peat) is strongly decomposed peat, with the dominance of amorphous humus and unidentifiable plant remains (Rydin and Jelgum, 2008). Peat porosity describes the size of peat pores and determines the water retention. Fibric peat horizons (weakly decomposed peat) have high porosity and thus also high rate of water movement, but large pores collapse on a progressive decomposition and the total pore space significantly decreases. The total porosity of peat ranges between 78 and 93%, with highest values in bog peat (Ilnicki and Zeitz, 2003). The water content in peat shows on current hydrological and hydrogeological conditions of mire. Water content is expressed as the percentage of original mass or volume of the peat sample. Due to drying peat tends to hold on to water, whereas already dried peat tends to resist re-wetting. Water content is the subject to variation, because of geographical characteristics, variability of peat types, degree of pore space, water conductivity characteristics in particular peat layers and temperature (Rydin and Jelgum, 2008; Kellner and Lundin, 2001).

Main chemical characteristic of peat according to Fuchsman (1980) is the amount of organic and inorganic compounds and their interrelations (Table 1.6). Peat characteristics of high importance are: 1) pH of peat; 2) oxygen content and redox potential; 3) gases in peat; 4) greenhouse gases; 5) the amount of CH_4, CO_2, N_2O, H_2S, SO_2, CH_3SCH_3; 6) the amount of essential elements, toxic elements and compounds; 7) base saturation and 8) the sum of extractable values for main base cations – Ca, Mg, K, Mn, as a percentage of total cation exchange capacity (Rydin and Jeglum, 2008).

The chemical composition, physical characteristics, structure, texture and colour of peat depend on peat forming plants and conditions of their growth (Black et al., 1955). Peat characteristics are based on the material of its origin and chemical processes in it (Orru and Orru, 2006). Chemical characteristics of fen peat OM depend also on mire

Table 1.6

The average content of fen peat forming elements (Fuchsman, 1980)

Compound	Content
Bitumen	4.2±1.96%
Readily hydrolysable compounds	25.2±6.10%
Hemicellulose	21.6±10.54%
Humic acid	40.0±5.99%
Fulvic acid	15.5±3.80%
Cellulose	2.4±1.44%
Lignin	12.3±3.83%
Ash	7.6±3.18%
C	59-63%
H	5.1-6.1%
O	31-34%
N	0.9-1.9%
S	0.2-0.5%

location, feeding conditions (hydrological and hydrogeological conditions), geological and geobotanical conditions (Yeloff and Mauquoy, 2006).

In general, peat mass consists of 4 main groups of substances (Orru and Orru, 2008), it is: 1) bitumen (a natural compound found in peat, which can be extracted by organic solvents); 2) lignin (kind of mixture including lignin, lignin-like matter, cutin, suberin, etc., and these components do not hydrolize in water); 3) humus (HA and FA); and 4) carbohydrates (water-soluble matter, easily hydrolyzed matter and cellulose. The content of water-soluble matter and easily hydrolyzed matter have a large variability, which is decreasing with rise of the decomposition degree). A significant part of peat mass is also nitrogen components and MM, which may form up to 25% of peat dry matter (Fuchsman, 1980). Among essential inorganic nutrients, there are nine macronutrients, which can be ranked in order of decreasing concentration in mire plants: C, O, H, N, K, Ca, P, Mg, and S. The important micronutrients are Fe, Cl, Cu, Mn, Zn, Mo, Br; some plants also require Na, Si, Co and Ni (Rydin and Jeglum, 2008).

The availability of oxygen in peat and thus also peat decomposition depend on the environmental pH level: if it is alkaline then peat attracts oxygen, microbial activity is high and decomposition of organic material is at high rate, but if pH is acidic then peat lacks oxygen and decomposition is weak and slow (Rydin and Jeglum, 2008; McBride, 1994). The oxygen content in peat is associated with the water table depth, thus also with the hydrological regime of mire. Both oxidation and reduction process are microbially mediated. The oxygen content is broadly correlated with the content of Mn and Fe, which in case of oxygen depletion becomes more stable and can reach toxic levels (Stumm and Morgan, 1996).

The major ionized elements in peat are H, K, Na, Ca, Mg and Al, which are adsorbed on the surface of peat particles when they have negative charges. Due to decomposition OM produces organic acids, lignin and many other products, which can exhibit element exchange properties (Rydin and Jeglum, 2008; Orru and Orru, 2006).

1.2.4 Characteristics of peat humic substances in terms of fluorescence spectroscopy

Mires commonly exhibit distinct spatiotemporal gradients in both reduction-oxidation potential and OM provenance and reactivity. The long-term persistence of saturated peat often results in vertical reduction-oxidation gradients near the mire surface (Thomas et al., 2009) and depth heterogeneity, which is resulting from mire micro-topography and can establish horizontal gradients in peat reduction-oxidation potential (Ahn et al., 2009; Vivian-Smith, 1997). Horizontal gradients in the OM provenance and reactivity can result from heterogeneity in the composition of local vegetation community, although, hydrologic transport may change or obscure those gradients (Saunders et al., 2006; Neto et al., 2006). Meanwhile, non-conservative behaviour of the decomposed OM, including photo-bleaching, metabolic process and

sorption, can contribute to vertical gradients in OM quality (McKnight et al., 2001; Benner and Biddanda, 1998; McKnight et al., 1992). Seasonal groundwater fluctuation and disturbance events contribute to temporal gradients in OM quality that are reflected in fluorescence spectra (Maie et al., 2006; Mladenov et al., 2005; Maie et al., 2005; Lu et al., 2003).

Using fluorescence spectroscopy to trace the degradation of OM is a prominent analytical technique not only in the characterization of OM, but also particularly for the characterization of HS (Rodriguez and Núñez, 2011; Kalbitz et al., 1999). Fluorescence spectroscopy can detect organic compounds sensitive to the primary production and decomposition of OM, reduction-oxidation gradients, hydrologic transport and photochemistry. However, different environmental gradients can have confounding effects on fluorescence spectra of the OM (Larsen et al., 2010). Fluorescence spectroscopy provides an important information on the chemical nature of HS; it provides the data on their position, shift and intensity of fluorescence signal and all this information can be correlated with the structural information such as functional groups, polycondensation, aromaticity, heterogeneity and various dynamic properties related to their intramolecular and intermolecular interactions (Chen et al., 2003; Mobed et al., 1996). Fluorescence spectroscopy is also simple, rapid, sensitive and non-destructive method and requires a small volume of aqueous sample at low concentration (Swietlik and Sikorska, 2004). The most recent and complete fluorescence technique is TLS, which is also known as EEM. TLS, at present, is the most complete technique, as it provides "fingerprints" for a single compound or a mixture of fluorescent components (Peiris et al., 2010; Henderson et al., 2009; Hudson et al., 2007; Sierra et al., 2005). The general behaviour of humic macromolecules can be described even if structural units have very variable effects on the wavelength and intensity of fluorescence (Swietlik and Sikorska, 2004; Peuravuori et al., 2002; Coble, 1996; Senesi, 1990). The fluorescence intensity decreases with the increase of molecular size of humic macromolecule. The intensity decreases also if the organic substance contains a high content of electron-withdrawing groups (COOH). In turn, the content of electron-donating groups such as OH, NH_2, OCH_3, significantly increase the fluorescence intensity, especially in aromatic compounds. The carboxyl-containing substituents, hydroxyl, alkoxyl and amino groups tend to shift fluorescence maxima to longer wavelengths, but at the same time – decrease in the number of aromatic rings, reduction of conjugated bonds in a chain structure and conversion of a linear ring system to a nonlinear system can cause fluorescence maxima shifting towards shorter wavelengths (Peuravuori et al., 2002). A direct fluorescence measurement of peat is not suitable for studying HA and FA separately, because their fluorescence, in most cases, overlap making the identification inaccurate – the comparatively weaker fluorescence signal of less abundant HA is overshadowed by stronger fluorescence signal of more abundant FA (Peiris et al., 2010; Hudson et al., 2007; Sierra et al., 2005; Baker, 2001).

1.3 Metallic elements in peat

The accumulation of Me in peat is controlled by the botanical composition of peat and the abundance of MM. With regard to the distinctive trophic status of ombrotrophic (bogs) and minerotrophic (fens) systems, there is a complex of characteristics to be taken into account; – the trophic status is determined by the peat botanical composition, pH, ash content, CM and MM content, etc. characteristics. Environmental conditions during the mire development and peat formation also are of a considerable importance (Kalniņa et al., 2003).

In this PhD thesis the concentration and scattering of Fe, Mn, Zn, Na, K, Pb, Mg, Ca, Cu, Cd, Cr, Co and Ni was described, thus in following chapters characteristics of only these Me are described. Selection of the particular Me was based on their importance in environmental processes and their dominance in peat composition.

The importance of mires in geochemical cycles of major and trace elements is significant on a global scale (Shotyk, 1988; Damman, 1978). In addition, mires have a significant importance in the global carbon biogeochemical cycle and their capacities to store and release large amounts of carbon most definitely have a considerable impact on the global climate (Ellis and Rochefort, 2006; Shindell et al., 2004; Brix et al., 2001).

The study of Me accumulation is also important to understand the biogeochemical cycle of elements and how it affects peat, and to evaluate the possible peat contamination and its variability through time, which is especially important for the industrial production of peat. 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 Me cycles (McMorrow et al., 2002).

Throughout the Northern Hemisphere, the geochemical cycle of Me has been profoundly affected by anthropogenic impact for more than 3000 years (Nriagu, 1983). There has been a significant impact of human activities on the atmospheric emissions of a broad range of trace metals, such as Pb, Cu, Cd, Mg, Zn, Cd, etc., as a result of, for instance, coal combustion (Pacyna et al., 2009), but at the same time a variety of pre-anthropogenic emissions of heavy metal-bearing particles are insignificant, compared to human-produced emissions. Moreover, low Me solubility in natural conditions render them largely harmless for the environment (Shotyk and Le Roux, 2005).

Fen plants are fed predominantly of groundwater and that is why fen peat is rich with lithogenic Me. 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 weathering metal ions are released into groundwater and supplied to peat. Metal ion supply, either it is 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). Hypothetically, compared to bogs, fens are chemically more

affected by upward diffusion of metal ions because of underlying calcareous sapropel, clay or till deposits.

As it has been demonstrated in numerous studies, carried out over the last decades, a significant increase in the accumulation of heavy metals in peat has been observed and can lead to the characterization of gradual environmental pollution. However, to reconstruct the major and trace metal accumulation character using peat, strict selection criteria should be followed. The criteria must include topography and depth of mire, water table, peat characteristics and all possible impact sources. Notably, not all mires are suitable for comparative studies of peat characteristics or accumulation history (Givelet et al., 2004). To characterize Me accumulation, in purpose of comparison among mires, it is possible to use peat from any given mire; however, there are important rules to follow:

1. It is relevant to remove upper and bottom peat layers, because they are not suitable for the characterization of natural accumulation, as the accumulation of major and trace elements in these parts is affected and disturbed by the ambient environment. Highest disorder is observable directly in the top peat layer, which is affected by atmospheric contaminant fluxes, anthropogenic pollution etc. factors;
2. It is relevant to find correct sampling area – sampling must be performed in an area in absence of any possible drainage of ground or surface waters;
3. Sampling must be performed further possible from the edges of mire to limit changes inducted by interaction between mire and surroundings.

The developed surface area and large number of acidic functional groups common to peat determine the ability to bind Me included in remains of the plant OM, either as sedimentary, deposited, particulate matter, or as sorbed or complexed metal ions (Brown et al., 2000). The ability of peat to accumulate Me depends on the ability of metal ions to bind with common functionalities in the structure of peat, and, as a consequence of this, the ability of metals can be arranged in the sequence Cu>Pb>Ni>Zn>Co>Cd>Mn (Rinquist and Öhorn, 2002). The ability of peat to accumulate Me 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 Me in peat mass can be attributed to atmospheric precipitation, to Me present in peat-forming plants, as well as to supply with groundwater and surface runoff. Another important source of Me in peat are sedimentary rocks in the base of mire, as due to weathering metal ions migrate upward by diffusion into the peat layer (Shotyk and Steinmann, 1994).

The accumulation and cycling of Me in fens have not been widely studied; notwithstanding the fact that the anthropogenic impact on Me concentration in mires is a common finding in raised bog research (Tipping et al., 2003; Mitsch and Gosselink, 2000; Crowder, 1991). Although, great deal of research of Me in peat focuses on historical records of trace metal deposition; however, fens are unwieldy for such research, as early diagenesis significantly remobilise metals within deposits and variety of input sources prevails other impact factors (Norton, 2007; Gambrell, 1994). Further

remobilisation of chemical elements depends on local factors on-site, such as hydrological conditions, geomorphology, climate fluctuations, flora and even wildlife in mire (Knorr et al., 2009; Koretsky et al., 2006).

All studied Me 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).

Ca and Mg are lithophile elements (Goldschmidt, 1937) and are found in rocks and minerals. Both alkaline earth metals are also biophile – they are intermediate nutrients and thus play an important role in the development of mire vegetation. Ca and Mg have strong affinity to oxygen and in the reaction with water they form strong alkaline hydroxides. Ca is major cation and its availability in peat is related to the cation-exchange capacity. Ca is also in the competition with other major cations (Mg, Na, K, and Fe) for uptake by mire plants, thus the content of these Me in peat is also interdependent. The content of Ca in peat according to A. Damman's study (Damman, 1978) is related to water table and the highest concentration is characteristic to the anaerobic zone. In contradiction with the date of Damman's study more recent research works (Krumins and Kuske, 2012; Silamiķele, 2010) show that the content of Ca significantly depends also on the botanical composition of peat. Presumably changes in Ca content in surface peat layers are affected by the seasonal water level, but in deeper layers more complex variability of factors takes place. An increased concentration of Ca in bottom peat layers can be explained with the presence of Ca in groundwater. In general, Ca is mobile and is tended to leach out of peat profile; however, the migration is strictly affected by the presence of iron oxide and various organic colloids in peat, because Ca forms complexes with those compounds (Syrovetnik et al., 2004). The prevalence of Mg in peat is partly explainable with proximity of the sea and Mg concentration does not depend on depth range of peat profile. An increased concentration of Mg in bottom peat layers can also be explained with the presence of Mg in groundwater. The highest Mg content is characteristic to aerobic peat layers where living plant cells are still in the production, but in anaerobic peat layers the content of Mg is significantly lower. This speciality can be explained with Damman's conclusion (Damman, 1978) that Mg is rapidly leaching from well-drained raised bog domes. The availability and thus also the concentration of Mg in peat depend on mire pH level, because low pH is decreasing Mg availability, but high pH is increasing it – accordingly, fen peat profile contains more magnesium than bog peat profile.

K and Na are lithophile elements (Goldschmidt, 1937) and usually are found in salts. Both alkali metals are also primary nutrients and are required by plants in larger quantities than Ca or Mg. K and Na are essential Me and have a major biological role as electrolytes, thus their content depends on mire vegetation and peat formation conditions. The distribution of Na in peat, in a regional scale, can also be related to oceanic air masses (Reimann and de Caritat, 2005), but elevated concentrations can also be related to rock weathering and agricultural land use. K is produced due to OM decay; however plant roots may also take it up from the substrate. K compounds cannot be leached out of peat by groundwater flow, although, they can migrate upward

in living plant cells. High K content in peat is reducing the uptake of Ca and Mg by current mire vegetation, but high concentration of Na leads to Ca leaching. Both Me at their highest levels remain close to the surface and combine readily with oxygen. K is biophile element and is adherent to plant feeding, plants are using K in the biomass production, thus the highest content of K can be seen in aerobic peat layers, where non-decomposed plant remains are still in contact with plant OM (Damman, 1978).

Fe, Mn, Co, and Ni are siderophile elements (Goldschmidt, 1937) and, in general, have no affinity for oxygen. Fe, Mn, Co and Ni are also biophile micronutrients and required as plant nutrients. Fe at low pH level becomes soluble and combines readily with Ca and forms insoluble compounds. The concentration of Fe strongly depends on peat decomposition degree, because it accumulates after plants die-off. The form in which Fe exists in peat depends on peat physical character and OM transformation degree. Fe is vital constituent of plant and animal life, and is the key component of haemoglobin. Fe is also considered as sedentary element and is tended to leach only from a permanent anaerobic zone. In several studies the distribution of Fe is explained with anthropogenic impact (Glooshenko et al., 1986). Mn typically is not found in the association with OM. In the presence of oxygen Mn is forming quaternary oxides, which can be important reservoirs for such transition metals as Co, Zn and Cr, but in the lack of oxygen or in sub-oxidable conditions Mn quaternary oxides are reductively dissolving and releasing dissolved bivalent Mn. Mn dioxide, which is the result of reduction reaction in anaerobic mire environment, is forming very mobile Mn cation, which is leaching out of mire permanent anaerobic and water fluctuation zone (Damman, 1978). Mn migration is strictly affected by the presence of Fe oxide and various organic colloids in peat, as Mn accumulates on the surface of those compounds (Syrovetnik et al., 2004). Co is frequently found in the association with Fe (Schoonen, 2004). The amount of Co is also related to Cu-Ni ore mining. Co plays a significant role in plant growth and metabolism, but the distribution of cobalt in plants is species dependent, Co is an essential component of several enzymes and co-enzymes (Allen et al., 2007). The distribution of Ni can be explained by both natural and anthropogenic processes, as Ni is related not only to anthropogenic activities, but also to bedrock weathering. The leaching out of mineral soils provides presence of Ni in bottom anaerobic peat layers. Ni is also disseminating from atmospheric pollution and it can occur, for instance, in the combustion of petroleum products, thus the highest Ni amount is in freshly formed aerobic peat layers. The amount of Ni is rapidly decreasing with depth – it can be explained by the fact that Ni pollution came later than other pollutants like Pb, Zn and Cd. Cd, Cu, and Zn are chalcophile elements (Goldschmidt, 1937) and readily combine with sulphur, but have low affinity for oxygen. An increased or decreased concentration of Cd in peat is related to its migration upwards from mineral soil and migration downwards from the atmosphere or surface waters. The amount of Cd is also related to human activities; therefore upper peat layers contain the highest Cd concentration. Cd is also a phytophile element and its concentration depends on the botanical composition of peat, it is mobile and has a higher mobility in bog acidic environment (Biester et al., 2002). Cu and Zn are micronutrients

and are required by living plants, thus their content in peat depends on peat botanical composition. Cu forms discrete sulphide minerals and it is often found in the association with OM. Cu is the key component of reduction-oxidation enzymes and of haemocyanin. The highest Cu content usually is in freshly formed aerobic peat layer (Gilucis, 2007), where Cu oxides are forming strong complexes with HS (Syrovetnik et al., 2004). Zn content is directly related to the amount of OM in peat. The amount of Zn is also related to human activities; therefore its highest concentration can be found in the upper peat layer. Zn is a phytophile element, thus its concentration also depends on the botanical composition of peat (Biester et al., 2002). Due to water level increasing, Zn is reducing to non-soluble Zn sulphide, but due to water level decrease, Zn sulphide ions oxidize to sulphate ions and Zn becomes mobile (Damman, 1978). Zn has higher mobility in bog acidic environment than in fens. Cr is a lithophile element, but also has characteristics of siderophile elements (Goldschmidt, 1937). Cr has strong affinity for oxygen and remains close to surface. Cr is also associated with the OM, but changes in Cr concentration indicate variability in dust composition. Usually Cr content and distribution are both controlled by plant feeding conditions and the absorption onto organic ligands in decomposed OM. Cr is an essential Me and plays an important role in glucose metabolism. In anything other than trace amounts, Cr compounds need to be regarded as highly toxic. Although, studies on Cr content in peat is scare, an increase of this Me in mires usually is linked to the industrial activities and the highest Cr content can be identified in mires close to large cities (Nikodemus et al., 2004). The variability of peat botanical composition has no significant effect on the concentration of Cr, it is highly mobile Me in an acidic environment, thus in bogs Cr is more mobile than in fens (Damman, 1978).

Lead is a chalcophile element (Goldschmidt, 1937) and has similar characteristics to chalcophile elements in the transition metal group. Lead has no known biological functions, although, the concentration also depends on botanical composition of peat and Pb is forming organic compounds (Biester et al., 2002). The highest Pb content usually can be found in freshly formed aerobic peat layers. However, in some cases, catotelm layer can contain an increased amount of Pb as well – it can be explained with the decrease of Pb in atmosphere during last decades (Nikodemus et al., 2004).

1.3.1 Heavy metal contamination indicators

Many studies (Coggins et al., 2006; Ukonmaanaho et al., 2004; Shotyk et al., 2002; Martinez-Cortizas et al., 2002; Shotyk et al., 2001; Damman, 1978 etc.) have shown a gradual increase of heavy metals in peat mass during the last hundred years as a result of anthropogenic pollution. Due to the ability to bind pollutants, which are supplied by the precipitation and water flow, peat and mire plants can be successfully used as pollution indicators. Me concentration variations in a peat profile can be determined using geo-accumulation index, but to evaluate if peat is contaminated with particular heavy metals it is required to compare Me content with their natural concentration in Earth crust (Table 1.7). At high concentrations all Me, but in particular, heavy metals, are serious contaminants and can cause not only degradation of vegetation,

but also human health problems. Heavy metals are not biodegradable and they tend to accumulate in living organisms and cause a variety of disorders and diseases such as peripheral neuropathy, multiple sclerosis, cancer and others (Brennan et al., 1996). An increasing amount of heavy metals in the environment is a global problem and it is a growing threat to the humanity (Martin and Griswold, 2009).

Table 1.7

Metallic elements in Earth crust (Bettelheim et al., 2015)

Element	mg/kg	Element	mg/kg
Fe	50000	K	25900
Mn	1000	Cd	0.15
Zn	70	Co	25
Cu	100	Cr	100
Mg	20900	Ni	84
Ca	36300	Pb	0.015
Na	28300	Ti	4400

Heavy metals are naturally occurring substances, but they are also forming as by-products of the industrial activities and thus their spreading must be limited to the minimum. In general, humans and other organisms are exposed to heavy metals from food and water; therefore, one of the largest challenges is the heavy metal potential for the bioaccumulation and bio-magnifications in the food chains (Couillard, 1994).

To identify and characterize a possible peat contamination with heavy metals it is possible to use variety of multi-proxy research methods, but most commonly it is being executed by means of EF, PI and GI (Pekey, 2006; Birch, 2003; Atgin et al., 2000). EF is a powerful tool to distinguish between anthropogenic and naturally occurring heavy metal sources and it is being used to determine the degree of composition in atmospheric aerosols, deposits, soils (including peat) and soil waste (Pekey, 2006). The contamination with heavy metals based on EF values can be divided into six classes. According to Birch (2003) EF < 1 demonstrates no enrichment, EF: 1-3 is moderate enrichment, EF: 5-10 is moderately severe enrichment, EF: 10-25 is severe enrichment, EF: 25-50 is very severe enrichment and EF > 50 is extremely severe enrichment. Element enrichment depends on variety of complex factors – one of the most significant ones is the biogeochemistry, which is redistributing chemical elements between environmental compartments and the Earth surface. Thus element EF cannot conclusively demonstrate the anthropogenic impact on element cycle in local, remote, research sites, although, it shows on trends and relations between human activity and environmental processes (Reimann and de Caritat, 2005). Contamination with particular heavy metal can be also described using PI, which is the relation of heavy metal concentration in a sample to value for the element in Earth crust. According to Håkanson (1980) PI can be classified into four groups: PI<1 demonstrates low contamination, PI: 1-3 is moderate contamination, PI: 3-6 is considerable contamination and PI > 6 is very high contamination.

1.3.2   Bio-sorption of metallic elements onto peat

Peat has emerged as strong adsorbent for heavy metals such as Pb, Cu, Ni, Zn and Cd (Bulgarlu et al., 2011; Gupta et al., 2009; Ho and McKay, 2004; Rinqvist et al., 2002). The majority of studies on peat as metal adsorbent are focused on the extraction of HS (Gondar et al., 2005; Li et al., 2004; Baran, 2002; Niemeyer et al., 1992); this requires disintegration of original peat material and is altering functional groups. Thus studying peat with minimal break down of the original material is more realistic for describing of its capabilities as bio-sorbent (Burba et al., 2001).

Industrial development and other anthropogenic activities have a huge impact on the environment and forces to find new and cost-effective environment treatment technologies. One of the most effective and environmentally friendly methods is use of bio-sorbents and for this option peat is one of the most cost-effective materials. In general, bio-sorption may be simply defined as the removal of substances from solution by biological material (Gadd, 2009).

To promote clean environment, high on the agenda is to limit heavy metal contamination, particularly of that in wastewaters of metal plating facilities, tanneries and many other industries. Most popular methods in the decontamination of wastewater are coagulation, membrane separation, oxidation and other physico-chemical methods (Bulut and Tez, 2007). These methods are expensive and have a lot of technical constrains and disposal problems. Thus there is an urgent need to find an universal, simply operable and cost effective method in wastewater treatment – not only in decontamination of industrial waters, but also in decontamination of any waste material, which might end up into water. One of the most promising solutions is use of bio-sorbents. Several of currently used bio-sorbents have proven their effectiveness, for instance – peat moss, seaweeds, bacteria, wool and rice have high potential in environmental decontamination. The quality of peat and range of applications largely depend directly on Me concentration in it. Physico-chemical characteristics – high porosity, acid to alkaline pH reaction, modifiable specific surface area and high ion-exchange capacity allow using peat as a high-quality material for variety of bio-sorbents (Joosten and Clarke, 2002). In the matter of fact, using peat and peat products in purposes of heavy metal bio-sorption is technically feasible and an economically viable solution, because it is a low cost organic material, which requires a little processing and is abundant in nature (Dżugan et al., 2012; Sun et al., 2003).

1.4   The interaction among peat characteristics and metal ions

Due to peat composition and structure, it has an ability to bind Me (Coupal and Lalancette, 1976). The variation of these two peat characteristics supports Me accumulation at different rates and in form of various complexes. There is no generally accepted Me accumulation system, but there are five mechanisms (Table 1.8) proposed to metal binding in peat (Orru and Orru, 2006; Brown et al., 2000).

Table 1.8

Metallic element binding mechanisms in peat

Mechanisms	Factors
Mechanical accumulation of metals in a particulate form	Peat properties, Metal properties, Environmental conditions
Biologically mediated binding during the life cycle of plants and microorganisms	
Physicochemical ion exchange	
Physical and chemical adsorption and complex formation	
Chemical transfer of readily degradable compounds into less readily degradable compounds	

It has been proven that the sequence of elements in peat column is subject of specific order (Weiss et al., 2002; Damman, 1978):

1. Elements with higher concentration near surface, but with significant decrease in the depth of 10 to 15 cm (Na, K);
2. Elements with high concentrations in the depth of 35 cm and with a noticeable decrease in the depth (Ca, Mn, Mg), in upper 35 cm thick peat layer usually is concentrated around 10% of all Ca and even up to 60% of total amount of Mn;
3. Elements with high concentration in bottom peat layer.

Although, as it will be seen in following chapters (Chapter 3.2) fen peat seems not to be subjected to this order and has independent Me accumulation mechanisms.

1.5 Use of peat

Wise use of mires and peat are essential to ensure that sufficient areas of mires remain intact or are returned close to their natural state to carry out their vital natural resource functions, while satisfying essential requirements of the civilization. This involves detailed evaluation of their functions, uses, impacts and constraints and, through such assessment and reasoning; it is required to highlight priorities for the management and use of mires, including the mitigation of damage done to them to date (Joosten and Clarke, 2002). In general, up to date, there are three major directions of peat use – for energy, horticultural and agricultural use, and for other use (Krumins et al., 2013). Over decades until today, peat has been used for the electricity and heat generation, as well as directly for various industrial and residential purposes. Peat has been known to use as litter and compost ingredient, soil improver and growing medium. One of the noteworthy fields is medicine, where peat is used in variety of medical products and therapeutic applications (Clarke and Rieley, 2010).

Peat in agriculture, horticulture and animal husbandry

Peat moss and milled peat can be successfully used in horticulture as soil improvers; it is also a valuable resource for agriculture, where mixed with soil it improves soil structure and increases acidity. One of the major peat agricultural characteristics is

the ability to retain moisture when soil is dry, thus retaining water access for plants. Although, peat is widely used in horticulture, it is highly recommended to thermally process peat substrate before use to kill pests and reactive nutrients.

Peat has been widely used as an organic raw material in the production of organic fertilisers and combined organic-mineral fertilisers and in the improvement of degraded soils. Most important value of organic and organo-mineral fertilisers, produced with peat, is biologically active substances in OM. Organic substances enrich soil with trace elements and improve physical properties, pH level and the productivity. In future peat might have an economically effective role in remediation of degraded soils and as topsoil replacement in regeneration of areas used in open-cast mining (Mayhew, 2004; Joosten and Clarke, 2002). Due to the limited volume of a pot, container or tray module, the growing media must provide appropriate physical, chemical and biological conditions for plant growth. In countries with modern horticultural industry peat has emerged as the foremost constituent of growing media and production and processing of peat-based growing media have become preconditions for horticulture (Alexander et al., 2008). Peat substrates are used particularly in glasshouse horticulture for cultivation of young plants, pot plants and for growing of crops, such as bedding plants and vegetable plants in containers. In Europe, approximately 90% of all growing media for the professional and amateur markets are peat-based (Joosten and Clarke, 2002). Dry peat moss can absorb about ten times of its own weight in liquids, is reducing unpleasant smells and has favourable effect on health of animals. Another advantage of peat is the after-use as substrate for local vegetable-growers (Joosten and Clarke, 2002).

Peat in medicine, chemistry and food industry

Peat, due to low thermal conductivity and high heat capacity, is being used in physiotherapy in the form of peat compresses, bandages etc. In the 20th century peat has also been used as food additive for livestock feed, because it was considered that peat addition to food prolongs digestion and allows obtaining more nutrients from food. Interest of peat as fodder food additive, in recent years, has increased; it can be explained with peat ability to limit spreading of digestive diseases, to stimulate livestock growth and to strengthen immune system (Shermer et al., 1998; Stevenson, 1982). A long tradition in many countries is using mud for human and veterinary therapeutic purposes. By any chance peat was substituted for mud, and from 1802 (first in in Nennodorf and Marienbad – Mariánske Lázné in the Czech Republic) this balneological speciality spread across Central Europe and later to some other European countries including Estonia, Ukraine and Poland (Joosten and Clarke, 2002). Fields in which peat is indicated for human medical treatment are: gynaecology; illnesses of the locomotion system; dermatology; interior illnesses and ophthalmology (Joosten and Clarke, 2002). The positive effect of peat therapy arises from thermophysical and biochemical mechanisms. Peat baths are able to cause overheating effect, are favourable to changes in digestive system, act as a relaxing medium. Peat contains biologically active substances, of which HA are the most important, thus it has positive effect on immune system and against bacteria, viruses and inflammation. Peat chemical

processing has resulted in development of number of preparations with growth-stimulating, fungicidal and bactericidal properties. Peat hydrolysates contain wide spectrum of amino, carbonic and uronic acids, HS and other compounds, which can activate or inhibit variety of biological processes. Peat oxidate has been found to be helpful in treatment of skin diseases. Compounds combining volatiles with water steam have been used in treatment of eye diseases. Use of peat has also been successful in veterinary medicine. In Central and Eastern Europe peat preparations were used in a large-scale rearing of cattle, pigs and poultry as growth promoters and as medicine, immunological stabiliser, nutrient yeast, carbohydrate fodder additives, and absorbents of harmful substances. Peat preparations have also been used in plant production as growth promoting, fungicidal and bactericidal substances. Peat oxidates have been used as a treatment for microbiological diseases of agricultural crops, for example, to fight phytophtorose of potato and tomato (Joosten and Clarke, 2002).

Peat OM is a valuable raw material for chemistry. Chemical peat processing is carried out by hydrolysis, pyrolysis, extraction and chemical modification (Klavins and Porshnov, 2013; Лиштван, 1996).

Examples of the use of peat in chemical processing include:

1. Water soluble humic preparations have been found to be effective in purification of metallic surfaces from radioactive substances, it is considered that they may have potential in purification of technological equipment in active nuclear power stations;
2. Humic preparations, which are soluble in acids, have been used for the extraction of valuable metals from raw materials;
3. Activated carbon from peat is effective in number of applications including purification of soil and water from organic contaminants;
4. Peat has been found to be an inhibitor of corrosion. Special preparations for the transformation of rust into metal have been widely used in Belarus, for example to remove rust from automobiles (Bambalov, 2012; Joosten and Clarke, 2002).

Historically peat has been used as flavour enhancer for whisky. Scotch whisky is being produced by distillation of beer and there are two distinct types of whisky, malt and grain, produced in Scotland. Single malts are distilled in simple copper pot-stills from a mash derived entirely from malted barley. First stage in malting is to steep screened barley in water for two to three days until the grain becomes soft and swollen. The "green malt" is then dried slowly over a smouldering peat fire. In general, highly decomposed peat, known locally as blue or black peat, seems to be preferred. Despite the disadvantages associated with small-scale production units, some distilleries and individual malting still select, cut and harvest their own peat supplies annually. More recently use of air-dried peat sods to fuel open fires in traditional malting process is being superseded by combustion of peat pellets in special burners resulting in better overall control and efficiency and a significant reduction in quantity of peat what is required (Joosten and Clarke, 2002).

Peat in construction and pollution treatment

Peat, mixed with binders, can be used in production of building materials. Physical and chemical characteristics of peat – high porosity, high specific surface area, ion exchange capacity etc. make of peat a valuable material in production of various sorbents. In many countries peat has been used as a building material. In Ireland, the Netherlands and Germany, poor people built their homes from sods of turf. Peat has been used in Germany as an insulation material in wooden cottages. In some parts of Finland sod peat is being used as foundation material on roads (instead of gravel). In Norway compressed peat bales have been used as foundation for rail tracks in areas prone to soil movement from frost. In Russia and Belarus peat has been widely used as an insulation material in the form of dry pressed sheets, for example in industrial refrigerators or as peat boards in poultry stables (Korjakins et al., 2013; Joosten and Clarke, 2002). Peat has also valuable filter and absorbent material functions. Pollution treatment capabilities of peat materials include physical filtration; chemical adsorption/ absorption and biological transformation (Joosten and Clarke, 2002).

Peat in clothing production

Peat has been used to produce paper and experimenting accelerated the discovery of its potential for peat fibre and as an insulating material. The basal sheaths of cotton-grass (*Eriophorum vaginatum*) in peat under the long-term influence of humus and humin substances undergo a change into brown, 5-20 cm long fibres, which are soft enough to be used for textiles. These fibres are warmer than wool, because of their cavity-like, air-filled structure, which makes them also very light. The fibres easily absorb and release liquids and have the ability to absorb secretions of the skin, including perspiration and salts, in addition to absorbing smells. They do not acquire an electric charge and burn poorly, like wool does (Joosten and Clarke, 2002).

2 MATERIALS AND METHODS

2.1 Study sites and sampling

To characterize the influence of peat composition on Me accumulation, four fens in the territory of Latvia were chosen, those were Elku, Salas, Svētupes and Vīķu mire (Fig. 2.1 and Table 2.1).

Figure 2.1   **Location of study sites**
        (1. Svētupes Mire, 2. Salas Mire, 3. Vīķu Mire, 4. Elku Mire)

Table 2.1

Study site characteristics

Study site	Geographical region	Geobotanical region	Mire type	Peat layer depth (m), avg., max.
Elku Mire	Eastern Kursa Upland, Lielauce Hillock	Western Latvia geobotanical region	Transitional, fen	1.10, 3.50 (fen peat layer: 2.00)
Salas Mire	Eastern Latvia Lowland, Lubāns Plain	Northern-eastern geobotanical region	Bog, Transitional, fen	1.00, 8.00 (fen peat layer: 0.50)
Svētupes Mire	Central Latvia Lowland, Idumeja Upland, Limbaži Wavy Plain	Northern Vidzeme geobotanical region	Fen	1.20, 3.00 (fen peat layer: 2.20)
Vīķu Mire	Eastern Kursa Upland, Lielauce Hillock	Western Latvia geobotanical region	Fen	2.00, 4.50 (fen peat layer: 2.50)

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.

Studied fens were formed in similar conditions (lake overgrowing) and characterize environmental conditions in fens in the territory of Latvia. Relatively simple environmental conditions, similar origin, but differences in further fen development suggest variable development of peat properties. Therefore, fens can be dealt with only as heterogeneous systems. Moreover, fen environment is so variable that wide range of peat properties will be different even within borders of particular mire.

Elku Mire is located in Lielauce Hillock at coordinates: 56°37'22"N, 22°59'16"E, 86 m asl. The nearest populated places are Zebrene (7 km to the SW) and Kaķenieki (7 km to the NE). The total area of Elku Mire occupies 285 hectares, 188 ha of which is covered by fen. The average depth of peat profile is 1.1 m, but the maximum known depth is 3.5 m.

Vīķu Mire is located in Lielauce Hillock at coordinates: 56°30'58"N, 22°54'32"E, 100 m asl. The nearest populated place is Lielauce (1 km to the E). Vīķu Mire completely surrounds Lake Lielauce and the total area of mire occupies 875 hectares, 397 hectares of which is fen. The average thickness of peat layer is 2.0 m, but the maximum known depth – 4.5 m.

Salas Mire is located in Lubāns Plain at coordinates: 56°46'59"N, 27°00'42"E, 110 m asl. The nearest populated places are Varakļāni (24 km to the SW), Lubāna (15 km to the NW), Bērzpils (7 km to the NE), and Gaigalava (8 km to the SE). Salas Mire occupies 2104 hectares and the most part of it (1885 hectares) is covered with bogs, while fens occupy 130 hectares. The depth of peat profile varies between 1 and 4 m, but in some places it can attain 8 m. The sampling in this study site (0.50 m) was carried out for the purpose of peat properties comparison without harming the environment.

Svētupes Mire is located in Idumeja Upland at coordinates: 57°32'49"N, 24°41'48"E, 71 m asl. The nearest populated places are Ozolaine (3 km to the S), Katvari (5 km to the E), and Viļķene (8 km to the N). The total area of Svētupes Mire occupies 917 hectares; the most part of fen is covered by forest (640 ha). The average depth of peat profile is 1.2 m, but the maximum known depth – 3.0 m.

Dissimilarities in mire formation time, development conditions and in interaction with environment promote differences in peat botanical composition making it multifarious even in nearby located mires.

During peat sampling a special care was taken to select appropriate sites in the line with objective of this study (Givelet et al., 2004). Peat samples were taken from selected research points with the stainless steel "Russian" type corer (standard peat corer). All use constrains of this type corers were taken into account following Zaccone et al. (2012) conclusions. Semi-cylindrical corer with shutter was pushed into deposits, twisted and recovered to display a full and undisturbed peat profile (de Vleeschouwer et al., 2007; Jowsey, 1966). In this study the model with 50 cm long

sample chamber and with inner diameter of 70 mm was used. Coring, sounding and sampling have been accomplished in central areas of mires, where the most complete geological section is present (Coggins et al., 2006; Shotyk et al., 2001). 0.5 m long monolithic peat samples were put in special plastic cartridges and wrapped in poly-ethylene film to preserve their natural moisture and other peat parameters. Outside edges of each 0.05 m sample were discarded, because of possible contamination during the sampling.

2.2 Metallic element content determination procedure

Peat from Svētupes, Salas, Vīķu and Elku Mire was studied using standardized methods (Tan, 2005). Peat profiles from each study site were separated into 5 cm thick layers and it was followed by Me content determination by acid digestion using AAS (Krachler et al., 2003) and by using TXRF (Potts, 1987). Acid digestion was carried out using 25 ml 50% HNO_3 and 5 ml 30% H_2O_2 on 1 g of oven-dried peat sample. Each sample was mixed up with the acid solution and left for 24 h; mixtures were then boiled at 150 °C until half of the liquid evaporates and then another 25 ml of 50% HNO_3 were added and mixture boiled until first vibrate. 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 AAS. Me concentrations were measured with the acetylene-air flame, acetylene-N_2O flame and GFAAS with the background correction (Table 2.2).

Table 2.2

Precision of analytical determination of metallic element content

	Ca	Mg	Fe	Na	K	Mn	Zn	Cu	Ni	Pb	Cr	Co	Cd
Detection limit, mg/kg	21	6	4	3	3	0.6	0.2	0.2	0.15	0.09	0.07	0.02	0.006
Measurement uncertainty, %	3	4	3	6	9	5	3	4	7	11	18	11	7

Me concentration was normalized against Ti content in peat samples (determined using TXRF). The author has performed the acid digestion procedure, but K. Viligurs at the University of Latvia, Faculty of Geography and Earth Sciences performed AAS. 5 g of homogenous peat powder, derived from approximately 50 g fresh peat, was irradiated with an X-ray beam. The interaction of primary X-ray with the sample causes ionization of discrete inner orbital systems, causing rearrangement of the remaining electrons accompanied by an emission of X-ray fluorescence (Le Roux and de Vleeschouwer, 2010). J. Kostjukovs at the University of Latvia, Faculty of Chemistry, performed TXRF analysis.

2.3 Peat characterization methods

Depending on the aim of study, samples are attributed to a different set of analyses and methodology (Gnatowski et al., 2010). In this PhD thesis the detailed characterization of fen peat was performed using multi-proxy analysis method with a view to link peat properties to Me accumulation characteristics in studied peat profiles and are describing the importance of peat composition on Me accumulation in fens.

2.3.1 Sample dating

Sample Carbon-14 dating was performed by Professor Enn Kaup in Tallinn University of Technology using the conventional liquid scintillation counting technique, but as the scintillation solvent – benzene (Piotrowska et al., 2011; Tamers, 2010). Absolute age was calculated using "Clam" v. 1.0.2 add-on for "R" v. 2.11.0 software. This program performs "classic" age-depth modelling and uses linear interpolation between dated levels (Blaauw, 2010). To calibrate the obtained data, the author was using curve IntCal09.14C (Reimer et al., 2009).

2.3.2 Botanical composition and decomposition degree

The analysis of peat decomposition degree was followed by the centrifugation method according to ГОСТ 10650-72 standard, and peat decomposition degree was expressed as percentage of the total peat sample mass (Malterer et al., 1992). An approximate decomposition degree was also determined on the field, because peat in contact with air rapidly oxidizes, changes its characteristics and loses its natural colour (von Post, 1924).

Peat botanical composition was determined in binocular microscope at 56 to 140 time's magnification according to ГОСТ 28245-89 standard. Principle of this analysis is to identify the percentage of specific plant residues in a defined area – as the result all recognized plant remains sets 100% (Lamacraft, 1979; Кац и др, 1977). Anete Dinķīte from Ltd. "Balt-OST-GEO" determined decomposition degree and botanical composition. Author using "Tilia" v. 1.7.16 software created representative diagrams of peat botanical composition and decomposition degree.

2.3.3 Humification index D_{540}

HI was determined by means of the spectro-photometric method of Blackford and Chambers (1993), with Borgmark's (2005) modifications. 1.00 g of peat with the addition of 25 ml 8% NaOH was heated 1.5 h at 95 °C in water bath. After the heating samples were filtered and half of the solution diluted with de-ionized water up to 100 ml. HI was evaluated as peat extract absorption value at 540 nm. Although D_{540} is a simplistic measurement, it is a reliable and informative indicator describing the living matter transformation process and can be also considered as K-value (Hughes et al., 2012).

2.3.4   Loss on Ignition procedure

The content of OM, CM and MM was determined and values calculated using LOI method (Heiri et al., 2001). Samples were dried in an oven at 105 °C for 24 h, heated in muffle at 550 °C for 4 h and at 950 °C for 2 h.

OM content was calculated using equation 2.1:

$$OM = \frac{DW_{105} - DW_{550}}{DW_{105} - W_{cru}} \times 100 \tag{2.1}$$

In the equation above OM is the content of organic matter in percentage; DW_{105} is the weight of oven-dried peat sample together with a crucible; DW_{550} is the weight of peat sample heated at 550 °C with a crucible and W_{cru} is the weight of an empty crucible.

CM content was calculated using equation 2.2:

$$CM = \frac{DW_{550} - DW_{950}}{DW_{105} - W_{cru}} \times 136 \tag{2.2}$$

In the equation above CM is the content of carbonate matter in percentage; DW_{105} is the weight of oven-dried peat sample together with a crucible; DW_{550} is the weight of peat sample heated at 550 °C with a crucible; DW_{950} is the weight of peat sample heated at 950 °C with a crucible and W_{cru} is the weight of an empty crucible.

MM content was calculated using equation 2.3:

$$MM = 100 - (OM + CM) \tag{2.3}$$

In the equation above MM is the content of mineral matter in percentage; OM is the content of organic matter and CM the content of carbonate matter.

2.3.5   Elemental composition

The analysis of elemental composition was carried out in Latvian Institute of Organic Synthesis and the Institute of Solid State Physics. Elemental composition (C, H, N and S) was determined using Carlo Erba Elemental Analyzer EA-1108 with PC based data system. This analytical method is based on the complete and instantaneous oxidation of sample by flash combustion, which converts all organic and inorganic substances into combustion products. Resulting combustion gases pass through the reduction furnace and are swept into chromatographic column by the carrier gas, where they are separated and detected by thermal conductivity detector, which gives an output signal, which is proportional to the concentration of the individual components of the mixture. 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). The elemental composition was further used to calculate elemental correlations H/C; O/C; N/C; oxidation index (ω) and hydrogen deficient (ϕ) (Fong et al., 2007).

Elemental correlations were calculated using equations 2.4, 2.5 and 2.6:

$$O/C = \frac{(M_{xC} \times O)}{(M_{xO} \times C)} \quad (2.4) \quad H/C = \frac{(M_{xC} \times H)}{(M_{xH} \times C)} \quad (2.5) \quad N/C = \frac{(M_{xC} \times N)}{(M_{xN} \times C)} \quad (2.6)$$

Where M_x is the molar mass of a particular element, but O; C; H and N is the quantity of particular element in percentage.

Oxidation indices (ω) and hydrogen deficient (φ) were determined using equations 2.7 and 2.8:

$$\omega = \frac{(2O+3N)}{H/C} \qquad (2.7) \qquad\qquad \varphi = \frac{((2C+2) - H)}{2} \qquad (2.8)$$

Where ω is oxidation index; φ is hydrogen deficient; O, N and C is the quantity of oxygen, nitrogen and carbon in sample.

2.3.6 Differential thermal analysis and thermogravimetry

DTA represents the data about temperature range with the most pronounced changes in peat sample. In most cases data coincides with the most significant sample weight loss. In turn, TG allows monitoring sample weight loss – which, accordingly, is dependent on the heat input. DTA and TG allows monitoring of both endothermic and exothermic reactions, thus it is possible to trace the sequence of physico-chemical processes in a peat sample. For instance, this method allows monitoring the time, temperature and weight loss when sample collapses in an event of gas release. The illustration of an early diagenesis is one of the most significant results what can be represented using these methods. Results also give the representation of OM transformation into peat deposits and further into coal.

These analyses were performed using derivatograph SII Exstar 6300 TG/DTA. As an optimal sample mass for these analyses were selected 20 mg of an air-dried and grinded peat. Heating was performed in nitrogen atmosphere at temperature range from 25 °C to 550 °C. An initial temperature ($\sim$ 25 °C) was variable and corresponded to the room temperature at the moment of analysis. Temperature was automatically increased by 10 °C every minute. These analyses were performed by Agris Bērziņš in the Faculty of Chemistry.

2.3.7 X-ray diffraction

XRD measurements were performed on peat ash using PANalitical X'Pert PRO X-ray difractometer. Crystalline phases were identified according to data from International Centre for Diffraction Data using X'Pert HigScore and X'Pert Data viewer software. Juris Kostjukovs at the Faculty of Chemistry, University of Latvia and Agnese Stunda-Zujeva at the Faculty of Material Science and Applied Chemistry at Riga Technical University performed these XRD measurements.

2.3.8   Fourier-transform infrared spectroscopy

FT-IR is a method to obtain an IR spectrum of absorption, photo-conductivity, emission or Raman scattering of substances (Stuart, 2004). In this study it has been used to obtain IR absorption spectrum of powdered peat samples. FT-IR has several advantages against other peat research methods, such as elemental analysis or UV/Vis spectroscopy. General advantage is the simplicity of this method. Sample preparation and analysis is not time-consuming and results can be obtained almost immediately. The FT-IR application on peat provides data on the nature of oxygen and hydrogen containing functional groups, their structural array, relations etc. (Stuart, 2004; Chapman et al., 2001). However, it should be remembered that this method only indicates the presence of one or another functional group, but not on their amount. Certain functional groups absorb IR light at characteristic frequencies and thus it is possible to identify chemical structures common to particular peat sample (Tolstoy et al., 2003). The most part of absorption zones for functional groups, common to peat, are located in so-called middle range of IR spectra at wavelength interval 400-4000 cm^{-1}. General absorption range can be separated in three main areas:
1.   The "fingerprint region" in wavelength interval from 400-1500 cm^{-1};
2.   Absorption of double bounded groups in range from 1500-2500 cm^{-1};
3.   "R-H region" in range from 2500-4000 cm^{-1} (Stuart, 2004).

30 mg of KBr salt was manually compressed into a pellet through which IR radiation was then transmitted (Liu et al., 2002). 250 mg of KBr was mixed up with 25 mg of sample powder and 30 mg of mixture was extracted and compressed into a pellet. The IR radiation was transmitted through the sample pellet. Afterwards, IR spectra were recorded in the wavelength range from 4000-450 cm^{-1} with resolution of 4 cm^{-1}. IR spectra of peat samples were recorded by author using "Perkin Elmer Spectrum BX FT-IR" spectrophotometer. Several independent background samples were prepared to reduce errors on spectra (for instance, collection of CO_2 from the air). Typical error usually is observable in wavelength range from 2340 to 2300 cm^{-1} and it is caused by CO_2 and moisture (Stuart, 2004; Tolstoy et al., 2003). These background samples were made of potassium bromide (VWR International Ltd., England; KBr for infrared spectroscopy) (Liu et al., 2002; Stuart, 2004). The author corrected obtained data using baseline correction and normalization (Stuart, 2004; Tolstoy et al., 2003) and afterwards, using "Spekwin32" software, visualized spectral curves.

2.3.9   3D fluorescence spectroscopy

Peat itself has no fluorescent characteristics, however – chromophores in HS have a wide range of fluorescence intensity, what allows identifying functional groups containing compounds. To identify these compounds, it is necessary to extract HS from peat – presumably, using alkaline solutions. For this study fen peat alkaline extracts were made using 10 mg of air dried peat with addition of 8% KOH solution up to 50 ml. Alkaline solutions were shaken for 24 hours at room temperature and pH was normalized to 5. EEM spectra were recorded using total luminescence spectrometer AQUALOG. In further analysis FI was calculated from two points in FA influenced

region of EEM. FI is a relatively simple measure of the degree of impact of allochthonous or autochthonous processes in DOM processing (McKnight et al., 2001). FI was introduced by McKnight et al. (2001); they described it as the intensity value at f_{450}/f_{500}. Respectively, it is the ratio of fluorescence intensity at Em wavelength 450 nm to that at 500 nm at Ex 370 nm, to discriminate the sources of DOM. They reported that f_{450}/f_{500} is about 1.9 for aquatic and microbial sources and about 1.3 for terrestrial and soil sources (including peat).

2.3.10 Specific surface area

Specific surface area was determined in the Faculty of Material Science and Applied Chemistry at Riga Technical University using NOVA 1200e surface area analyser, but results were treated using NovaWin2 software. Specific surface area was calculated using Brunauer-Emmett-Teller method (Brunauer et al., 1938). Peat samples were heated 2 hours at 100 °C before the analysis. The method is based on the absorption of nitrogen molecules – at given pressure it is possible to measure differences in the pressure of nitrogen gas.

2.3.11 Scanning electron microscopy

Various fen peat types were viewed under lens of the scanning electron microscope (JOEL ISM T-200) at magnification of 50, 200, 500, 1000 and 2000 times. Before analysis was performed, peat sample surface was covered with a thin gold layer in a diode sputtering system for 10 min to increase the sample reflection. SEM was performed at the Faculty of Biology, University of Latvia.

2.3.12 Carbon-13 NMR spectroscopy

Carbon-13 nuclear magnetic resonance is the application of NMR spectroscopy to carbon. It allows the identification of carbon atoms in an organic molecule. Carbon-13 has a nuclear spin ($I = \frac{1}{2}$) and makes up 1.1% of all naturally occurring carbon, a high enough abundance along with modern technology to make ^{13}C-NMR a useful technique. Since carbon is an element central to organic chemistry, ^{13}C-NMR plays an important role in determining the structure of unknown organic molecules, study of organic reactions and processes (Keeler, 2010; Kemp, 1991). ^{13}C-NMR spectra were recorded using pulsed Fourier-transform method with an enhanced sensitivity by summation of several spectra – commonly a few hundred to several thousands, depending on the solubility of the compound, the amount available and the number of carbon atoms in the molecule (Kemp, 1991). Analysis was performed in the School of Engineering, University of Pisa in Italy by Oskars Purmalis.

2.3.13 Bio-sorption experiment

Sorption of Ca, Mg, K, Na, Cu and Pb onto fen peat was performed in an aquatic environment using water-soluble reagents ($CaCl_2$ x $2H_2O$; $MgCl_2$ x $6H_2O$; KCl; NaCl; $CuSO_4$ x $5H_2O$ and $Pb(NO_3)_2$), all of them diluted up to 250 ml. Equilibrium batch adsorption studies were carried out by mixing peat (100 mg of grinded and oven-dried

peat sample) with aqueous metal solutions (50 ml) of different concentrations in sealed containers at 25 °C for 24 h. Subsequently, solutions were filtered, but the amount of heavy metals in filtrate was measured using AAS (PerkinElmer AAnalyst 200). Sorption capacity was calculated using multiplication of analytical solution volume and difference between analytic concentration before and after adsorption against the mass of peat sample. The appropriate model of the adsorption mechanism was created using Langmuir adsorption model determination coefficients, which is the most often-used adsorption model. Langmuir adsorption model is based the following assumptions – "*adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighbouring sites occupancy*" (Febrianto et al., 2004).

2.4 Data statistical analysis

The variation of Me concentration in peat profiles is often determined by geo-accumulation, but EF and PI are significant to understand the character of heavy metal accumulation in peat.

Element enrichment factor

EF for given heavy metals is relative to Ti concentration and was calculated using equation 2.9 (Birch, 2003):

$$EF = \frac{(M_p/Ti_c)}{(M_c/Ti_c)} \tag{2.9}$$

Where EF is the enrichment factor; M_p is metallic element in peat; M_c is metallic element in Earth crust; but Ti_c is titanium content in Earth crust.

Pollution index

PI for given heavy metals was calculated using equation 2.10 (Birch, 2003):

$$PI = \frac{M_p}{M_c} \tag{2.10}$$

Where PI is the pollution index; M_p is metallic element in peat, but M_c is metallic element in Earth crust.

Geo-accumulation index

GI for given heavy metals was calculated using equation 2.11 (Birch, 2003):

$$GI = \log_2\left(\frac{M_p}{(1.5 \times M_c)}\right) \tag{2.11}$$

Where GI is the geo-accumulation index; M_p is metallic element in peat, but M_c is metallic element in Earth crust.

Parallel factor analysis

PARAFAC analysis of EEM data evolved from the need to identify spectral features and associated fluorophore concentrations more quantitatively (Stedmon et al., 2003). The algorithm, analogous to a trilinear PCA, makes no assumptions about the number of components or the shapes of their absorption and Em spectra, and simulates EEM by optimizing the absorption spectra, Em spectra, and concentrations of independent groups of fluorophores in the sample (Stedmon and Bro, 2008).

OM sample PARAFAC analysis (whole water, FA, hydrophilic fraction etc. features) acquired from aquatic environments worldwide revealed that reduction-oxidation reactive quinone like components, amino acid like components, and a few unnamed fluorophore groups are repeatedly responsible for EEM spectral features (Cory and McKnight, 2005). Due to spectral overlap in Ex and Em signatures of fluorophores, multivariate analyses such as PCA performed on whole EEM allow to identify sample groups less distinctly than multivariate analyses performed on PARAFAC model results (Ohno and Bro, 2006; Jaffe et al., 2008). However, even when sample groups are identified based on PARAFAC model results, their positions in multivariate space are function of provenance, reduction-oxidation potential and reactivity gradients. The way how each of gradients independently controls observed differences in HS fluorescence can still be unclear.

PARAFAC analysis was performed using MATLAB R2014a v. 5.3.0.532 software with DOMFluor (contains the N-Way toolbox v. 3.1, it has additional functions that facilitate running PARAFAC analysis on OM fluorescence data) and drEEM toolboxes using specially adjusted algorithm. Both toolboxes are freely downloadable from the Chemometrics site at University of Copenhagen.

PARAFAC analysis consisted of 8 general steps:
1. Setting up MATLAB to run with N-Way toolbox, DOMFluor toolbox and drEEM toolbox;
2. Loading the required data and plotting EEM. In this step was created the data structure consisting of fluorescence, Em and Ex data. In total this data structure consisted of 6 variables: Ex (a list of the Ex wavelengths), Em (a list of Em wavelengths), X (3D array of fluorescence data), nSample (the number of samples), nEx (the number of Ex wavelengths) and xEm (the number of Em wavelengths). the plotting of raw data was also performed at this step and, subsequently – 2D contour maps and 3D plots created;
3. Cutting the spectra region influenced by scatter peaks. In this step wavelengths what are affected by scatter peaks have been cut and replaced with zeros;
4. Initial explorative data analysis and outlier identification. In this step series of PARAFAC models were run in order to explore the data for outlier samples, noisy wavelengths, or other potential problems with the data that are not easily identified by visual analysis of EEM plots. This analysis is structured into two parts – at first this test is performed on original data and at the second – on modified data, from where all outliers have been removed. Series of PARAFAC models from

2 to 7 components were run in this step and series of scores, loadings and leverages was accordingly created;

5. Split half analysis and validation. In this step all data were divided into halves and two different splits was made – each splitting data in a different way. Afterwards, all data were validated by mathematically comparing model Ex and Em loadings using Tucker Congruence Coefficients and states whether the model is validated or not;

6. Random initialization. In this step series of models were fitted to the whole data using model random initialization. It is necessary to ensure that the derived model is the last squares result and not a local minimum;

7. The component plot creation;

8. Data export out of MATLAB.

EEM spectra have been spectrally corrected for instrument biases, corrected for inner filter effects and were Raman calibrated. All of Rayleigh scatter and most of the Raman scatter has been removed.

Principal component analysis

PCA is quantitatively rigorous method for achieving simplification of information when datasets contain many variables and when groups of variables tend to move together. The reason of variables moving together is that more than one parameter might be measuring the same driving principle governing behaviour of the whole system. In PCA from the set of parameters a new set of variables is generated, called principal components, each of these components is a linear combination of original parameters. All principal components are orthogonal to one another and there is no redundant information left. The first principal component is a single axis in space (x axis); the variance of each parameter on this axis is the maximum among all possible choices of first axis. The second principal component is the perpendicular axis (y axis); the variance of each parameter on this axis is the maximum among all possible choices of y axis (Jollife, 2002). MATLAB R2014a v. 5.3.0.532 and PCORD 5 software has been used to perform PCA.

The statistical treatment of atomic absorption analysis results

Each measured Me was subjected to the determination of metrological parameters, method detection limit (Equation 2.12) and the quantitative limit (Equation 2.13).

$$\text{MDL} = (3 \times \text{STDEV}) \times \frac{V}{m} \tag{2.12}$$

In the equation above MDL is method detection limit, STDEV is standard deviation, V is volume (50 ml) and m is the sample mass (1 g).

$$QL = MDL \times 3.3 \tag{2.13}$$

In the equation above QL is quantitative level and MDL is method detection level.

Other statistical and graphical data post-processing

Statistical and graphical data post-processing was also carried out using Microsoft Office Excel 2007, Tilia 1.7.16 and SPSS 17 software. Correlation analysis was carried out between concentration of particular Me, Me and peat characteristics. In order to access Me absorption and precipitation characteristics at particular pH level, author was used software Visual MINTEQ 3.1.

3 RESULTS AND DISCUSSION

3.1 Characteristics of studied fen peat

Studied peat profiles were characterized using multi-proxy analysis methods (Chapter 2.3 and 2.4) and show on the individuality and complexity of characteristics and factors among study sites, although expressed similarities can also be detected.

3.1.1 Quaternary deposit character in mire catchment areas

Me supply in fen ecosystems is supported by precipitation, surrounding environment and deposits in the base layer. Thus it is essential to identify and evaluate mire catchment areas, because groundwater has the major role in Me accumulation character in fens (Orru and Orru, 2006; Shotyk, 1996).

Wide range of geochemical barriers (biochemical, mechanical, physiochemical etc.) play an important role in the dynamics of Me distribution in peat profile and in the environment itself (Syrovetnik et al., 2004), what, fundamentally, are changes in the environment physico-chemical characteristics. However, according to the results and especially in respect to Me accumulation in peat profile, as the only significant limit works the border between acrotelm and catotelm layer (oxidation-reduction) and, in some cases (Elku Mire), also the border between mire deposits and base layer. However, these barriers are selective for studied Me (Chapter 3.2.1).

The composition of Me in Quaternary deposits is essential to Me accumulation dynamics and concentration in fens. Moreover, an important precondition is also agricultural land use, land use dynamics, agricultural pollution etc. anthropogenic considerations in the particular mire catchment area. Due to modern agricultural practices (use of variety of pesticides and fertilizers containing, for instance, – N, P and K), type of agricultural land use and the agricultural pollution are of major importance in fen peat, accumulated in last 1000 years, and has a direct impact on Me distribution character in fen acrotelm layer. However, particular type of agricultural land use in mire catchment area is an individual large-scale research object and has no direct impact on the influence of fen peat composition on Me accumulation in fens. Notwithstanding, anthropogenic considerations are essential to the uniqueness and heterogeneity of fen ecosystems and special attention to this aspect in further research must be paid.

Quaternary deposits in Elku Mire catchment area

Quaternary deposits in Elku Mire catchment area (Fig. 3.1) consist mainly of Latvian formation glaciofluvial deposits; it is sand, gravel and pebble (fQ$_3$ *ltv*). To a lesser extent, but also with a significant impact on MM composition and Me concentration in peat, are Latvian formation glaciolacrustine deposits, which is sand and clayey silt (lgQ$_3$ *ltv*), in some places (Fig. 3.1) also Latvian formation glacigenic deposits – till (gQ$_3$ *ltv*), take place.

Figure 3.1   **Schematic map of the Quaternary surface deposits in Elku Mire catchment area**

(Geological indices gQ_3 *ltv*, fQ_3 *ltv* and lgQ_3 *ltv* describe Upper Pleistocene deposits; geological index bQ_4 describes Holocene deposits)

Quaternary deposit character in Elku Mire catchment area is determining Me content in groundwater and, accordingly, also Me concentration in peat. High MM content in Elku Mire fen peat profile bottom part (Chapter 3.1.3), which is dominated by quartz minerals and to a lesser extent also by carbonate minerals, can be related to groundwater flow through glaciofluvial and glaciolacrustine sand deposits (Chapter 3.1.4). The base of Elku Mire consists of sandy and carbonate-rich sapropel, which hypothetically can be evaluated as a geochemical barrier and can cause an elevated concentration of Me in peat (Chapter 3.2.1). In the bottom of Elku Mire peat profile a significant increase in concentration of particular heavy metals (Fe, Zn, Cu, Cr, Ni, Co and Cd) has been observed, while the content of alkali and alkaline earth metals (K, Na, Ca and Mg) here is not affected (Chapter 3.2.1). This elevated Me concentration most likely can be explained with an increased groundwater flow and MM supply (Chapter 3.1.3).

Quaternary deposits in Vīķu Mire catchment area

Quaternary deposits in Vīķu Mire catchment area are not significantly different from Quaternary deposit composition in Elku Mire basin (Fig. 3.2). In the Quaternary surface occur Latvian formation glacigenic (gQ_3 *ltv*), glaciofluvial (lgQ_3 *ltv*) and glaciolacrustine (lgQ_3 *ltv*) deposits, what are of a sandy character.

Figure 3.2 **Schematic map of the Quaternary surface deposits in Vīķu Mire catchment area**

(Geological indices gQ$_3$ *ltv*, fQ$_3$ *ltv*, lgQ$_3$ *ltv* describe Upper Pleistocene deposits, geological index bQ$_4$ describes Holocene deposits)

The Quaternary deposit composition in Vīķu Mire catchment area partially explains Me content in peat. Vīķu Mire is surrounded by sandy deposits of various coarsenesses (also by glaciolacrustine and glaciofluvial sand, gravel and pebble) and they explain an elevated MM content in acrotelm layer (Chapter 3.1.3). In the base of Vīķu Mire lies carbonate-rich sapropel, however, its impact on Me accumulation in peat profile cannot be observed (Chapter 3.2.1).

Quaternary deposits in Svētupes Mire catchment area

Quaternary surface in Svētupes Mire catchment area is mainly formed of glacigenic deposits (till). However, glaciolacrustine deposits (clayey silt and a small hill of glaciofluvial sand deposits) also have been identified in this catchment area and has an impact on Me content in peat (Fig. 3.3).

The dominance of till in the catchment area and clayey silt deposits to the west from the study site is determining the composition of inflowing groundwater and thus also the dynamics of Me content in peat. The bottom part of Svētupes Mire peat profile contains an elevated amount of MM (Chapter 3.1.3) and X-Ray diffraction results (Chapter 3.1.4) point on quartz mineral dominance in peat inorganic matter. Results suggest the explanation of this elevated MM amount with groundwater flow through glacigenic and glaciolacrustine deposits, as well as with the supply of glaciofluvial

Figure 3.3 **Schematic map of the Quaternary surface deposits in Svētupes Mire catchment area**

(Geological indices gQ_3 *ltv*, fQ_3 *ltv*, lgQ_3 *ltv* describe Upper Pleistocene deposits, geological indices aQ_4 and bQ_4 describe Holocene deposits)

deposits in Lake Dūņezers and their further transport to the study site via River Svētupe. In the base of peat profile lies carbonate-rich sapropel, however, the character of Me accumulation in peat does not suggest the existence of any geochemical barrier in here (Chapter 3.2.1).

Quaternary deposits in the catchment area of Salas Mire

Quaternary deposits in Salas Mire catchment area consist of alluvial (aQ_4), lacrustine (lQ_4), eolian (vQ_4), glaciolacrustine (lgQ_3 *ltv*) and glaciofluvial (fQ_3 *ltv*) sand. However, to the northeast of Salas Mire occur also till deposits (gQ_3 *ltv*) (Fig. 3.4). Salas Mire is located in Lake Lubāns catchment area and is one of the mires in this complex mire array in here.

The composition of Quaternary deposits in Salas Mire catchment area characterizes the content of Me in groundwater and further also in the peat profile. The dominance of sand and silt deposits determines the high mineralization degree of Salas Mire peat (Chapter 3.1.3), which in the upper peat layers exceeds 38% of total peat mass. In the base of peat profile lies lacurstine sand deposits (lQ_4), but results show on no observable effect on the accumulation of Me in peat above (Chapter 3.2.1).

Figure 3.4 **Schematic map of the Quaternary surface deposits in Salas Mire catchment area**
(Geological indices gQ$_3$ *ltv*, fQ$_3$ *ltv*, lgQ$_3$ *ltv* describe Upper Pleistocene deposits, geological indices aQ$_4$, vQ$_4$, bQ$_4$ and lQ$_4$ describe Holocene deposits)

3.1.2   Peat botanical composition and origin

All study sites are of similar origin, but of varied botanical composition, which points on different conditions of mire development. However, in general, studied mires were formed in similar conditions (lake overgrowing, except Salas Mire, which was formed due to mineral soil paludification) 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 variability in peat properties.

Elku Mire peat profile

Nowadays Elku Mire is under stage of transitional mire and is covered by 0.25 m thick transitional wood peat layer. Therefore Me content in fen peat is relatively non-affected by modern human activities or atmospheric pollution. Studied Elku Mire peat profile consists of 5 different peat layers with total depth of 2 m (Fig. 3.5) and absolute age 8000 years. The superficial peat layer (0.00-0.25 m) is composed of transitional wood peat, but the rest of 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. The decomposition degree is decreasing by the depth; moreover, this change seems to follow the replacement of peat layers (Fig. 3.5).

Figure 3.5   **The botanical composition and decomposition degree of Elku Mire peat**

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. As an additional indicator of formation due to a lake overgrow serve identified freshwater mollusc remains – *Radix labiata, Valvata macrostoma* and *Bithynia tentaculata* (determined by palaeontologist M. Rudzītis) in reed peat layer at the bottom of peat profile. Assumingly that this lake overgrow has begun with the overproduction of reeds and sedges. Elku Mire originated due to a lake overgrowing (presumably parts of Lake Zebrus and Svēte) on a sandy–calcareous sapropel by accumulation of reed peat. The bottom peat layer is mainly composed of reed remains, what were growing on periodically flooded flood plains. These conditions indicate that at the beginning of mire formation, this area was shallow and flooded by the nearby lake. The re-emergence of reed remains in peat profile (1.50-0.75 m) indicates another appearance of flooding.

Vīķu Mire peat profile

The superficial peat layer in Vīķu Mire similar to the one in Elku Mire is consists of wood peat, although – this mire is still in the stage of fen, thus peat is more affected by anthropogenic activity than fen peat in Elku Mire. Vīķu Mire peat profile (Fig. 3.6) consists of 7 peat types (wood, grass, wood-*sphagnum*, wood-grass, wood-sedge, sedge-*hypnum* and sedge peat) with layer depth of 2.5 m and absolute age 8000 years. Peat decomposition degree in the studied section varies from 27 to 41%. The different nature of peat botanical composition indicates variability of plant growing conditions that have influenced peat composition.

Vīķu Mire has developed on algal sapropel by accumulation of the sedge-*hypnum* peat. First fen peat layer has formed as the result of plants growing in an excessively wet and nutrient-abundant conditions promoted by groundwater and surface water. This mire started to develop when a shallow bay of nearest lake was filled with lake sediments (algal sapropel), when they were covered by medium decomposed sedge-*hypnum* peat. High grasses remain proportion in peat botanical composition usually reflects environmental conditions with rich nutrient regime, presumably, inducted by surface waters. Most likely that source of nutrients was water form near located lake (Lake Lielauce). Peat layer in the depth range from 2.20 to 2.00 m contains remains

Figure 3.6 **The botanical composition and decomposition degree of Vīķu Mire peat**

of *Scheuzeria* (10% of the botanical composition) and this is marking an important step in the development of Vīķu Mire. *Scheuzeria* is commonly associated with fen and marshy lake coasts and established remains reflect stable fen development 7000 years ago. Wood remains first appear in the depth of 1.80 m and can be traceable until 0.40 m. This indicates an important change in mire hydrological and hydrogeological conditions 6400-5700 years ago. The environment kept getting drier and plant feeding mainly depended on groundwater, while the impact of surface water became irrelevant. Grass peat layer in the depth range from 0.40 to 0.20 m (generally consisting of sedge remains) reflects an increase of nutrient supply by groundwater, but last 0.20 of the peat profile (wood fen peat layer), show on the decrease of nutrient supply.

Svētupes Mire peat profile

The upper peat layer in Svētupes Mire consists of well decomposed wood remains, although, it contains also a significant amount of grass remains. Svētupes Mire peat profile (Fig. 3.7) consists of 3 different peat layers (wood-grass, wood-sedge and sedge peat) with the total depth of 2.2 m and absolute age 9000 years.

Figure 3.7 **The botanical composition and decomposition degree of Svētupes Mire peat**

Svētupes Mire has developed on calcareous sapropel by accumulation of sedge peat due to lake depression fill in what took place approximately 3000 years and forms the thickest peat layer of Svētupes Mire peat profile (Fig. 3.7). As an additional indicator of Svētupes Mire formation due to a lake overgrowing serve freshwater mollusc remains, – *Radix labiata* and *Bithynia tentaculata* (determined by palaeontologist M. Rudzītis) in the bottom part of peat profile.

Salas Mire peat profile

Salas Mire peat profile contains only wood fen peat (Fig. 3.8) with the total depth of 0.5 m. The choice of this mire as the fourth study site is argued by the thick and continuous wood fen peat layer what is one of the most common fen peat types.

Figure 3.8 **The botanical composition and decomposition degree of Salas Mire peat**

Salas Mire originated due to mineral soil paludification near Lake Lubāns. Amongst study sites Salas Mire is the most recently formed. It has begun to form when Elku, Vīķu and Svētupes Mire were all already fully formed as fens.

Peat botanical composition

Existing mire plant species and the botanical composition of peat profiles characterize plant feeding conditions and nutrient availability through the history of mire development. Thus allow to describe the local environment through time. Fen peat in studied mires generally is built up of *Betulaceae*, *Cyperaceae*, *Equisetaceae*, *Pinaceae*, *Scheuchzeriaceae*, *Sphagnaceae* and *Poaceae* family plant species remains with the dominance of various sedge species (Table 3.1). However, peat botanical composition is site specific and only few plant species are common to all study sites. This peat forming plant diversity depends on local environmental conditions.

Table 3.1

Determined plant macro-remains in peat along study areas

Common name	Elku Mire	Salas Mire	Svētupes Mire	Vīķu Mire
	Depth of peat profile, cm			
	200	50	220	250
Alder	x	x	x	x
Birch	x	x	x	x
Buckbean				x
Bulrush			x	x
			x	
Cotton grass	x			
Horsetail	x			x
Moss				x
	x			x
	x			
			x	
				x
Pine	x	x	x	x
Pod grass				x
Spinulose woodfern	x			x
Common reed	x		x	x
Slender sedge	x	x	x	x
Fibrous tussock sedge	x			x
Tufted sedge				x
Bog sedge				x
Greater pond sedge				x
Lesser tussock sedge				x

The most complex structure has Vīķu Mire peat, which contains remains of 16 different plant species. The evaluation of peat forming plants and the amount of their remains in particular peat layers allowed the determination of various fen peat types along study sites (Table 3.2). It is believed that peat mire plant species have the effect on peat humification (Overbeck, 1947). One of assumptions is that vegetation cause

seasonal water table lowering and it is moving the boundary between acrotelm and catotelm, thereby changing peat chemical properties, humification intensity and Me accumulation.

Table 3.2

Determined peat types along study areas

Peat type	Elku Mire	Salas Mire	Svētupes Mire	Vīķu Mire
	Depth of peat profile, cm			
	200	150	220	250
Fen grass				x
Fen reed	x			
Fen sedge	x		x	x
Fen sedge-*hypnum*				x
Fen wood	x	x		x
Fen wood-grass			x	x
Fen wood-reed	x			
Fen wood-sedge			x	x
Fen wood-*sphagnum*				x
Transitional wood	x			

Under an important consideration is the fact that peat botanical composition can be widely varied even in geographically close located mires, with similar origin and absolute age. Such an example is Elku and Vīķu Mire. They both are relatively close located mires, but with obvious differences in peat botanical composition.

K-values

HI determined by means of the spectro-photometric method of Blackford and Chambers (1993), with Borgmark's (2005) modifications were considered as K-values (Table 3.3). HI in studied peat varies between 0.20 and 0.81; this index is smaller in wood fen peat, while humification degree in grass fen peat is more pronounced.

Table 3.3

Changes in peat decomposition degree and K-values according to depth range

Depth, cm	DD	KV	Depth, cm	DD	KV	Depth, cm	DD	KV	Depth, cm	DD	KV
0-10	53	0.70	80-90	35	0.76	160-170	34	0.26	240-250	29	0.71
10-20	53	0.60	90-100	35	0.69	170-180	32	0.53			
20-30	32	0.21	100-110	40	0.61	180-190	32	0.62			
30-40	28	0.20	110-120	40	0.51	190-200	29	0.73			
40-50	28	0.37	120-130	39	0.35	200-210	29	0.71			
50-60	28	0.62	130-140	35	0.31	210-220	28	0.74			
60-70	41	0.81	140-150	35	0.29	220-230	28	0.76			
70-80	34	0.80	150-160	34	0.27	230-240	28	0.72			

Peat decomposition degree and K-values are marked with DD and KV.

The variability of peat botanical composition contributes a "species signal" to the records and is potentially confusing the relationship between mire water table and the apparent peat humification degree (Hughes et al., 2012). Although, HI is simplistic measurement, it is reliable and informative indicator to characterize living OM transformation processes (Hughes et al., 2012). Results show (Table 3.3) that there is no significant relation amongst depth range, decomposition degree and K-values. Although, peat decomposition degree seems to decrease by depth, however, K-value does not follow this order and value of this parameter can increase or decrease to extreme levels within few centimetres.

Fen peat specific surface area

Specific surface area is an important characteristic that shows on material total surface area per unit of mass or volume (Paykov and Hawley, 2013). It is a derived value and can be used in the determination of material type and properties. Specific surface area is significant for adsorption of various chemical reactions and Me accumulation in peat. Specific surface area of studied peat varies between 1.53 m^2/g and 4.34 m^2/g and seems to be dependent directly on botanical composition of particular peat layers (Table 3.4).

Table 3.4

Specific surface area of studied fen peat in comparison to bog peat

Peat type		m^2/g	Depth, cm	Peat type	m^2/g
Studied fen peat	Wood-*sphagnum* fen	2.76	45-50	Latvian bog peat	43.80
	Wood-grass fen	1.53	125-130		6.99
	Wood-grass fen	3.98	140-145		19.15
	Sedge fen	4.35	215-220		

Specific surface area characterizes the ability of fen peat to transport or retain nutrients (Me) and water via peat profile. Fen peat retains several times higher amount of nutrients and water than bog peat (Hajnos et al., 2000).

Peat organic matter degradation characteristics

Transformation of OM into peat depends on geological, physico-chemical and biological character of the area. Considering that mire formation takes place due to lake overgrowing and mineral soil paludification, and peat profile consists of an aerobic and anaerobic peat layer, it is possible to make a detailed schematic model of naturally occurring processes in mire environment (Table 3.5). Plant biomass has the main role in peat accumulation after either lake overgrows or mineral soil is bogging up. Further peat decomposition in acrotelm layer is inducted by aerobic bacteria and fungi what as the by-product of decomposition release water and carbon dioxide. Peat decomposition in catotelm layer practically does not take any place or it is very slow. However, anaerobic bacteria are interacting with peat and release water, carbon dioxide and

methane. It is also worth mentioning that catotelm layer is subjected to leaching and erosion what changes peat physico-chemical characteristics.

Table 3.5

Physico-chemical and biological processes in mires

Environment	Microbial activity	Process	Uptake	Release
Lake	Living organisms	Overgrowing	Precipitation Groundwater	Oxygen Carbon dioxide
	Aerobic bacteria	Sapropel formation and accumulation		
Mineral soil	Living organisms	Paludification	Precipitation Groundwater	Oxygen Carbon dioxide
	Aerobic bacteria			
Plant biomass	Living organisms	Mortification (disintegration of living plants)	Oxygen Carbon dioxide	Oxygen
	Aerobic bacteria		Precipitation Surface runoff Groundwater	Carbon dioxide
Aerobic peat	Aerobic bacteria	Decomposition	Surface water Groundwater Carbon dioxide	Water
		Accumulation	Oxygen Precipitation	Carbon dioxide
Anaerobic peat	Anaerobic bacteria	Decomposition	Groundwater	Water Carbon dioxide Methane
		Accumulation		
		Leaching		
		Erosion		

Mires generally are subjected to atmospheric, surface and groundwater uptake. Every type of water has different chemical characteristics, Me content and impact on mire development. Not least important are chemical reactions in mires what are causing release of various chemical compounds in the atmosphere. Thus mires should be observed as interactive habitats, where an impact of environment on mire and an impact of mire on environment take place.

OM degradation in peat can be well observed in SEM images (Fig. 3.9). Scanning electron microscopy allows describing the structural degradation of peat forming plant remains in microscopic level. In general, SEM images allow observing the relative ratio between still recognizable plant structural elements and the amorphous, decomposed peat mass.

(a) (b)

(c) (d)

(e) (f)

Figure 3.9 **Scanning electron microscopy images describing the degradation of organic matter in (a, b) wood fen peat; (c, d) wood-grass fen peat and (e, f) wood-*sphagnum* fen peat**

In addition, the characterization of OM degradation using SEM images is valuable to the characterization of peat fibrosity and humification. In fibric peat a variety of leaf, stem and branch remains can be easily recognized. In mesic peat the major part of peat mass is forming an amorphous substance, although some plant remains can still be recognized. In humic peat plant remains cannot be recognized and the whole peat mass consists of an amorphous material.

3.1.3 Peat elemental composition

Five base elements in fen peat elemental composition are C, H, N, O and S (Appendix 1). S level in studied peat was below the apparatus detection level, thus it was not further investigated. The most part of peat elemental composition is built up of C what is the base constructing element in 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 (Chapter 3.1.3).

C is primarily added to mire surface layers through net primary production. In deep peat layers (catotelm) C amount is reducing due to methanogenesis and sulphate reduction (Kuhry and Witt, 1996). The concentration of C in studied peat (Table 3.6) is in range from 27.6 to 48.9%, but the exact value depends on peat botanical composition, thus this element has no particular accumulation pattern. C content in Elku Mire peat is in range from 41.2 to 48.9% and it seems to gradually increase by the depth, although, C content is practically stable within the peat profile. In Svētupes Mire peat profile C content varies from 27.6 to 41.5%. Although, there are wide differences between C extreme values, however, C concentration is rather stable. In Vīķu Mire peat profile C content is from 28.7 to 42.2%, with slightly lower concentration in the bottom part of peat profile.

Table 3.6

Carbon content in studied peat (%)

Elku Mire			Svētupes Mire			Vīķu Mire		
min	max	mean	min	max	mean	min	max	mean
41.2	48.9	44.8	27.6	41.5	36.5	28.7	42.2	36.3

H concentration in studied fen peat is in the range from 1.0 to 5.2%, but the exact value seems to depend on peat botanical decomposition and the depth range (*Table 3.7*). In Elku Mire peat H content is in the range from 3.9 to 5.2% and has the tendency to increase by depth. H content in Svētupes peat profile is in range from 1.0 to 4.7% and acrotelm seems to have higher H content than catotelm layer. In Vīķu Mire peat profile H concentration is between 3.0 and 4.8%, with higher amount in acrotelm layer.

Table 3.7

Hydrogen content in studied peat (%)

Elku Mire			Svētupes Mire			Vīķu Mire		
min	max	mean	min	max	mean	min	max	mean
3.9	5.2	4.7	1.0	4.7	3.6	3.0	4.8	4.1

Primary N input source is precipitation, dry fall and N fixation, while secondary sources include mineralization and translocation. A significant amount of N in fen acrotelm layer is lost through denitrification, grazing, surface runoff and erosion, while

in bogs the greatest amount of N is lost when it becomes immobilized in the catotelm (Kuhry and Vitt, 1996). N content in fen peat is in range from 0.5 to 2.9%. Although, N prevalence is variable, it seems that acrotelm layer has a higher N content than catotelm layer (Table 3.8). In Elku Mire peat N content varies from 0.8 to 2.5% and seems to increase by depth. N concentration in Svētupes Mire peat is in the range from 0.5 to 2.7%, with the highest content in acrotelm layer. N content in Vīķu Mire peat is from 1.5 to 2.9%, with highest amount in the upper peat profile part.

Table 3.8

Nitrogen content in studied peat (%)

Elku Mire			Svētupes Mire			Vīķu Mire		
min	max	mean	min	max	mean	min	max	mean
0.8	2.5	1.8	0.5	2.7	1.9	1.5	2.9	2.1

O content in studied fen peat is in the range from 43.6 to 67.9%. O concentration significantly depends on the depth range (Table 3.9). O content in Elku Mire peat varies from 43.6 to 53.5% and the highest concentration can be detected in acrotelm layer near the mire surface. In Svētupes peat profile O content is in the range from 51.1 to 67.9% and here the highest concentration is in the catotelm. O content in Vīķu peat is in the range from 52.2 to 66.5%, with slightly elevated amount in the middle part of peat profile.

Table 3.9

Oxygen content in studied peat (%)

Elku Mire			Svētupes Mire			Vīķu Mire		
min	max	mean	min	max	mean	min	max	mean
43.6	49.3	48.2	51.1	67.9	57.9	50.1	66.5	57.0

C and N content in peat are directly related to one another. Preferential loss of C in catotelm results in N enrichment and N/C molar ratio decrease (Kuhry and Vitt, 1996). N/C molar ratio in Elku Mire peat is in the range from 0.01 to 0.05 and low molar ratio is directly related to the increase of N content, while high ratios are followed by the increase of C content. However, this phenomenon does not depend on the depth range. N/C molar ratio in Svētupes Mire peat is between 0.01 and 0.07. Due to low N content in Svētupes Mire catotelm layer N/C molar ratio in this part of peat profile slightly higher than it is in acrotelm layer. N/C molar ratio in Vīķu Mire peat profile is in the range from 0.04 to 0.06.

In the characterization of OM transformation into peat it is necessary to evaluate H/C and O/C molar ratios. H/C molar ratio in Elku peat profile is between 1.14 and 1.38, with an increase in catotelm layer. H/C molar ratio in Svētupes Mire peat is in range from 0.36 to 1.51; noticeably that 0.36 is an extreme value and can be observed

only in a thin layer in the bottom part of peat profile. It can be explained with low C content in bottom part of the peat profile, but, – overall, H/C molar ratio in Svētupes peat profile is between 1.24 and 1.51 and is rather stable. H/C molar ratio in Vīķu Mire peat is no different from those in other studied peat profiles and is in range from 1.24 to 1.59. O/C molar ratio in Elku peat profile is in range from 0.67 to 0.97 and it can be considered as the lowest amongst study sites, moreover, acrotelm layer seems to have higher O/C molar ratio than catotelm layer. O/C molar ratio in Svētupes Mire peat is the highest amongst study sites and is in the range from 0.92 to 1.85, high ratio is characteristic to catotelm layer. O/C ratio in Vīķu Mire peat is in the range from 0.89 to 1.72, with highest value in catotelm layer. Placing the molar ratio data on Van Krevelen (1984) graph (Fig. 3.10), it can be seen that fen peat sits down next to bog peat and exactly under mire vegetation data. This graph shows that fen peat is an intermediate between mire vegetation and bog peat.

Figure 3.10 **Representative Van Krevelen graph showing O/C and H/C molar ratio in organic deposits**

(Data on bogs taken from Silamiķele, 2010; data on coal: International Humic Substances Society reference samples)

According to the results it was concluded that H/C molar ratio of fen peat is in the range from 0.36 to 1.59 and it depends on peat botanical composition, thus it has no traceable pattern amongst study sites. In comparison to bog peat (Silamiķele, 2010), fen peat has lower overall H/C molar ratio. Low H/C molar ratio of fen peat (Fig. 3.10) suggests H secession, although, H content in fen peat is no different from H amount in bog peat. O/C molar ratio of fen peat is in the range from 0.67 to 1.85 and depends on oxygen availability; moreover, the range is similar to O/C molar ratio of bog peat (Silamiķele, 2010). Low O/C molar ratio points on O secession (Fig. 3.10). N/C molar

ratio of studied fen peat is from 0.01 to 0.07, with highest value in anaerobic peat layers and in comparison to bog peat (Silamiķele, 2010) this characteristic has higher value in fen peat. Low N/C molar ratio is related to N secession and this process is more characteristic to bog peat, while fen peat naturally contains high N amount. O and H secession gradually transforms peat into coal, however – bog peat hypothetically is closer to coal deposits than fen peat.

Oxidation index (ω) and hydrogen deficient (φ) are highly variable parameters amongst study sites and also depend on peat layer depth. Oxidation index of Elku Mire peat varies between 71.6 and 97.9 (81.2 in average), with tendency to decrease by the depth. Oxidation index of Vīķu Mire peat is in the range from 78.1 to 110.8 (84.0 in average). Oxidation index of Svētupes Mire peat is in the range from 81.2 to 364.4 (86.5 in average). The abnormal oxidation index values (exceeding 100.0) can be found in Vīķu Mire peat layer at the depth range 150-190 cm, where peat contains more than 25% of MM (Chapter 3.1.3). Hydrogen deficient of Elku Mire peat is in the range from 40.2 to 47.3 (43.4 in average) and it tends to be stable throughout whole peat profile with the exception of peat layer at 110 cm, where H deficient is increased (47.3). H deficient in Vīķu Mire peat is between 29.1 and 40.8 (35.2 in average). In Svētupes Mire peat H deficient is in the range from 27.2 to 40.2 (35.8 in average).

Similarities and differences in the elemental composition of fen and bog peat

Overall, bog and fen peat contain similar amount of C, O and H, while N content is slightly increased in fen peat (Fig. 3.11). High N content can be explained with fen peat specialities – peat forming reeds naturally contain relatively high N amount (Lucas, 1982).

Figure 3.11 **Comparison of elemental composition in mires**
(Data on bogs taken from Silamiķele, 2010)

Results point out that even though bog and fen peat contain similar amount of O, H and C, the transformation of OM in peat of different origins takes different place. Peat elemental composition forms various functional compounds what are engaged in Me binding, although results show that functional groups common to fen peat do not form statistically significant relations with Me (Chapter 3.3). Hypothetically, in fen peat, alkali and alkaline earth metals are engaged in Me binding.

3.1.3   Quantitative composition of fen peat

Peat deposits consist of OM, MM and water. The quantity of these components can be successfully evaluated using LOI method (Chapter 2.3.4). Formation and accumulation of peat take place due to transformation and decomposition of mire vegetation remains. Thus OM content in peat is highly dependent on peat forming plants, because every plant species and distinct plant structural elements have different decomposition characteristics. While some plant remains are included into peat composition, other might not get included in peat botanical composition.

In studied fen peat OM content is broad (Table 3.10). Fen peat contains around 90% of OM and peat is built up mainly of euthrophic plant remains, any OM content deviation is related to an increased MM supply via groundwater.

Table 3.10

The organic matter content in studied peat (%)

Mire	Organic matter content
Elku Mire	81.3–96.8
Salas Mire	61.6–91.8
Svētupes Mire	45.7–91.3
Vīķu Mire	58.6–97.0

An average OM content in Elku Mire peat is above 90% with slight decrease in middle peat layer (Fig. 3.12). At the same time CM content is around 4.4% (from 0.3 to 6.5%). An elevated CM content can be explained by groundwater flow from mire catchment area. The lowest OM content in Svētupes Mire peat (45.7%) can be observed in the bottom part of profile, where peat is mixed up with sandy sapropel (Fig. 3.13). Moreover, Svētupes Mire peat has the highest average CM content amongst study sites (4.9%) and the widest distribution range (1.2-30.4%). This can be explained by an intensive groundwater flow; however, simple botanical composition (Fig. 3.13) points on water level decrease afterwards. Significantly decreased OM content (58.6%) in Vīķu Mire peat can be recognized in the upper part of profile (Fig. 3.14), but in the rest of cross-section peat contains more than 90% of OM. This can be explained by an increased amount of CM in the upper part of peat profile (6.4%). An average OM content in Salas Mire peat is 79.3% (Fig. 3.15), while CM makes 1.8% and peat can be considered as sandy.

Figure 3.12 **Distribution of Loss on Ignition parameters within Elku Mire peat profile**

Figure 3.13 **Distribution of Loss on Ignition parameters within Svētupes Mire peat profile**

Figure 3.14 **Distribution of Loss on Ignition parameters within Vīķu Mire peat profile**

Figure 3.15 **Distribution of Loss on Ignition parameters within Salas Mire peat profile**

AC was determined according to Heiri et al. (2001) and results show on its variability amongst study sites and within peat profile (Table 3.11), these differences can be explained by different groundwater flow impact and heterogeneity of mire catchment areas.

The ash content in studied peat (%)

Mire	Ash, 4 h in 550 °C (carbonates)	Ash, 2 h in 950 °C (mineral matter)
Elku Mire	3.2–18.7	2.2–15.2
Salas Mire	8.2–38.4	7.5–36.7
Svētupes Mire	8.7–54.3	5.3–34.3
Vīķu Mire	3.0–41.4	2.1–39.0

Due to the fact that AC in fen peat depends on groundwater flow, fen peat naturally contains higher MM content than bog peat and in some cases it can reach more than 50% of total peat mass.

3.1.4 Functional groups containing compounds and inorganic matter in fen peat

Characterization of organic compounds, functional groups and peat inorganic material can be performed using various spectroscopic methods (Chapter 2.3) and in the following chapter a detailed description of fen peat chemical characteristics, using these methods, has been given.

Fourier-transform infrared spectroscopy results

Basic peat forming elements are C, H, N, S and O. These elements mutually form chemical bounds and construct various functional groups and compounds. In general, the ability of peat to accumulate Me depends on metal ion binding capabilities with functional groups. In particular, these are carboxylic groups and hydroxyl groups. However, study results point out that fen peat functional composition has no statistically significant relation to Me content (Chapter 3.3) and that Me accumulation does not depend on metal ion binding with acidic functional groups. Main fen peat and fen peat HA forming functional group constituent elements are C, H and O.

Although, fen peat IR spectra can be divided into several regions (Fig. 3.16) and represents the presence of particular functional groups, results demonstrate no significant differences amongst various fen peat types. Absorption at 3376 cm^{-1} (O-H) indicates the presence of H bounded OH group – high concentration of alcohols and phenols. O-H bands are board and least variable amongst different peat types, thus pointing on no significant dependence on peat characteristics. However, flat O-H stretching might be affected by water in adsorbed form. Absorption at frequencies 2924 and 2852 cm^{-1} (C-H) shows on aliphatic hydrocarbons.

Figure 3.16 **Fourier-transform infrared spectra of studied fen peat**

Absorption band at 2924 cm^{-1} demonstrates asymmetrical stretching, while band at 2854 cm^{-1} shows on symmetrical stretching of C-H. Frequencies might point on the presence of methylene group of aliphatic hydrocarbons in fen peat. Absorption at 1630 cm^{-1} (C=O) describes the presence of cyclic and acyclic compounds and ketones in peat. Absorption at 1385 cm^{-1} (C=O) points on the presence of carboxylic acid salts. Absorption at 1265 cm^{-1} (C-O) represents esters, ethers and phenols. Absorption at 1034 cm^{-1} (C-O) demonstrates polysaccharide valence fluctuations.

IR spectra of fen peat HA can be divided into several regions (Fig. 3.17). HA IR spectrum shows more detailed picture that fen peat IR spectrum. Spectra point out the presence of alkynes (C=C) in peat HA (absorption at 2157 and 2030 cm^{-1}). It can be explained by FA suppressing signal removal.

Data statistical analysis indicates no significant associations amongst functional groups or their relation to Me accumulation character in peat (Chapter 3.3) and it can be considered that functional groups in fen peat are virtually independent.

In the correlation analysis all functional groups were attributed to alcohols and phenols (O-H), because this functional group does not rapidly changes by depth or peat layer age. Thus using O-H as virtually stable value, it is possible to trace changes in other functional groups. Results indicated that the amount of aliphatic hydrocarbons in peat is directly related to decomposition degree and depth of the peat layer – respectively, upper peat layers contain more hydrocarbons than bottom part of the peat profile. Also carboxylic acids can be associated with peat depth and decomposition degree. High polysaccharide content is related to freshly formed, well decomposed fen peat layers and, accordingly, their amount decreases by the depth.

Figure 3.17 **Fourier-transform infrared spectra of fen peat humic acids**

In comparison to bog peat (Silamiķele, 2010) results demonstrate simplified IR spectrum of fen peat. This can be explained by high fen peat decomposition degree what causes the functional group degradation.

Three-dimensional fluorescence spectroscopy results

Fen peat HS Em spectrum shows on well-marked peak at 475 nm (Fig. 3.18) and it points on the presence of carbonyl and carboxyl groups what are substituting aromatic core structures.

Figure 3.18 **Emission spectrum of fen peat humic substances** (excitation at 340 nm)

Fen peat HS EEM spectra (Appendix 2) demonstrate high FA luminescence intensity (350 nm Ex and 460 nm Em); while HA luminescence intensity (470 nm Ex and 540 nm Em) is rather low. Luminescence intensity depends on how condensed organic

structures are. HA are high condensed structures and thus have weak luminescence signal. At the same time FA are chromophore groups with high phenolic group content and have strong luminescence signal.

Obtained EEM data were further analysed using PARAFAC analysis according to mathematical algorithm (Appendix 3). Results show on the benefits of PARAFAC analysis – to gather detailed data on peat composition, it is possible to use low concentration organic solutions (Fig. 3.19).

Figure 3.19 **The original excitation-emission matrix record (a) and the record after processing with parallel factor analysis (b)**

EEM results show on OM degradation through the vertical peat profile, and what is important, FA degradation (decay and dissolution) is more pronounced than HA degradation (Appendix 2). According to obtained data author has created 2-7 factor/component models (Appendix 4). To test the suitability each model was evaluated and run twice through standard outlier identification, non-negativity constrains outlier identification and sum of squared residuals. Gathered results allowed the assumption that only 3 and 4 component models can be fitted to studied fen peat HS. 3 and 4 component models were run through split half analysis and data validation and results confirmed that fen peat HS consist of 4 main components (Fig. 3.20).

4-component model was run 10 times through random initialization and as the result – 10 different sums of squared errors models were created. Obtained fluorescence fingerprints demonstrated that first component is phenolic group containing compounds; second component is carboxylic group containing compounds; third component is protein; and fourth component is made of polycyclic aromatic compounds.

EEM spectra decomposition showed that 1-3 components have approximately the same luminescence intensity, while fourth component (aromatic compounds) has the least luminescence intensity. The cross-correlation between these components (Fig. 3.21) has shown that there is relation between phenolic group containing compounds and proteins; phenolic group containing compounds and aromatic compounds and between proteins and aromatic compounds.

Figure 3.20 **Decomposition of fen peat humic substances excitation-emission matrix record**
(Comp. 1 – compounds containing phenolic groups; Comp. 2 – compounds containing carboxylic groups; Comp. 3 – proteins; Comp. 4 – aromatic compounds)

Figure 3.21 **Correlations amongst fen peat humic substances components**
(Comp. 1: phenolic groups; Comp. 2: carboxylic groups; Comp. 3: proteins; Comp. 4: polycyclic aromatic compounds)

Data from EEM spectra were used to calculate FI (Table 3.12). This index demonstrates degree of allochthonous (FI < 1) or autochthonous (FI > 1) influence in OM processing (McKnight et al., 2001). FI, generally, shows on the impact of allochthonous factors (FI > 1) on fen peat formation in upper layers.

Fluorescence index of fen peat humic substances

Peat type	Fluorescence index
Wood	0.92-1.20
Grass	1.07-1.08
Wood-*sphagnum*	1.04-1.06
Wood-grass	0.76-1.12
Wood-sedge	0.80-0.81
Sedge-hypnum	0.75-1.04
Sedge	1.00-1.20

However, an increased *FI* can also be identified in the middle and bottom parts of the peat profile, this fact can be explained by groundwater impact on peat profile.

Differential thermal analysis and thermogravimetry results

DTA and TG results show that more decomposed fen peat requires a high temperature and long combustion time for functional compounds to collapse (Appendix 5). DTA/TG results are visualised as thermogramms containing DTG, DTA and TG spectrum data (Fig. 3.22). DTG spectrum shows on the speed of sample weight loss in percentage per minute. DTA spectrum demonstrates heat input in Celsius. TG spectrum shows on amount of sample weight loss in percentage. The character of DTA and

Figure 3.22 **Derivative thermogravimetry (DTG), differential thermal analysis (DTA) and thermogravimetry (TG) spectrum of fen peat**

TG results indicates frequent changes in fen peat due to heat input and an important factor causing these changes is peat botanical composition. Fen peat consists of simple, but variable plant remains, they contain high amount of lignin, various its derivatives and cellulose. The temperature range (DTA spectrum), what is causing significant sample degradation, differs amongst fen peat types and it depends not only on peat botanical composition, but also on the decomposition degree. DTA and DTG spectrum usually are similar; however, there is a major difference at temperature range from 90 to 120 °C (Fig. 3.22) where DTG spectrum has peak intensity, while DTA spectrum has a slope.

This can be explained by endothermic processes in fen peat samples – peat is losing hydroscopic moisture. All input heat due to gas release is absorbed and it appears as an extensive slope on spectrum (Francioso et al., 2003; Almendros et al., 1982). Sample destruction due to exothermal reaction begins at 120 °C, although, this process still interchanges with less expressed endothermic reactions. All of the input heat in exothermal reaction is released and it appears as an expressive peak on spectrum. The highest sample weight is lost during exothermic reactions, while mass loss due to endothermic reactions is negligible. It is inherent that most of its weight fen peat losses at 300 °C, while in the temperature range from 250 to 400 °C peat losses 60% of the weight (Fig. 3.22 and Appendix 5) and it mean that chemical compounds what collapse at this temperature range are dominating in fen peat (Rustschev and Atanasov, 1983; Almendros et al., 1982). Sheppard and Forgeron (1987) have stated that the range from 300 to 350 °C is characteristic for polysaccharide destruction and

Table 3.13

Thermogravimetric index of fen peat

Fen peat type	Decomposition degree (%)	Plant remains (%)				Thermogravimetric index
		Wood	Sedges	Reeds	Others	
Wood-grass	41	25	25	10	40	1.37
Wood-sedge	41	20	35	15	30	1.23
Sedge	31	-	70	15	15	1.04
	31	-	60	15	25	1.11
	32	-	55	30	15	1.56
	32	-	65	10	25	0.63
	32	-	65	10	25	0.96
Wood	40	40	25	-	35	1.20
	53	90	-	-	10	0.32
	53	90	-	-	10	1.15
Sedge-*hypnum*	29	-	35	-	65	1.03
	29	-	35	-	65	0.94
Wood-*sphagnum*	28	20	15	5	50	1.18
Wood-grass	39	25	25	5	45	0.93
	35	20	35	-	45	0.86
Grass	32	10	25	15	50	1.09

degradation of humic functional groups, cellulose and aliphatic chains, acidic group decarboxylation and aliphatic structure dehydration. The temperature range from 400 to 450 °C, where the peak intensity of DTG and DTA spectra appear (Fig. 3.22 and Appendix 5), characterizes aromatic lignin component pyrolysis, lignin aromatic skeleton degradation and aromatic structure collapse (Sheppard and Forgeron, 1987). Fen peat TGI points on the resistance against heat exposure (Table 3.13).

TGI enables the comparative evaluation of peat thermal stability – high TGI is associated with high proportion of thermally unstable organic structures.

Total reflection X-ray fluorescence spectroscopy results

TXRF is being used evaluate the nature of mineral phases and to detect particular minerals. MM content amongst studied sites is variable (Chapter 3.1.3), however, inorganic matter composition is similar in MM of all studied peat profiles. Peat inorganic matter essentially consists of dolomite, calcite and quartz minerals (Fig. 3.23).

Figure 3.23 **X-ray diffraction spectra of studied fen peat**

Dolomite, calcite and quartz minerals are in the composition of Quaternary deposits – sand, silt, till etc., but their origin might be also sedimentary rocks.

^{13}C NMR spectroscopy results

^{13}C NMR spectra demonstrate the variability of C atoms. There are no major differences between fen peat (Fig. 3.24) and fen peat HA ^{13}C NMR spectrum (Fig. 3.26); however, results point on differences between fen peat types. Wood fen peat ^{13}C NMR spectrum (Fig. 3.24) is cardinally different from sedge fen peat spectrum (Fig. 3.25). In general, ^{13}C NMR spectrum represents 8 regions associated to carbon atoms in major structural units. 0-50 ppm region shows on aliphatic carbon (CHn) resonance (methylene and methine carbon). 50-60 ppm region represents methoxylcarbon (-OCH$_3$) resonance signal. 60-90 ppm region shows on carbon atom resonance line bound by a simple bond to a heteroatom. 90-110 ppm region represents primarily carbon atom bound by simple bonds to two heteroatoms (O or N), mainly acetal C in cyclic polysaccharide (OC-O, N) resonance. 110-140 ppm region is related to unsubstituted

and alkysubstituted aromatic carbon (CAr) resonance. 140-160 ppm region shows on aromatic carbon resonance substituted by O and N (e.g., phenols, aromatic ethers or amines).

Figure 3.24 **¹³C nuclear magnetic resonance spectrum of wood fen peat**

160-190 ppm region is associated with the resonance of carbon in carboxyl, ester and amide groups. 190-220 ppm region contains the resonance of carbons in quinone and ketone groups (C=O) substituted by O and N (e.g., phenols, aromatic ethers or amines) (Spaccini et al., 2006; Amir et al., 2010).

Figure 3.25 **¹³C nuclear magnetic resonance spectrum of sedge fen peat**

Dominant structures are characterized by the resonance at all eight characteristic regions showing that fen peat and fen peat HA contain all common functionalities with carbon.

Figure 3.26 **¹³C nuclear magnetic resonance spectrum of wood fen peat humic acids**

In fen peat HA (160-190 ppm) carboxyl, ester and amide groups, and polysaccharides (90-110 ppm) give stronger signal, while peat gives stronger hydrocarbon signal (60-90 ppm).

3.1.5   Interaction between fen peat physico-chemical characteristics

Data analysis indicated that each study site has an individual set of statistically significant correlations ($p < 0.05$) between fen peat physico-chemical characteristics (Figure 3.27-3.32 and Appendix 6) and it points on the heterogeneous nature of fen peat due to differences in geomorphological, geological, hydrological and hydrogeological conditions in mire catchment areas. Results show on an individual peat physico-chemical characteristic interaction pattern for each study site, thus it can be concluded that all relations among peat properties are highly site dependent.

However, despite distinct interactions between peat characteristics, the quantity of OM and MM, elemental composition, botanical composition, decomposition degree, depth, age and groundwater impact are all of great importance on the variability of fen peat characteristics.

Figure 3.27 **Statistically significant positive correlations (p < 0.05) between Elku Mire fen peat physico-chemical characteristics (n = 40)**

Figure 3.28 **Statistically significant negative correlations (p < 0.05) between Elku Mire fen peat physico-chemical characteristics (n = 40)**

Figure 3.29 **Statistically significant positive correlations (p < 0.05) between Svētupes Mire fen peat physico-chemical characteristics (n = 44)**

Figure 3.30 **Statistically significant negative correlations (p < 0.05) between Svētupes Mire fen peat physico-chemical characteristics (n = 44)**

Figure 3.31 **Statistically significant positive correlations (p < 0.05) between Vīķu Mire fen peat characteristics (n = 50)**

Figure 3.32 **Statistically significant negative correlations (p < 0.05) between Vīķu Mire fen peat characteristics (n = 50)**

3.2 Metallic elements in studied fen peat

This study demonstrates the dependence of Me content on peat layer depth, type and characteristic properties. Concentration and distribution of 13 most common Me (Fe, Mn, Zn, Na, K, Pb, Mg, Ca, Cu, Cd, Cr, Co and Ni) have been determined and normalised against Ti concentration in fen peat. Selection of these particular Me was considered due to their importance in plant forming processes that eventually leads to peat development and accumulation and to their content in groundwater and precipitation. Most of these Me can be both of lithogenic and anthropogenic origin (Chapter 1.3), thus it is possible to describe the effect of human inducted and natural processes on fen peat formation.

3.2.1   Metallic element content

In order to obtain the most complete picture of Me accumulation character, it is necessary to analyse full peat profile and not particularly selected parts, because the location of specific peat layer can significantly affect data interpretation. Thus in this PhD thesis, to evaluate the influence of peat characteristics on Me accumulation and concentration in fens, full peat profiles from each study sites have been analysed (Chapter 3.1.2). Me concentration was determined in every 0.05 m, what is corresponding to approximately 60 year period. Me 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). Full set of Me concentrations in studied peat with 0.05 m intervals can be found in Appendix 7.

Alkaline earth metals

Ca and Mg are biophile elements and are closely related to mire vegetation growing conditions. Both Me are main plant nutrients and are amongst most important Me what are involved in fen development (Chapter 1.3). 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 area – it can be sapropel, sand, silt, till etc. Quaternary deposits with high carbonate mineral content. Agricultural land use may cause anthropogenic alkaline earth metal supply form mire catchment area – for instance, soil liming can lead to high Ca concentration in upper peat layers.

The highest Ca concentration in Elku Mire is located in wood-reed fen peat layer, in the middle part of peat profile (Fig. 3.33), 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 Ca accumulation pattern (Fig. 3.33) 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 Me is decreasing by the depth, although there is also relation to peat botanical composition and decomposition degree.

Figure 3.33 **The accumulation pattern of alkaline earth metals in Elku Mire peat profile**

The highest Ca concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.34), where peak concentration exceeds 22 g/kg. It can be explained by both groundwater and surface water supply. The lowest Ca content is in the bottom part of peat profile, where peat contains 7.6 g/kg Ca. Overall, Salas Mire peat contains the least amount of Ca among study sites and it can be explained by completely different character of Quaternary deposits in mire catchment area (Chapter 3.1.1), in here Quaternary surface generally consists of sandy Holocene deposits, while in other catchment areas dominant are Upper Pleistocene deposits. The distribution of Mg (Fig. 3.34) is similar to Ca accumulation pattern, which means that both alkaline earth metals have common supply source. However, Mg concentration in Salas Mire peat is significantly lower (1.7 g/kg) than Ca content.

The highest Ca concentration in Svētupes Mire is located in sedge fen peat in the middle part of peat profile (Fig. 3.35), where peak concentration exceeds 171 g/kg. It can be explained by an intensive groundwater supply from mire catchment area, which mainly consists of glacigenic till deposits (Chapter 3.1.1). The lowest Ca content is in the upper part of peat profile, where peat contains 4.6 g/kg Ca and this can be explained by groundwater impact reduction. The distribution of Mg in Svētupes

Figure 3.34 **The accumulation pattern of alkaline earth metals in Salas Mire peat profile**

Figure 3.35 **The accumulation pattern of alkaline earth metals in Svētupes Mire peat profile**

Mire peat (Fig. 3.35) is different from Ca accumulation pattern; this can be explained by different sources of supply. It can be assumed that Ca has been supplied by groundwater with high calcite mineral content – this fact would explain an elevated amount of Ca in peat, but would not affect Mg concentration. Peak Mg concentration is located in wood-sedge fen peat in the upper part of peat profile, where peat contains 3.1 g/kg Mg. The lowest Mg content is in the bottom part of peat profile, where peat contains 0.5 g/kg Mg. The highest Ca concentration in Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.36), where peak concentration exceeds 33.9 g/kg. It can be explained by both groundwater supply and anthropogenic impact (soil liming) in mire catchment area (Chapter 3.1.1). The lowest Ca content is in wood-grass fen peat in the middle part of peat profile, where peat contains 7.1 g/kg Ca. The distribution of Mg (Fig. 3.36) is similar to Ca accumulation pattern, which means that both alkaline earth metals have common supply source (Chapter 3.1.1). However, Mg concentration in Vīķu Mire peat is significantly lower than Ca content. The highest Mg concentration is in wood-grass peat in the middle part of peat profile (Fig. 3.36), where peat contains 1.8 g/kg Mg, but the lowest Mg concentration was identified in wood-*sphagnum* peat (0.7 g/kg) in the upper part of peat profile.

Figure 3.36 **The accumulation pattern of alkaline earth metals in Vīķu Mire peat profile**

Summarizing the results, it can be concluded that alkaline earth metal accumulation mechanism is fens follows the untied rule – the amount of both Me is decreasing by depth. However, the character of mire catchment area, hydrological and hydrogeological conditions are of high importance. Moreover, Me content depend on mire vegetation, because different plants contain and can uptake different amounts of alkaline earth metals.

Alkali metals

K is biophile element and is closely related to the growing conditions of mire vegetation, while Na content can also be associated with atmospheric deposition (Chapter 1.3). Alkali metals in fen peat are supplied by groundwater from deposits in mire catchment area (Chapter 3.1.1), 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 peat profile (Fig. 3.37), where peat contains 269 mg/kg K. The location

Figure 3.37 **The accumulation pattern of alkali metals in Elku Mire peat profile**

of mire and K content in upper peat layer allows assuming that K has natural supply source (Chapter 3.1.1). The lowest K content is in reed fen peat in the middle part of peat profile, where peat contains 1.6 mg/kg K. The highest Na concentration in Elku Mire (Fig. 3.37) is located in 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 through peat profile, because of K high mobility, Na content is rather stable; this can be explained by different sources of supply.

The highest K concentration in Salas Mire is located in the bottom part of peat profile (Fig. 3.38), where peat contains 217 mg/kg K. The location of mire and K content in peat allows assuming that K might have anthropogenic supply source – fertilizers used in agriculture (Chapter 3.1.1). The lowest K content is in the middle part of peat profile, where peat contains 29 mg/kg K. The highest Na concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.38), where peat contains 67 mg/kg Na. The lowest Na content is in the bottom part of peat profile, where peat contains 35 mg/kg Na.

Figure 3.38 **The accumulation pattern of alkali metals in Salas Mire peat profile**

The highest K concentration in Svētupes Mire is located in wood-grass fen peat in the upper part of peat profile (Fig. 3.39), were peat contains 202 mg/kg K. The lowest K content is in sedge fen peat layer in the middle part of peat layer, where peat contains 8 mg/kg K. The highest Na concentration in Svētupes Mire is located in wood-grass fen peat in the upper part of peat profile (Fig. 3.39), while the lowest is in sedge fen peat in the middle part of peat profile, where peat contains 25 mg/kg Na.

Figure 3.39 **The accumulation pattern of alkali metals in Svētupes Mire peat profile**

The highest K concentration in Vīķu Mire is located in wood fen peat in the middle part of peat profile (Fig. 3.40), where peat contains 498 mg/kg K and this can be explained by the high mobility of K. The lowest K content is in the upper part of peat profile and does not exceed 17 mg/kg. The highest Na concentration in Vīķu Mire is located in wood-*sphagnum* fen peat in the upper part of peat profile (Fig. 3.40), where peat contains 119 mg/kg Na, while the lowest concentration was identified in wood-grass fen peat, where peat contains 47 mg/kg Na.

Figure 3.40 **The accumulation pattern of alkali metals in Vīķu Mire peat profile**

Summarizing the results, it can be concluded that alkali metal accumulation mechanism cannot be fully characterized using one model as K and N have different sources of supply and different accumulation characteristics. K seems to be sensitive to various internal and external factors, but, on the other hand – Na accumulation character is similar in all studied mires. Similarly, as it is with alkaline earth metals, K and Na content in peat is highly dependent on the character of mire catchment area and agricultural land use within its borders. Moreover, alkali metals are in the competition with alkaline earth metals, thus their content in peat is also interdependent.

Transition metals

Transition metal accumulation in peat can be explained by both natural and anthropogenic causes (Chapter 1.3). Me can be supplied with groundwater from deposits in mire catchment area (Chapter 3.1.1) and with precipitation from atmosphere, but agricultural land use can also be of possible consideration. All transition metals in reasonable amount are essential plant micronutrients, however if their concentration in soil is high, they must be seen as heavy metals and 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 bond 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 what are not tended to migrate downwards. Cr is lithophile element and forms chemical compounds with oxygen what are not migrating in peat profile (Chapter 1.3).

The highest Fe concentration in Elku Mire is located in sedge fen peat in the bottom part of peat profile (Fig. 3.41), where peat contains 5.6 g/kg Fe. An increased Fe concentration in the bottom part of peat profile can be explained by groundwater impact and pH level changes. The lowest Fe content is in wood fen peat in the upper part of peat profile, where peat contains 0.75 g/kg Fe. The highest Mn concentration in Elku Mire is located in transitional wood peat in the upper part of peat profile (Fig. 3.41), where peat contains 0.92 g/kg Mn. The lowest Mn content is in wood fen peat in the upper part of peat profile, where peat contains 8.8 mg/kg Mn. The highest Ni concentration in Elku Mire is located in sedge fen peat in the bottom part of peat profile (Fig. 3.41), where peat contains 5.47 mg/kg Ni. The lowest Ni content is in wood fen peat in the upper part of peat profile, where peat contains 0.2 mg/kg Ni. The highest

Figure 3.41 **The accumulation pattern of transition metals in Elku Mire peat profile**

Co concentration in Elku Mire is located in reed fen peat in the bottom part of peat profile (Fig. 3.41), where peat contains 1.2 mg/kg Co. The lowest Co content is in wood-reed fen peat in the middle part of peat profile, where peat contains 0.03 mg/kg Co. The highest Zn concentration in Elku Mire is located in transitional wood peat in the upper part of peat profile (Fig. 3.41), where peat contains 20 mg/kg Zn. The lowest Zn content is in reed fen peat in the middle part of peat profile, where peat contains 0.2 mg/kg Zn. The highest Cu concentration in Elku Mire is located in sedge fen peat in the bottom part of peat profile (Fig. 3.41), where peat contains 6 mg/kg Cu. The lowest Cu content is in reed fen peat in the middle part of peat profile, where peat contains 0.4 mg/kg Cu. The highest Cd concentration in Elku Mire is located in transitional wood peat in the upper part of peat profile (Fig. 3.41), where peat contains 0.54 mg/kg Cd. The lowest Cd content is in wood-reed fen peat in the middle part of peat profile, where peat contains 0.03 mg/kg Cd. The highest Cr concentration in Elku Mire is located in transitional wood peat in the upper part of peat profile (Fig. 3.41), where peat contains 2 mg/kg Cr. The lowest Cr content is in wood-reed fen peat in the middle part of peat profile, where peat contains 0.13 mg/kg Cr. According to the results (Fig. 3.41) Zn, Cu, Cr, Ni, Co and Cd have similar accumulation characteristics – these Me 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 what caused transition metal migration in the bottom part of peat profile, while Me content in upper part of peat profile is affected by atmospheric precipitation.

The highest Fe concentration in Salas Mire is located in the upper part of peat profile (Fig. 3.42), where peat contains 15.1 g/kg Fe. The lowest Fe content is in the bottom part of peat profile, where peat contains 7.8 g/kg Fe. Salas Mire peat contains high amount of Fe and it can be explained by an intensive groundwater and surface water supply from mire catchment area (Chapter 3.1.1), in here Quaternary surface consists on sandy deposits. The highest Mn concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.42), where peat contains 417 mg/kg Mn. The lowest Mn content is in the bottom part of peat profile, where peat contains 126 mg/kg Mn. The highest Ni concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.42), where peat contains 4.71 mg/kg Ni. The lowest Ni content is in the upper part of peat profile, where peat contains 1.73 mg/kg Ni. The highest Co concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.42), where peat contains 2 mg/kg Co. The lowest Co content is in the bottom part of peat profile, where peat contains 0.9 mg/kg Co. The highest Zn concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.42), where peat contains 9 mg/kg Zn, also the lowest Zn content is in the middle part of peat profile (3 mg/kg Zn). The highest Cu concentration in Salas Mire is located in the middle part of peat profile (Fig. 3.42), where peat contains 20 mg/kg Cu. The lowest Cu content is in the bottom part of peat profile, where peat contains 11 mg/kg Cu. The highest Cd concentration in Salas Mire is located in the upper part of peat profile (Fig. 3.42), where peat contains 0.26 mg/kg Cd. The lowest Cd content is in the bottom part of peat profile, where peat contains 0.06 mg/kg Cd.

Figure 3.42 **The accumulation pattern of transition metals in Salas Mire peat profile**

The highest Fe concentration in Svētupes Mire is located in sedge peat in the bottom part of peat profile (Fig. 3.43), where peat contains 43.1 g/kg Fe. The lowest Fe content is in wood-sedge fen peat in the upper part of peat profile, where peat contains 0.52 g/kg Fe. The highest Mn concentration in Svētupes Mire is located in sedge peat in the bottom part of peat profile (Fig. 3.43), where peat contains 95 mg/kg Mn. The lowest Mn content is in wood-sedge peat in the upper part of peat profile, where peat contains 10 mg/kg Mn. The highest Ni concentration in Svētupes Mire is located in wood-grass fen peat in the upper part of peat profile (Fig. 3.43), where peat contains 1.5 mg/kg Ni. The lowest Ni content is in sedge fen peat in the bottom part of peat profile, where peat contains 0.16 mg/kg Ni. The highest Co concentration in Svētupes Mire is located in sedge fen peat in the middle part of peat profile (Fig. 3.43), where peat contains 1.2 mg/kg Co. Lowest Co content is traceable through full peat profile and peat on average contains 0.12 mg/kg Co. The highest Zn concentration in Svētupes Mire is located in wood-grass fen peat in the upper part of peat profile (Fig. 3.43), where peat contains 32 mg/kg Zn. The lowest Zn content is in sedge fen peat in the middle part of peat profile, where peat contains 0.2 mg/kg Zn. The highest Cu concentration in Svētupes Mire is located in wood-grass fen peat in the upper part

of peat profile (Fig. 3.43), where peat contains 7 mg/kg Cu. The lowest Cu content is in sedge fen peat in the middle part of peat profile, where peat contains 0.1 mg/kg Cu. The highest Cd concentration in Svētupes Mire is located in wood-grass fen peat in the upper part of peat profile (Fig. 3.43), where peat contains 0.8 mg/kg Cd. The lowest Cd content is in sedge fen peat in the middle part of peat profile, where peat contains less than 0.04 mg/kg Cd.

Fig. 3.43   **The accumulation pattern of transition metals in Svētupes Mire peat profile**

The highest Fe concentration in Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.44), where peat contains 4.7 g/kg Fe. The lowest Fe content is in wood-sphagnum peat in the middle part of peat profile, where peat contains 216 mg/kg Fe. The highest Mn concentration in Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.44), 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 Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.44), where peat contains 3.2 mg/kg Ni. The highest Co concentration in Vīķu Mire is located in wood fen peat, in the upper part of peat profile (Fig. 3.44), where peat contains 2 mg/kg Co. The highest Zn

concentration in Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.44), 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 Vīķu Mire is located in wood fen peat in the upper part of peat p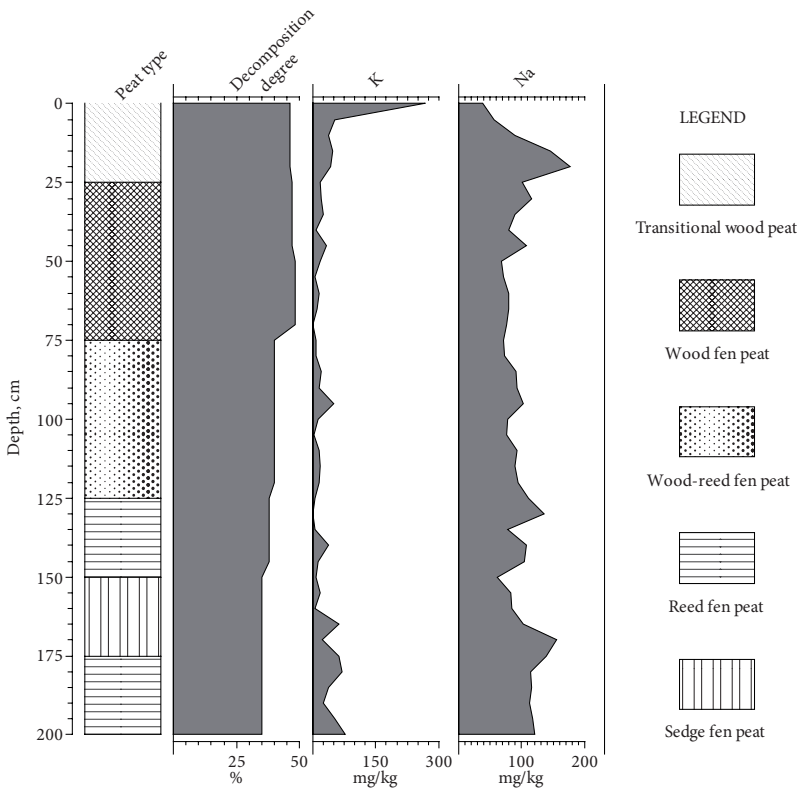rofile (Fig. 3.44), where peat contains 6.9 mg/kg Cu. The lowest Cu content is in sedge-*hypnum* peat in the bottom part of peat profile, where peat contains 0.8 mg/kg Cu. The highest Cd concentration in Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.44), where peat contains 0.26 mg/kg Cd. Low Cd content is in peat in the most part of peat profile, where peat contains approximately 0.01 mg/kg Cd. The highest Cr concentration in Vīķu Mire is located in wood fen peat in the upper part of peat profile (Fig. 3.44), where peat contains 1.9 mg/kg Cr.

Figure 3.44 **The accumulation pattern of transition metals in Vīķu Mire peat profile**

Summarizing the results, it can be concluded that an 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 area. An elevated Me concentration in bottom layers can be explained by significant groundwater level changes, what is causing the migration of particular Me.

Post-transition metals (Pb)

Pb has no known biological functions and can be considered as heavy metal. The highest Pb concentration in Elku Mire is located in transitional wood peat in the upper part of peat profile (Fig. 3.45), where peat contains 38 mg/kg and it can be considered as Pb pollution (Chapter 3.2.2). The lowest Pb content is below 0.5 mg/kg and the concentration remains low throughout full peat profile. The highest Pb concentration in Salas Mire is located in the bottom part of peat profile (Fig. 3.46), where peat contains 4.5 mg/kg; the lowest concentration is below 0.5 mg/kg.

Figure 3.45 **The accumulation pattern of lead in Elku Mire peat profile**

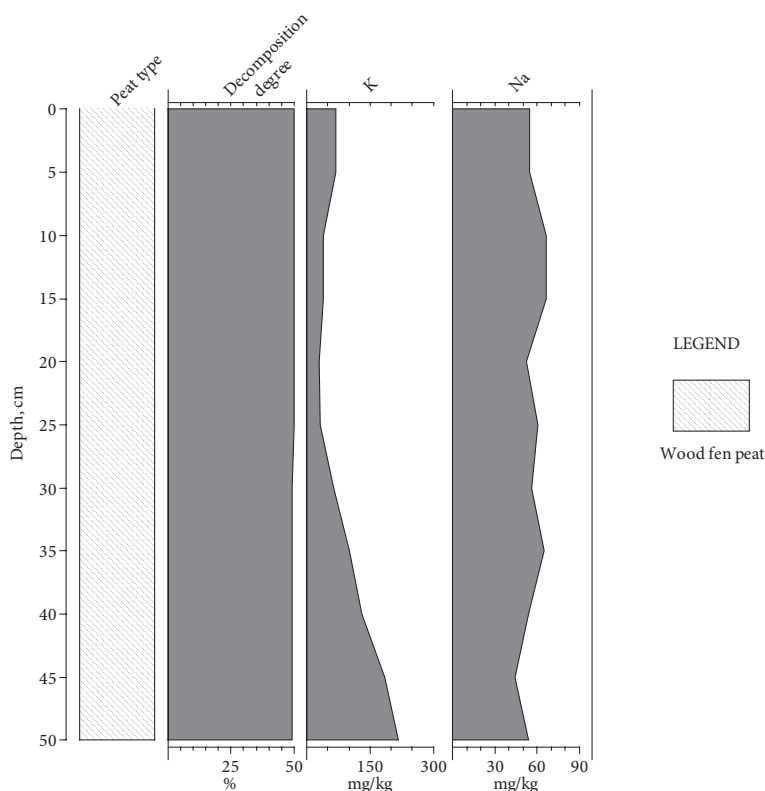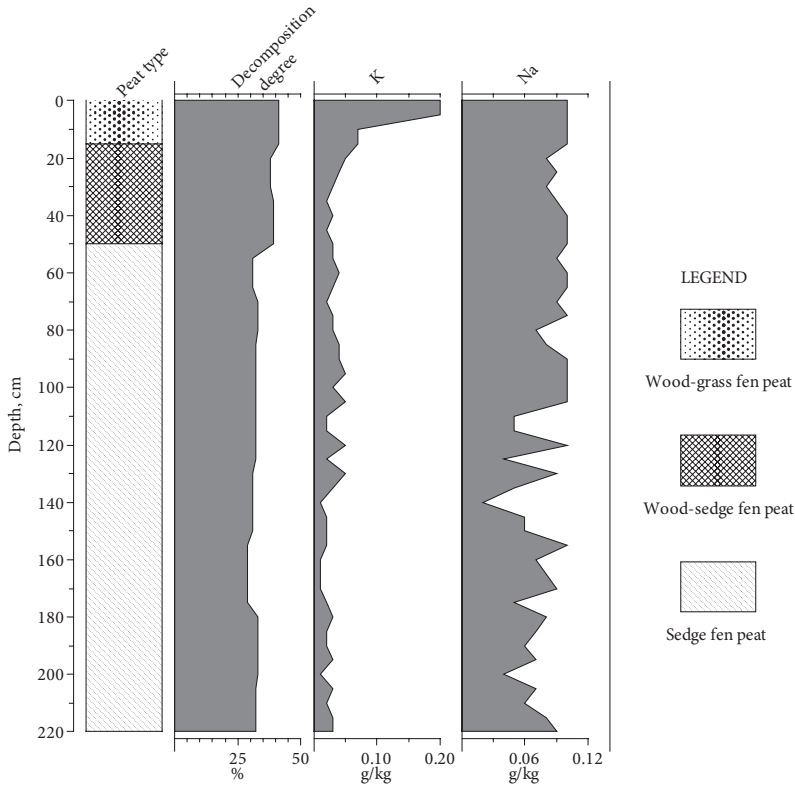*Figure 3.46* **The accumulation pattern of lead in Salas Mire peat profile**

Figure 3.47 **The accumulation pattern of lead in Svētupes Mire peat profile**

The highest Pb concentration in Svētupes Mire is located in wood-grass fen peat, in the upper part of peat profile (Fig. 3.47), where peat contains 44 mg/kg Pb. In the rest of peat profile Pb content remains low (below 0.5 mg/kg). The highest Pb concentration in Vīķu Mire is located in wood fen peat, in the upper part of peat profile (Fig. 3.48), where peat contains 23.5 mg/kg Pb, but in the rest of peat profile Pb content remains low (below 0.5 mg/kg).
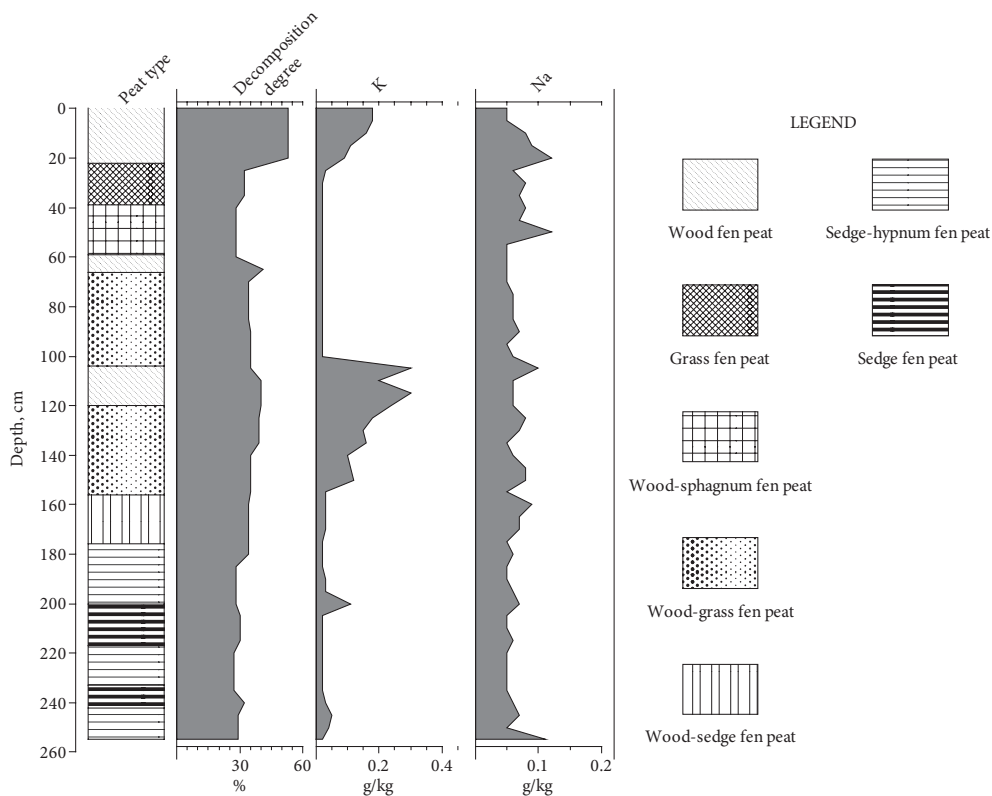

Figure 3.48 **The accumulation pattern of lead in Vīķu Mire peat profile**

Summarizing the results, it can be concluded that an 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.

Metallic element content in fen peat in comparison with bog peat

Me in studied fen peat generally are in higher average concentration that in bog peat (Fig. 3.49), although, the sequence of element distribution (with exception of Pb, Ni and Co) is the same in both mire types.

Figure 3.49 **The average metal content in mires** (Data on bogs taken from Silamiķele, 2010)

In general, Me concentration in studied peat (Table 3.14) is similar to that reported in peat from other countries – Baltic States, Norway, Russia, Germany etc. (Zaccone et al., 2007; Orru and Orru, 2006; Frontasyeva and Steinnes, 2005; Syrovetnik et al., 2004; Simon and Thomas, 2003; Dellwig et al., 2002; Kalaitzidis et al., 2002; Jennifer and Hao, 1993; Markert, 1991).

Table 3.14

Mean concentration (mg/kg) of metallic elements in peat

Element	Estonia[1]	UK[2]	Russia[3]	S Norway[4]	N Norway[5]	Australia[6]	NE Greece[7]	NW Germany[8]	Switzerland[9]
Ca		80.8							842
Mg		246							
Fe	1155	3.5	1783	1130	727	1686			1223
Mn	146	25.4	68.6	3.6	4.3			183	6.9
Cu	102	54.8	26.3	5.6	1.6	4.2	15.6	6.3	6.3
Pb	200	358	15.0	23.2	6.9	28.6	18.8	3.1	19.1
Zn	446	56.2	59.6	19.6	12.3	11.3	84.6	17.2	30.1
Cd	17	2.1		1.2	0.2	2.7	0.7	0.1	
Ni	47	10.9		1.4	2.6		7.0	6.0	
Cr		15.9		0.8	0.9		42.2	15.0	
Co				1.2	1.1		4.5	2.3	

([1]Orru and Orru, 2006; Syrovetnik et al., 2004; [2]Jennifer and Hao, 1993; [3]Markert, 1991; [4-5]Frontasyeva and Steines, 2005; [6]Simon and Thomas, 2003; [7]Kalaitzidis et al., 2002; [8]Dellwig et al., 2002; [9]Zaccone et al., 2007)

Table 3.14 demonstrates an average amount of Me in mires around the world. Me concentration reflects the impact of local environmental conditions and main differences depend on the character of mire catchment area and anthropogenic activities.

3.2.2 Heavy metal enrichment, geo-accumulation and pollution index

In this chapter as heavy metals are described transition and post-transition metals (Fe, Zn, Mn, Co, Cu, Cd, Cr and Pb). Heavy metal EF, GI and PI (Chapter 1.3.1) demonstrate possible pollution in mires, whereas it is a significant issue or minor process without any reasonable impact on fen ecosystem.

Enrichment factor

According to Birch (2003) heavy metal EF in studied peat profiles is fit to "no enrichment" class, thus heavy metal enrichment can be considered as insignificant, because EF is close to 0 (Table 3.15). However, Pb concentration is an exception and results show on extremely severe Pb enrichment in all four study sites (EF > 50); this process takes place in the upper part of peat profiles (Chapter 3.2.1). High EF is first indication of a potential anthropogenic contribution for an element; however, a visible enrichment can also be caused by some natural sources (Atgin et al., 2000).

Table 3.15

Heavy metal enrichment in studied peat profiles

	Elku Mire			Salas Mire			Svētupes Mire			Vīķu Mire		
	Range		Mean	Range		Mean	Range		Mean	Range		Mean
	From	To		From	To		From	To		From	To	
Fe	0.01	0.07	0.03	0.1	0.2	0.2	0.01	0.6	0.1	0.003	0.1	0.01
Zn	0.001	0.2	0.03	0.03	0.1	0.1	0.002	0.3	0.04	0.0004	0.002	0.001
Cu	0.002	0.04	0.01	0.1	0.13	0.1	0.001	0.05	0.02	0.005	0.05	0.01
Cd	0.001	0.01	0.004	0.001	0.01	0.005	0.0005	0.02	0.003	0.0002	0.01	0.001
Co	0.00003	0.001	0.0001	0.001	0.001	0.001	0.0001	0.001	0.0001	0.00002	0.001	0.0001
Cr	0.001	0.01	0.004	0.001	0.01	0.004	0.001	0.01	0.003	0.001	0.01	0.002
Ni	0.002	0.04	0.01	0.01	0.04	0.03	0.0001	0.01	0.005	0.002	0.03	0.004
Pb	3.6	1712	79	23	205	113	22	1971	132	8	1063	73

Nevertheless, an extremely severe Pb enrichment is the result of anthropogenic activities what are leading to Pb dispersion throughout the environment (Özkan, 2012; Karageorgis et al., 2003). High Pb EF in upper peat layers can be explained by growing anthropogenic impact on mires nowadays, it can be caused by automobile exhaust emissions, local domestic and industrial sewage and other factors. However, high and pollution related EF cannot be generalized over large areas and each case must be viewed separately (Reimann and de Caritat, 2005).

Pollution index

Heavy metal PI in studied peat profiles is generally low and fen peat can be considered as non-polluted. However, there are also some exceptions – Pb with PI > 6, which can be viewed as high contamination and Cd with PI > 1, what is moderate contamination (Table 3.16). An elevated PI is in the upper part of peat profiles, where direct anthropogenic impact takes place (Chapter 3.2.1).

Table 3.16

Heavy metal pollution index in studied peat profiles

	Elku Mire			Salas Mire			Svētupes Mire			Vīķu Mire		
	Range		Mean	Range		Mean	Range		Mean	Range		Mean
	From	To		From	To		From	To		From	To	
Fe	0.01	0.1	0.05	0.17	0.30	0.24	0.01	0.86	0.1	0.04	0.09	0.02
Zn	0.001	0.3	0.05	0.04	0.13	0.09	0.003	0.46	0.07	0.03	0.18	0.05
Cu	0.003	0.1	0.02	0.11	0.20	0.14	0.001	0.07	0.02	0.008	0.07	0.02
Cd	0.2	3.6	1.0	0.4	1.74	1.27	0.13	5.27	0.88	0.05	1.76	0.30
Co	0.002	0.04	0.01	0.04	0.09	0.06	0.005	0.05	0.01	0.001	0.08	0.007
Cr	0.001	0.02	0.01	0.001	0.2	0.03	0.001	0.04	0.008	0.001	0.02	0.003
Ni	0.002	0.1	0.01	0.02	0.06	0.04	0.0001	0.02	0.01	0.002	0.04	0.007
Pb	5.33	2530	116	33	303	167	32	2912	196	12	1570	108

High PI demonstrates an anthropogenic contribution for Pb and Cd accumulation in studied fens. However, PI also depends on peat botanical composition, physico-chemical characteristics and ability to absorb Me.

Geo-accumulation index

Heavy metal GI in studied peat is generally negative and it means that heavy metal geo-accumulation in fens does not take place (Table 3.17). However there are also exceptions (Pb and Cd). Calculations point on a small-scale Cd geo-accumulation and rapid Pb geo-accumulation in the upper part of peat profiles, what can be attributed to anthropogenic activities in mire catchment area and atmospheric pollution.

Table 3.17

Heavy metal geo-accumulation indices in the studied peat profiles

	Elku Mire			Salas Mire			Svētupes Mire			Vīķu Mire		
	Range		Mean	Range		Mean	Range		Mean	Range		Mean
	From	To		From	To		From	To		From	To	
Fe	-6.6	-3.7	-5.0	-3.3	-2.3	-2.6	-7.2	-0.8	-5.1	-8.4	-3.9	-6.9
Zn	-10.0	-2.4	-6.0	-5.1	-3.5	-4.2	-9.0	-1.7	-5.2	-5.51	-3.1	-5.1
Cu	-8.72	-4.6	-6.8	-3.7	-2.9	-3.4	-10.5	-4.4	-6.4	-7.6	-4.4	-6.4
Cd	-2.9	1.3	-1.1	-1.9	0.2	-0.3	-3.5	1.8	-1.1	-5.0	0.2	-2.8
Co	-9.6	-4.9	-7.9	-5.4	-4.1	-4.8	-8.3	-4.9	-8.1	-10.3	-4.2	-8.8
Cr	-10.2	-6.2	-8.3	-10.7	-6.2	-9.1	-10.5	-4.9	-8.6	-10.9	-6.1	-9.9
Ni	-9.3	-4.5	-7.5	-6.2	-4.7	-5.3	-13.4	-6.4	-8.2	-9.3	-5.3	-8.3
Pb	1.8	10.7	4.0	4.5	7.7	6.4	4.4	10.9	5.4	3.0	10.0	3.9

Highest Pb and Cd GI are in the upper part of peat profile regardless of mire location, this point on heavy metal geo-accumulation in mires in the whole territory of Latvia. Noteworthy that only Pb geo-accumulation can be viewed as serious pollution, because according to GIC only Pb shows on pollution (Table 3.18).

Table 3.18

Heavy metal geo-accumulation index class in studied peat profiles

	Fe	Zn	Cu	Cd	Co	Cr	Ni	Pb
Elku Mire	0	0	0	0	0	0	0	4
Salas Mire	0	0	0	0	0	0	0	6
Svētupes Mire	0	0	0	0	0	0	0	5
Vīķu Mire	0	0	0	0	0	0	0	3

(0: uncontaminated; 3: moderately to strongly contaminated; 4: strongly contaminated; 5: strongly to extremely contaminated; 6: extremely contaminated)

Pb GIC in studied peat profiles shows on moderately-strongly contaminated to extremely contaminated peat. Moreover, in study sites in the east part of Latvia, GIC is higher than in study sites in the western part of Latvia (Chapter 2.1).

3.2.3   Metallic element associations in fen peat

In bog peat profile, corresponding to acrotelm, catotelm and hedotelm parts of peat profile (Silamiķele, 2010), it is possible to divide three separate zones with different Me associations. However, results demonstrate no particular Me associations in fen peat according to hydrological zones in peat profile and all Me interactions are highly site dependent. Data tables showing Me correlation in studied fen peat can be found in Appendix 8.

Associations between Me in Elku Mire peat profile were viewed separately for each peat type, following their sequence in the peat profile (Chapter 3.1.2).

In transitional wood peat, Me form 23 statistically significant correlations (n = 5; α = 0.88; p < 0.05) and they vary from strong to very strong, showing on covariation (Fig. 3.50). Strongest Me associations form: K-Mn (r = 0.99), K-Co (r = 0.99), Mn-Pb (r = 1.00), Co-Pb (r = 1.00). In wood fen peat, Me form 16 statistically significant correlations (n = 10; α = 0.63; p < 0.05) and they vary from moderate to very strong (Fig. 3.50). Strongest Me associations form: Ca-Fe (r = 0.91), Na-Pb (r = 0.82) and Fe-Mn (r = 0.81). A variety of Me in wood fen peat layer form statistically significant, but negative correlations. Strongest negative associations form: Mg-Co (r = -0.66), Mg-Cu (r = -0.68), Ca-K (r = -0.70), Fe-K (r = -0.66), Cd-K (r = -0.66), Ca-Co (r = -0.74) and Mn-Co (r = -0.66). In wood-reed fen peat, Me form 20 statistically significant correlations (n = 10; α = 0.62; p < 0.05) and they vary from moderate to very strong (Fig. 3.50). Strongest Me form Mn-Pb (r = 0.96) and Mn-K (r = 0.85). In reed fen peat the most significant correlations (Fig. 3.50) form: Co-K (r = -0.90), Co-Cu (r = -0.93) and Co-Pb (r = -0.90). In sedge fen peat, Me form 21 statistically significant correlations (n = 5; α = 0.88; p < 0.05) and they vary from strong to very strong and results show on covariation (Fig. 3.50). Strongest Me associations form: Mg-Na (r = -1.00), Mg-Pb (r = -1.00), Ni-Cr (r = -1.00), Ca-Mn (r = -0.99), Ni-Co (r = 0.99), Ni-Zn (r = 0.99), Cr-Cu (r = 0.99), Cr-Zn (r = 0.99) and Cu-Zn (r = 0.99). In reed fen peat, in the bottom part of peat profile, Me form 8 statistically significant correlations (n = 5; α = 0.88; p < 0.05) and they vary from strong to very strong and point on data covariation (Fig. 3.50). Strongest Me associations form Ca-Mg (r = 0.96) and Ni-Cu (r = 0.98).

Associations between Me in Salas Mire peat profile (Fig. 3.51) were viewed in the whole profile at once (Chapter 3.1.2). Me form 20 statistically significant moderate to very strong correlations (n = 10; α = 0.63; p < 0.05). Strongest positive Me associations form: Fe-Mn (r = 0.99), Fe-Mg (r = 0.97) and Mn-Mg (r = 0.97), while statistically significant negative correlation is between Mg-K (r = -0.96), Mg-Ni (r = -0.75), Mg-Pb (r = -0.75), Ca-K (r = -0.90), Fe-K (r = -0.95), Mn-K (r = -0.95), Ca-Pb (r = -0.76), Fe-Ni (r = -0.82) and Mn-Ni (r = -0.75).

Figure 3.50 **Correlations between metallic elements in Elku Mire peat profile**
(a – transitional wood peat, 0.00-0.25 m; b – wood fen peat, 0.25-0.75 m; c – wood-reed fen peat, 0.75-1.25 m; d – reed fen peat, 1.25-1.50 m; e – sedge fen peat, 1.50-1.75 m; f – reed fen peat, 1.75-2.00 m)

Figure 3.51 **Correlations between metallic elements in Salas Mire peat profile** (wood fen peat, 0.00-0.50 m)

Associations between Me in Svētupes Mire peat profile were viewed separately for each peat type, following their sequence in the peat profile (Chapter 3.1.2).

In wood-grass fen peat Me form 14 statistically significant correlations (n = 4; α = 0.95; p < 0.05) and they tend to be very strong (Fig. 3.52). Strongest Me associations

form: Ca-Mg, Cd-Ni, Cd-K, Ni-K and Cu-Zn. In wood-sedge fen peat Me form 13 statistically significant correlations (n = 7; α = 0.75; p < 0.05). The association between Ca and Mg demonstrates very strong positive interdependence (r = 1.00), while Mg-Zn, Ca-Zn, Mn-Pb and Ni-Zn form statistically significant negative associations (Fig. 3.52). In sedge fen peat Me form 22 statistically significant correlations (n = 43; α = 0.30; p < 0.05); however, most of these associations are weak to moderate strong and negative (Fig. 3.52). Strongest Me associations form: Mg-Na (r = 0.88), Mg-K (r = 0.74) and Na-K (r = 0.71). Ca-K, Ca-Cu, K-Pb, Fe-Ni and Fe-Cd form negative associations.

Figure 3.52 **Correlations between metallic elements in Svētupes Mire peat profile**
(a – wood-grass fen peat, 0.00-0.15 m; b – wood-sedge fen peat, 0.15-0.50 m; d – sedge fen peat, 0.50-2.20 m)

Associations between Me in Vīķu Mire peat profile were viewed separately for each peat type, following their sequence in the peat profile (Chapter 3.1.2).

In wood fen peat Me form 22 statistically significant correlations (n = 4; α = 0.95; p < 0.05), all of them are very strong and show on data covariation (Fig. 3.53). Na-K and Na-Mn form statistically significant, but negative association. In grass fen peat Me form 12 strong to very strong statistically significant correlations (n = 5; α = 0.88; p < 0.05). The strongest are associations between Cd-Pb (r = 0.99), K-Ni (r = 0.98) and Cd-Cr (r = 0.95). In wood-*sphagnum* peat Me form 30 very strong statistically significant correlations (n = 4; α = 0.95; p < 0.05) and results show on data covariation (Fig. 3.53). Strongest Me associations form Na-K, Na-Cr, Na-Zn, Na-Pb, K-Cr, K-Zn, K-Pb, Zn-Cr, Zn-Pb and Cr-Pb, thus there is an obvious interdependence between alkali metals and heavy metals in peat profile. In wood-grass fen peat (0.65-1.05 m) Me form 46 strong to very strong statistically significant correlations (n = 7; α = 0.75; p < 0.05) and, as in the peat layer above, also there is an evidence of Me concentration covariance (Fig. 3.53). Strongest associations form: K-Fe, K-Co, K-Ni, K-Cr, K-Pb, Fe-Co, Fe-Ni, Fe-Cr, Fe-Pb, Co-Ni, Co-Cr, Co-Pb, Ni-Cr, Ni-Pb and Cr-Pb. In wood-grass fen peat (1.20-1.60 m) Me form 23 statistically significant correlations (n = 9; α = 0.67; p < 0.05), all of them are from moderate to very strong (Fig. 3.53). Strongest associations form: Fe-Mn and Ni-Cr. K correlates negatively with Mn (r = -0.73), Co (r = -0.80), Zn (r = -0.79) and Cd (r = -0.90). In wood-grass fen peat (1.60-1.80 m)

Me form 4 statistically significant correlations (n = 4; α = 0.95; p < 0.05): Na-K, Fe-Ni, Mn-Ni and Cu-Ni (Fig. 3.53), however all of these associations point on data covariation. In sedge-*hypnum* fen peat significant correlations are between: K-Mn, K-Cr, Ca-Mn, Fe-Mn, Cr-Mn and Zn-Cd (Fig. 3.53).

In sedge fen peat Me form 8 very strong statistically significant correlations (n = 4, α = 0.95; p < 0.05) and the strongest is association between: Na-Zn, Fe-Mn and Co-Cr (Fig. 3.53).

Figure 3.53 **Correlations between metallic elements in Vīķu Mire peat profile**

(a – wood fen peat, 0.00-0.20 m; b – grass fen peat, 0.20-0.40 m; c – wood-*sphagnum* fen peat, 0.40-0.60 m; d – wood-grass fen peat, 0.65-1.05 m; e – wood-grass fen peat, 1.20-1.60 m; f – wood-grass fen peat, 1.60-1.80 m; g – sedge-*hypnum* fen peat, 1.80-2.00 m, h – sedge fen peat, 2.00-2.20 m)

Summarizing the results, it can be concluded that associations between Me in studied peat are highly individual and depend on the characteristics on mire catchment area including agricultural land use. Thus there are no particular Me associations depending on the depth range or peat botanical composition what could be attributed to all fen peat profiles. However, it is possible to trace similarities regarding Me associations in geographically close located mires (Vīķu and Elku Mire peat profiles), where statistically significant heavy metal correlations between: Cu-Zn, Cu-Ni, Cu-Co, Co-Ni and Co-Zn were identified. This can be explained by anthropogenic activities in the area.

Results demonstrate the heterogeneity of studied peat profiles and site-specific Me associations, although, the depth range seems to have an impact on the quantity of Me associations – they are becoming rarer.

3.2.4 Relation of Ca and Mg content on metallic element accumulation in fens

The hypothesis of this PhD thesis was that Me accumulation in fen peat is being activated due to the replacement of Ca and Mg ions by other more tightly metal ions. According to this idea, the amount of Ca and Mg in peat (Chapter 3.2.1) must be related to Me accumulation character in peat profile. Ca and Mg content in studied peat are highly variable (Appendix 7) and so are associations between alkaline earth metal and other Me in peat (Appendix 8). Me associations depend on variety of complex properties, thus each study site must be viewed separately.

Associations between alkaline earth metals and other Me in Elku Mire peat were viewed separately for each peat type, following their sequence in the peat profile (Chapter 3.1.2). In transitional wood peat (0.00-0.25 m) Ca forms statistically significant association with Mg, while Mg has negative relation with K, Mn and Co. In wood fen peat (0.25-0.75 m) Ca forms statistically significant associations with Fe, Mn, K and Co. Mg has negative association with Co and Cu. In wood-reed fen peat (0.75-1.25 m) there is significant correlation between: Ca-Fe, Ca-Ni, Mg-Ni, Mg-Cu and Mg-Cr. In reed fen peat (1.25-1.50 m) Ca forms association with Fe. In sedge fen peat (1.50-1.75 m) Ca forms association with Pb and Na, moreover – Mg forms same associations: Mg-Pb and Mg-Na and results show on data covariation. In reed fen peat (1.75-2.00 m) Ca has statistically significant correlation with Mg, but Mg correlates also with Cd.

Both alkaline earth metals in Salas Mire peat profile form statistically significant association with one another and similar association with other Me in peat: Ca-Na, Ca-K, Ca-Fe, Ca-Mn, Ca-Pb, Mn-Na, Mg-K, Mg-Fe, Mg-Mn and Mg-Pb.

Associations between Ca and Mg and other Me in Svētupes Mire peat were viewed separately for each peat type, following their sequence in the peat profile (Chapter 3.1.2). In wood-grass fen peat (0.00-0.15 m) alkaline earth metals do not form statistically significant correlations with other Me in peat layer. In wood-sedge fen peat layer (0.15-0.50 m) Ca and Mg form associations with Zn, Na, Mn, Cu and

Ni. In sedge fen peat (0.50-2.20 m) Ca is associated with K and Cu, but Mg with Na, K, Mn and Cu.

Associations between alkaline earth metals and other Me in Vīķu Mire peat were viewed separately for each peat type, following their sequence in the peat profile (Chapter 3.1.2). In wood fen peat (0.00-0.20 m) layer neither Ca nor Mg form significant association with Me in peat layer. In grass fen peat (0.20-0.40 m) Ca forms association with K and Ni. In wood-*sphagnum* peat (0.40-0.60 m) Ca content correlates with Na, Fe, Mn and Cu, but Mg is associated with Ni. In the first wood-grass fen peat layer (0.65-1.05 m) Ca has correlation with Zn. In the second wood-grass fen peat layer (1.20-1.55 m) there is statistically significant correlation between: Mg-Cu, Ca-Fe, Ca-Mn, Ca-Co, Ca-Cu and Ca-Zn. In the third wood-grass fen peat layer (1.60-1.80 m) alkaline earth metals form no statistically significant associations with other Me in peat. In sedge-*hypnum* fen peat (1.80-2.00 m) Ca is associated only with Mn. In sedge fen peat layer (2.00-2.20 m) alkaline earth metals form association with Fe.

Summarizing the results, it can be concluded that associations between alkaline earth metals and other Me in studied peat profiles are highly variable and generally depend on Ca and Mg content in peat mass. Alkaline earth metals can have either natural or anthropogenic sources, thus also the character of mire catchment area and agricultural land use is also of high importance. Moreover, Ca and Mg are in competition with alkali metals, thus their content in peat mass is interdependent. However, in upper peat layers alkaline earth metals generally do not tend to form associations with other Me in peat.

3.2.5   Metallic element bio-sorption onto fen peat

In order to assess fen peat characteristics as potential bio-sorbent Ca, Mg, K, Na, Cu and Pb were sorbed onto peat samples (Chapter 2.3.13). Results demonstrate that fen peat has huge variability as bio-sorbent due to its variable botanical composition and complex physico-chemical characteristics. However, due to the naturally high Me content in fen peat (Chapter 1.3) overall sorption capacity is lower than it is for bog peat. Although, weak acidic/alkaline fen peat pH encourages high Me mobility and it is pointing on different from bogs Me accumulation character.

Fen peat has high Ca, Mg and Cu concentration, while K, Na and Pb content (Chapter 3.2.1) is considerably less than in bog peat (Silamiķele, 2010). Me sorption capacity onto fen peat depends on variety of peat characteristics, where one of the most important are oxygen-containing functional groups in peat. The concentration of these groups is growing along with peat decomposition degree. In addition, bog peat seems to be largely unsaturated in respect to metal ions, while situation is just the opposite with fen peat, where Me binding does not take place because of functional group content in peat.

In the bio-sorption experiment, to describe Me adsorption, author has used fen peat with its natural pH (wood-grass fen peat with pH 5.7 and 5.8 and grass fen peat with pH 6). Data analysis with the software Visual MINTEQ 3.1 has shown that Me

precipitation at these pH levels does not take place and 100% of particular element at chosen concentration is being absorbed.

Results demonstrate (Fig. 3.54) that Me adsorption capability is followed by geometric progression and it depends on Me concentration already in peat – higher is the "natural" Me concentration, lower is Me adsorption capacity and contrariwise.

a)

b)

Figure 3.54 **Metallic element adsorption isotherms (wood-grass fen peat)**
(a – copper, potassium, lead; b – calcium, magnesium, sodium)

To quantitatively describe adsorption isotherms (Fig. 3.54), Langmuir and Freundlich equations were used and highest r^2 values were obtained by fitting Langmuir equation. Results indicate that it Langmuir model is the most appropriate to describe Me adsorption by fen peat. Results have shown that 1 g of fen peat adsorbs 3 mg of Ca and 6 mg of Mg. However, Me adsorption is slightly different between wood-grass fen and grass fen peat; capacities are similar, but in wood-grass fen peat adsorbtion capacity is being reached faster. Moreover, alkaline earth metal absorption depends on their content already in peat as both elements are in competition with one other. 1 g of fen peat can adsorb approximately 15 mg of K and Na and adsorption characteristics are generally similar. 1 g of fen peat adsorbs 25 mg of Cu and obtained results are

comparable with results reported in other studies (Ho and McKay, 1999). 1 g of fen peat can adsorb 125 mg of Pb and this is one of the most significant fen peat characteristics as bio-sorbent. Pb sorption capacity in fen peat is similar to capacity in bog peat used in other studies (e.g. 122 mg/g) (Ho and McKay, 1999) and is much higher than sorption capacity of modified peat-resin particles (e.g. 47.39 mg/g) (Sun et al., 2003). Results also demonstrate that by increasing analytical concentration alkaline earth metal content in peat sample is decreasing.

3.3 Associations between metallic element content and fen peat characteristics

Me content in studied peat is linked to peat decomposition degree and botanical composition; however the main factor is peat inorganic matter, minerals supplied with groundwater. Peat decomposition degree and humification degree are similar characteristics (Chapter 3.1.2), but with different impact on Me content. Typically Me content correlates with peat humification degree, but this may not be always the case. That being said, Me content in upper peat layers can rather reflect anthropogenic impact and atmospheric deposition (Zaccone et al., 2009).

Results demonstrate that there is direct relation between ash content and Me concentration in peat; this can be explained by high importance of groundwater flow in fen peat forming. Respectively, Me are supplied with groundwater from mire catchment area and their concentrations in peat are highly dependent on deposit character, groundwater is flowing through.

Determining factors for metallic element accumulation in fen peat

PCA can be successfully used to characterize possible Me sources and primary peat forming factors, which cannot be observed directly and/or are not correlatively connected to one another, but describe mire origin and peat accumulation characteristics. In this PhD thesis PCA results are described as statistically significant correlation ($r > 0.50$) between principal components and characteristic peat parameters. Data points on PCA coordinate plane to the right from axis 2 demonstrate positive correlation with axis 1, while data points to the left from axis 2 show negative correlation with axis 1. Data points above axis 1 have negative correlation with axis 2, but data points below axis 1 have positive correlation with axis 2. PCA coordinate planes are bounded by four segments, each of which is characterized by different factors.

Me content absolute values and distribution pattern have been affected by combination of several major factors. Geographical location and spatial characteristics, mire formation conditions and variability in Me supply sources play the key role amongst Me accumulation determining factors in fen peat profile.

Created PCA matrices, taking into account several variables, allow explaining what processes – natural or anthropogenic – have an impact on Me accumulation in peat. Although, studied fen peat parameters are heterogeneous in nature, PCA results

outline three separate segments with the distinction between elemental composition, Me accumulation and factors it is depending on.

Vīķu Mire peat profile PCA results (Fig. 3.55) demonstrate that CM and MM content, peat decomposition degree and elemental composition is of the major importance for Me accumulation in fen peat. As a further matter, the accumulation character of Mn, Co, Ni, Cr, Zn, Fe, Cu and Ca has a strong resemblance.

Figure 3.55 **Principal component analysis results of Vīķu Mire peat characteristics and metallic element content (n = 50)**

(Only statistically significant principal component loadings (r > 0.50) are presented in the figure. Org. m. – organic matter; Min. m. – mineral matter; Decomp. deg. – decomposition degree; Ox. ind. – oxidation idex; Hum. ind. – humification index; H def. – hydrogen deficient)

The distribution of such parameters as peat decomposition degree, elemental composition, OM and MM content and Me concentration on the coordinate plane is statistically significant with axis 1 (p-value: 0.001) and axis 2 (p-value: 0.002), what explain 65.17% of the total data dispersion (Fig. 3.55). With axis 1, which explains

44.72% from the total dispersion, a statistically significant (r > 0.50) positive correlation between decomposition degree (r = 0.84), HI (r = 0.48), CM content (r = 0.70), MM 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) has been found. Whereas axis 1 has a statistically significant, but negative correlation with depth (r = -0.56) and OM content (r = -0.96). Axis 2 explains 20.45% of the dispersion of characteristic peat parameters. In this case, there is a positive correlation with HI (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 negative is the correlation with depth (r = -0.47), O (r = -0.78), Cd (r = -0.56) and oxidation index (r = -0.56). Both axes have a statistically significant correlation with H content and it shows on Me concentration dependence on the content of this element.

In sector 1 are grouped peat parameters, which are characteristic to peat composition and its variability, including peat decomposition degree, HI, elemental composition, alkali and alkaline earth metals. All of these parameters are determining factors for Me binding and accumulation in fen peat. In sector 2 is distributed the variability of Me concentration, including CM and MM content what is the source of these elements. Furthermore, in this sector is distributed the variability of natural origin Me, for instance, Ca and Fe, and also the variability of anthropogenic origin Me – Ni, Cu and Pb. However, the variability of Me in sector 2 is generally related to the parameter variability in sector 3, which is peat depth range and oxygen content in peat.

Svētupes Mire peat profile PCA results (Fig. 3.56) demonstrate wide variability in the interdependence between fen peat parameters, although there is also clear similarity with Vīķu Mire peat PCA results. Inorganic matter content, peat decomposition degree and elemental composition are all also determinant factors for Me accumulation in Svētupes Mire peat profile. Moreover, Mn, Co, Ni, Zn and Cu have strong resemblance, which is also similar to Vīķu Mire peat profile. Data dispersion for Svētupes Mire peat physico-chemical characteristics, elemental composition and Me concentration on the coordinate plane is statistically significant with axis 1 (p-value: 0.001) and axis 2 (p-value: 0.002), what explain 62.85% of the total data dispersion (Fig. 3.56). With axis 1, which explains 41.70% from the total dispersion, a statistically significant positive correlation between decomposition degree (r = 0.69), K-value (r = 0.64), OM (r = 0.91), C (r = 0.65), N (r = 0.76), H (r = 0.81), Cu (r = 0.70), K (r = 0.59), Cd (r = 0.50), Co (r = 0.49), Pb (r = 0.52) and H deficient (r = 0.57) has been found. At the same time axis 1 also has a negative correlation with depth (r = -0.83), pH (r = -0.75), CM (r = -0.91), MM (r = -0.86), O (r = -0.81), Fe (r = -0.53), Ca (r = -0.77) and oxidation index (r = -0.79). Axis 2 explains 21.15% of the data dispersion. However, the majority of correlations are negative and the only statistically significant positive correlation is with H (r = 0.46). Negative is the correlation with Zn (r = -0.52), Cu (r = -0.53), Na (r = -0.73), K (r = -0.72), Cd (r = -0.75), Co (r = -0.76) and Pb (r = -0.75). Both axes have a statistically significant correlation with H content and it is showing on Me content dependence on the concentration of H in peat.

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Figure 3.56 **Principal component analysis results of Svētupes Mire peat characteristics and metallic element content (n = 44)**

(Only statistically significant principal component loadings (r > 0.50) are presented in the figure. Org. m. – organic matter; Min. m. – mineral matter; Decomp. deg. – decomposition degree; Ox. ind. – oxidation idex; Hum. ind. – humification index; H def. – hydrogen deficient)

In sector 1 are grouped peat parameters what are describing the variability of peat elemental composition, including alkali and alkaline earth metal concentration. In sector 2 is distributed the variability of Me concentration in fen peat, including peat decomposition degree and K-values, what might indicate on the importance of plant decomposition on Me content in peat. However, parameters in sector 2 are mainly dependent on O content, pH value and the amount of inorganic matter in peat (sector 3).

The data dispersion for Elku Mire peat physico-chemical parameters and variability of Me concentration is highly heterogeneous (Fig. 3.57). Only axis 1 is statistically significant and it explains 38.21% of total data dispersion (p-value: 0.001). Axis 1 has a statistically significant positive correlation with depth (r = 0.94), MM (r = 0.50), H (r = 0.47), Fe (r = 0.84), Zn (r = 0.74), Cu (r = 0.69), Cd (r = 0.49), Co (r = 0.77)

and Ni (r = 0.79). While negative is the correlation with peat decomposition degree (r = -0.83), K-value (r = -0.92), HI (r = -0.65), OM (r = -0.76), O (r = -0.61), Mg (r = -0.83) and oxidation index (r = -0.82).

Figure 3.57 **Principal component analysis results of Elku Mire peat characteristics and metallic element content (n = 40)**

(Only statistically significant principal component loadings (r > 0.50) are presented in the figure. Org. m. – organic matter; Min. m. – mineral matter; Decomp. deg. – decomposition degree; Ox. ind. – oxidation idex; Hum. ind. – humification index; H def. – hydrogen deficient)

Although the data dispersion is high, it is possible to identify similarities with Vīķu and Svētupes Mire peat PCA results. The results outline three separate segments with the distinction between peat elemental composition, organic/inorganic matter ratio and Me accumulation in studied fen peat (Fig. 3.57). Full information on the nature of associations between Me content and peat characteristics can be found in Appendix 9. Obtained data show on the heterogeneity of associations between Me content and peat characteristics, thus set of peat characteristics with impact on Me concentration is individual (Fig. 3.58-3.60). However, similarities can also be identified.

Figure 3.58 **Statistically significant correlations between metallic elements and peat characteristics in Vīķu Mire peat profile (p < 0.05; n = 50)**

Figure 3.59 **Statistically significant correlations between metallic elements and peat characteristics in Svētupes Mire peat profile (p < 0.05; n = 44)**

Figure 3.60 **Statistically significant correlations between metallic elements and peat characteristics in Elku Mire peat profile (p < 0.05; n = 40)**

Data demonstrate that alkaline earth and alkali metal content in peat generally depend on peat elemental composition, peat botanical composition and decomposition degree, while transition metal content has a significant impact from peat inorganic matter and groundwater.

CONCLUSIONS

Aim of this work was to ascertain fen peat physico-chemical properties and composition using multi-proxy analysis methods in regard to evaluate peat composition influence on metallic element accumulation in fens. The author concludes that the objective has been achieved, main tasks fully accomplished and thesis for defence instrumentally proven.

Main conclusions are as follows:

- Fen peat organic matter generally consists of phenolic and carboxylic group containing compounds, proteins and polycyclic aromatic compounds. Fen peat organic matter can be characterized using humic substance fluorescence index, which depends on peat botanical composition – humic substances are more concentrated in well decomposed grass fen peat, than in decomposed wood fen peat.
- Peat humification in weak acidic/alkaline environment of fens differs from peat humification in bogs. Peat decomposition in upper peat layers exceeds 40% and shows on intensive peat decomposition in oxygen rich peat layers; however, humification index (K-value) does not follow this pace and it can increase or decrease to extreme levels within few centimetres.
- Links between fen peat characteristics are site-dependent; however, in all cases, peat botanical composition, decomposition degree and relation between organic and inorganic matter in peat is of high importance in the variability of fen peat characteristics.
- Metallic element accumulation character in fen peat profile due to its heterogeneous nature (variable botanical composition and physico-chemical characteristics), hydrological and hydrogeological conditions in mire catchment area (including deposit character) has site-dependent character.
- Links between fen peat characteristics and metallic element content depend on the origin of particular metallic elements. Alkaline earth and alkali metal content is linked to peat botanical composition and elemental composition, while transition metal content in depends on mineral matter character.
- Upper peat layers in studied mires contain an increased amount of heavy metals what can be explained by modern anthropogenic impact. However, only Pb and Cd content can be considered as significant, while other heavy metal enrichment, their geo-accumulation and pollution can be considered as low and insignificant.

REFERENCES

1. Ahn, C., Gillevet, P. M., Sikaroodi, M., Wolf, K. L. 2009. An assessment of soil bacterial community structure and physicochemistry in two microtopographic locations of a palustrine forested wetland. Wetlands Ecology and Management 17, 397-407.

2. Aiken, G., Costaris, E. 1995. Soil and hydrology: their effect on NOM. Journal of American Water Works Association 87, 36-45.

3. Alexander, P. D., Bragg, N. C., Meade, R., Padelopoulos, G., Watts, O. 2008. Peat in horticulture and conservation: the UK response to a changing world. Mires and Peat 3, 1-10.

4. Allen, V., Barker, D., Pilbeam, J. 2007. Handbook of plant nutrition. CRC Press.

5. Almendros, G., Polo, A., Vizcayno, C. 1982. Application of thermal analysis to the study of several Spanish peats. Journal of Thermal Analysis and Colorimetry 24, 175-182.

6. Amir, S., Jouraiphy, A., Meddich, A., El Gharous, M., Winterton, P., Hafidid M. 2010. Structural study of humic acids during composting of activated sludge-green waste: elemental analysis, FTIR and 13C NMR. Journal of Hazardous Materials 177, 524-529.

7. Andrews, S. A., Huck, P. M. 1996. Using fractionated natural organic matter to study ozonation by-product formation, 411-447. In: Disinfection Byproducts in Water Treatment: Chemistry of Their Formation and Control (eds. Minear, R. A. and Amy, G. L.). Lewis Publishers, Boca Raton.

8. Atgin, R. S., El-Agha, O., Zararsız, A., Kocataş, A., Parlak, H., Tuncel, G. 2000. Investigation of the sediment pollution in Izmir Bay: trace elements. Spectrochimica Acta 55, 1151-1164.

9. Baker, A. 2001. Fluorescence excitation-emission matrix characterization of some sewage impacted rivers. Environmental Science & Technology 35(5), 948-953.

10. Bambalov, N. N. 2012. Use of peat as an organic raw material for chemical processing. Solid Fuel Chemistry 46(5), 282-288.

11. Baran, A. 2002. Characterization of Carex Peat using Extinction Values of Humic Acids. Bioresource Technology 85(1), 99-101.

12. Belyea, L. R., Clymo, R. S. 2001. Feedback control of the rate of peat formation. Proceedings of the Royal Society of London: Biological Sciences 268, 1315-1321.

13. Benner, R., Biddanda, B. 1998. Photochemical transformations of surface and deep dissolved organic matter: Effects on bacterial growth. Limnology and Oceanography 43, 1373-1378.

14. Bettelheim, F. A., Farrell, S. O., Brown, W. H., Torres, O. J., Campbell, M. K. 2015. Introduction to general, organic and biochemistry. 10th edition. Brooks/Cole.

15. Biester, H., Müller, G., Schöler, H. F. 2002. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. The Science of the Total Environment 284, 191-203.

16. Birch, G. 2003. A scheme for assessing human impacts on coastal aquatic environments using deposits. Paper No: 14. In: Coastal GIS 2003: an integrated approach to Australian coastal issues (eds. Woodroffe, C. D. and Furness, R. A.). Wollongong University Papers in Centre for Maritime Policy.

17. Blaauw, M. 2010. Methods and code for 'classical' age-modelling of radiocarbon sequences. Quaternary Geochronology 5(5), 512-518.

18. Black, W. A. P., Cornhill, W. J., Woodward, F. N. 1955. A preliminary investigation on the chemical composition of Sphagnum moss and peat. Journal of Applied Chemistry 5, 484-492.

19. Blackford, J. J., Chambers, F. M. 1993. Determining the degree of peat decomposition for peat-based palaeoclimatic studies. International Peat Journal 5, 7-24.

20. Bohlin, E., Hamalainen, M., Sunden, T. 1989. Botanical and chemical characterization of peat using multivariate methods. Soil Science 147, 252-263.

21. Borgmark, A. 2005. Holocene climate variability and periodicities in south-central Sweden, as interpreted from peat humification analysis. Holocene 15, 387-395.

22. Bragazza, L., Siffi, C., Iacumin, P., Gerdol R. 2007. Mass loss and nutrient release during litter decay in peatland: the role of microbial adaptability to litter chemistry. Soil Biology & Biochemistry 39, 257-267.

23. Bragg, O. M., Tallis, J. H. 2001. The sensitivity of peat-covered upland landscapes. Catena 42, 345-360.

24. Brennan, T. J., Vandermeulen, E. P., Gebhart, G. F. 1996. Characterization of a rat model of incisional pain. Pain 64, 493-501.

25. Brix, H., Sorrell, B. K., Lorenzen, B. 2001. Are Phragmites-dominated wetlands a net source or net sink of greenhouse gases? Aquatic Botany 69, 313-324.

26. Brown, P. A., Gill, S. A., Allen, S. J. 2000. Metal removal from wastewater using peat. Water Resources 34, 3907-3916.

27. Brunauer, S., Emmett, P. H., Teller, E. 1938. Adsorption of Gases in Multimolecular Layers. Journal of the American Chemical Society 60(2), 309-319.

28. Bulgarlu, L., Bulgarlu, D., Macoveanu., M. 2011. Adsorptive Performance of Alkaline Treated Peat for Heavy Metal Removal. Separation Science and Technology 46(6), 1023-1033.

29. Bulut, Y., Tez, Z. 2007. Adsorption studies on ground shells of hazelnut and almond. Journal of Hazardous Materials 149(1), 35-41.

30. Burba, P. Beer, A. M., Lukanov, J. 2001. Metal Distribution and Binding in Balneological Peats and their Aqueous Extracts. Fresenius Journal of Analytical Chemistry 37(4), 419-425.

31. Cabaniss, S. E., Zhou, Q., Maurice, P. A., Chin, Y. P., Aiken, G. R. 2000. A log-normal distribution model for the molecular weight of aquatic fulvic acids. Environmental Science Technologies 34(6), 1103-1109.

32. Chapman, S. J., Campbell, C. D., Fraser, A. R., Puri, G. 2001. FTIR spectroscopy of peat in and bordering Scots pine woodland: relationship with chemical and biological properties. Soil Biology & Biochemistry 33, 1193-1200.

33. Charman, D. 2002. Peatlands and Environmental Change. John Wiley & Sons Ltd, West Sussex, England.

34. Chen, W., Westerhoff, P., Leenheer, J. A., Booksh, K. 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environmental Science Technologies 37, 5701-5710.

35. Choudhry, G. G. 1984. Humic substances: structural, photophysical, photochemical and free radical aspects and interactions with environmental chemicals. Gordon and Breach Science Publishers.

36. Čivić, K., Jones-Walters, L. 2010. Peatlands in Ecological Networks in Europe Peatlands in Ecological Networks in Europe. November 2010 report. ECNC European Centre for Nature Conservation.

37. Clarke, D., Rieley, J. 2010. Strategy for Responsible Peatland Management, International Peat Society, Jyväskylä, Finland.

38. Clymo, R. S. 1983. Peat, 159-224. In: Mires: swamp, bog, fen and moor. General studies. Ecosystems of the world, General studies (ed. Gore, A. J. P.). Amsterdam, Elsevier.

39. Coble, P. G. 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry 51, 325-346.

40. 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.

41. Cory, R. M., McKnight, M. D. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environmental Science Technology 9, 8142-8149.
42. Couillard, D. 1994. The use of peat in wastewater treatment. Water Research 28, 1261-1274.
43. Coupal, B., Lalancette, J. M. 1976. The treatment of wastewaters with peat moss. Water Research 10(12), 1071-1076.
44. Crowder, A. 1991. Acidification, metals and macrophytes. Environmental Pollution 71, 171-203.
45. Damman, A. W. H. 1978. Distribution and movement of elements in ombrotrophic peat bogs. Oikos 30, 480-495.
46. 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 millenia: Human impact an e regional to global scale. Science of the Total Environment 377, 282-295.
47. Dellwig, O., Bottcher, M. E., Lipinski, M., Brumsack, H. J. 2002. Trace metals in Holocene coastal peats and their relation to pyrite formation (NW Germany). Chemical Geology 182, 423-442.
48. Driessen, P. M., Rochimah, L. 1976. The physical properties of lowland peats from Kalimantan. Peat and Podzolic Soils and Their Potential for Agriculture in Indonesia. Proc. ATA 106 Midterm Seminars. Soil Research Institute, Bogor, Indonesia. Bulletin No. 3, 56-67.
49. Dżugan, M., Zielińska, S., Hęclik, J., Pieniążek, M., Szostek, M., Dżugan, I. M. 2012. Evaluation of heavy metals environmental contamination based on their concentrations in tissues of wild pheasant (Phasianus Clochicus L.). Journal of Microbiology, Biotechnology and Food Sciences 2, 238-245.
50. Ellenberg, H. 1988. Vegetation ecology of Central Europe. Cambridge University Press, Cambridge, 731.
51. Ellis, C. J., Rochefort, L. 2006. Long-term sensitivity of a High Arctic wetland to Holocene climate change. Journal of Ecology 94, 441-454.
52. Febrianto, J., Kosasiha, A. N., Sunarsob, J., Jua, Y., Indraswati, N., Ismadji, S. 2004. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. Journal of Hazardous Materials 162, 616-645.
53. Finlayson, C. M., van der Valk, A. G. 1995. Classification and Inventory of the World's Wetlands. Springer Science+Business Media, B. V.
54. Fong, S. S., Seng, L., Mat, H. B. 2007. Re-use of nitric acid in the oxidative pretreatment step for preparation of humic acids from low rank coal of Mukah, Sarawak. Journal of The Brazilian Chemical Society 18, 41-46.
55. Fortescue, J. A. C. 1980. Environmental geochemistry a holistic approach. Springer-Verlag.
56. Foster, D. R., Fritz, S. C. 1987. Mire development, pool formation and landscape processes on patterned Fens in Dalarna, central Sweden. Journal of Ecology 75, 409-437.
57. Francioso, O., Ciavatta, C., Montecchio, D., Tugnoli, V., Sánchez-Cortes, S., Gessa, C. 2003. Quantitative estimation of peat, brown coal and lignite humic acids using chemical parameters, H-NMR and DTA analyses. Bioresource technology 88, 189-195.
58. Frontasyeva, M. V., Steinnes, E. 2005. Distribution of 35 elements in peat cores from ombrotrophic bogs studied by epithermal neutron activation analysis. Journal of Radioanalytical and Nuclear Chemistry 265(1), 11-15.
59. Fuchsman, C. H. 1980. Industrial chemistry and Technology. Academic press, New York.
60. Gadd, G. M. 2009. Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. Journal of Chemical Technology and Biotechnology 84, 13-28.

61. Galapate, R. P., Baes, A. U., Ito, K., Mukai, T., Shoto, E., Okada, M. 1998. Detection of domestic wastes in Kurose River using synchronous fluorescence spectroscopy. Water Research 32(7), 2232-2239.

62. Gambrell, R. P. 1994. Trace and toxic metals in wetlands – a review. Journal of Environmental Quality 23, 883-891.

63. Gilucis, A. 2007. Mikro- un makroelementu satura un izplatības likumsakarības Latvijas augšņu virsējos horizontos. Promocijas darbs. Latvijas Universitāte.

64. 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., Shotyk, 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.

65. Glooshenko, V., Blancher, P., Herskowitz, J., Fulthorpe, R., Rang, S. 1986. Association of wetland acidity with reproductive parameters and insect prey of the Eastern Kingbird (*Tyrannus tyrannus*) near Sudbury, Ontario. Water, Air and Soil Pollution 30, 553-567.

66. Gnatowski, T., Szatylowicz, J., Brandyk, T., Kechavarzi, C. 2010. Hydraulic properties of peat in Poland. Geoderma 154, 188-195.

67. Goldschmidt, V. 1937. The principles of distribution of chemical elements in minerals and rocks. Journal of the Chemical Society, 655–673.

68. Gondar, D., Lopez, R., Fiol, S., Antelo, J. M., Arce F. 2005. Characterization and acid-base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. Geoderma 126, 367-374.

69. Grebb, S. F., DiMichele, W. A., Gastaldo, R. A. 2006. Evolution and importance of wetlands in earth history, 1-40. In: Wetlands through time (eds. Grebb, S. F. and DiMichele, W. A.). Geological Society of America, Special Paper 399.

70. Gupta, A., Rai, D. K, Pandey, R. S., Sharma, B. 2009. Analysis of some heavy metals in the riverine water, deposits and fish from Ganges at Allahabad, Environmental Monitoring and assessment 157(1-4), 449-458.

71. Hajnos, M., Korsuskaia, L., Pachepsky, Y. 2000. Soil pore surface properties in management of grasslands. Soil and Tillage Research 55, 63-70.

72. Håkanson, L. 1980. An Ecological Risk Index for Aquatic Pollution Control: A Sedimentological Approach. Water Research 14, 975-1001.

73. 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.

74. Henderson, R. K., Baker, A., Murphy, K. R., Hamblya, A., Stuetz, R. M., Khan, S. J. 2009. Fluorescence as a potential monitoring tool for recycled water systems: A review. Water Resources 43, 863-881.

75. Ho, Y. S., McKay, G. 1999. Batch lead (II) removal from aqueous solution by peat: Equilibrium and kinetics. Process Safety and Environmental Protection 77, 165-173.

76. Ho, Y. S., McKay, G. 2004. Sorption of copper (II) from aqueous solution by peat. Water, Air and Soil Pollution 158, 77-97.

77. Hudson, N., Baker, A., Reynolds, D. 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters: A review. River Research and Applications 23, 631-649.

78. Huges, 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.

79. Ilnicki, P., Zeitz, J. 2003. Irreversible loss of organic soil functions after reclamation, 15-32. In: Organic soils and peat materials (eds. Parent, L. E. and Ilnicki, P.). CRC Press, Boca Raton.

80. Ingram, H. A. P. 1978. Soil layers in mires: function and terminology. Journal of Soil Science 29, 224-227.

81. Jaffe, R., Mcknight, D. M., Maie, N., Cory, R. M., McDowell, W. H., Campbel, J. L. 2008. Spatial and temporal variations in DOM composition in ecosystems; the importance of longterm monitoring of optical properties. Journal of Geophysical Research 113:G04032.

82. Jennifer, M. J., Hao, J. 1993. Ombrotrophic peat as a medium for historical monitoring of heavy metal pollution. Environmental Geochemistry and Health 15(2/3), 67-74.

83. Joliffe, I. T. 2002. Principal Component Analysis. 2nd edition. Springer-Verlag, Berlin.

84. Joosten, H., Clarke, D. 2002. Wise use of mires and peatlands. International Mire Conservation Group/International Peat Society.

85. Jowsey, P. C. 1966. An improved peat sampler. New Phytologist 65, 245-248.

86. Kalaitzidis, S., Christanis, K., Georgakopoulos, A., Fernandez-Turiel, J. L., Papazisimou, S. 2002. Influence of geological conditions during peat accumulation on trace element affinities and their behaviour during peat combustion. Energy & Fuels 16, 1476-1482.

87. Kalbitz, K., Geyer, W., Geyer, S. 1999. Spectroscopic properties of dissolved humic substances: a reflection of land use history in a fen area. Biogeochemistry 47, 219-238.

88. Kalnina, L., Nikodemus, O. Silamikele, I., Platniece, D. 2003. Influences of hydrological change on peat humification, microfossil stratigraphy and chemistry in mires of Kemeri National Park, 64-70. In: Eco-hydrological processes in Northern wetlands. (eds. Järvet, A. and Lode, E.) Selected papers. Tallinn-Tartu.

89. Karageorgis, A. P., Nikolaidis, N. P., Karamanos, H., Skoulikidis, N. 2003. Water and sediment quality assessment of the Axios River and its coastal environment. Continental Shelf Research 23, 1929-1944.

90. Keeler, J. 2010. Understanding NMR spectroscopy. 2nd edition. Wiley, New York.

91. Kellner, E., Lundin, L. C. 2001. Calibration of time domain reflectometry for water content in peat soil. Nordic Hydrology 32, 315-332.

92. Kemp, W. 1991. Organic spectroscopy. 3rd edition. McMillan Press, Hong Kong.

93. Klavins, M., Krumins, J., Bunere, S. 2015. Soil substrate for use in organic farming and method of producing thereof. No. LV15013. Applicant: Latvijas Universitāte. Classification: international (C05D9/00; C05F11/02), cooperative. Application number: LV20150000025 20140305.

94. Kļaviņš, M. 1993. Immobilization of humic substances. Latvijas Ķīmijas Žurnāls 1, 96-102.

95. Klavins, M., Porshnov, D 2013. Development of a new peat-based oil sorbent using peat pyrolysis. Environmental Technology 34(12), 1577-1582.

96. Klavins, M., Sire, J., Purmalis, O., Melecis, V. 2008. Approaches to estimating humification for peat. Mires and Peat 3, 1-17.

97. Knorr, K. H., Lischeld, G., Blodau, C. 2009. Dynamics of redox processes in a minerotrophic fen exposed to a water table manipulation. Geoderma 153(3-4), 379-392.

98. Koretsky, C. M., Haas, J. R., Miller, D., Ndenga, N. T. 2006. Seasonal variations in pore water and sediment geochemistry of littoral lake deposits (Asylum Lake, MI, USA). Geochemical Transactions 7:11.

99. Korjakins, A., Toropovs, N., Kara, P., Upeniece, L. 2013. Application of peat, wood processing and agricultural industry by-products in producing the insulating building materials. Journal of Sustainable Architecture and Civil Engineering 1(2), 1-7.

100. Krachler, M., Mohl, C., Emons, H., Shotyk, 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.

101. 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.

102. Krumins, J., Kuske, E. 2012. The distribution regularities of calcium and magnesium in fen peat profile, 42-55. In: Scientific papers of University of Latvia, Earth and environmental sciences 785. (ed. Zelcs, V.). University of Latvia, Riga.

103. Krūmiņš, J., Robalds, A., Purmalis, O., Ansone, L., Poršņovs, D., Kļaviņš, M., Segliņš V. 2013. Kūdras resursi un to izmantošanas iespējas. Materiālzinātne un lietišķā ķīmija 29, 82-94.

104. Kuhry, P., Vitt., D. H. 1996. Fossil carbon/nitrogen ratios as a measure of peat decomposition. Ecology 77, 271-275.

105. Kušķe, E., Silamiķele, I., Kalniņa, L., Kļaviņš, M. 2010. Peat formation conditions and peat properties: a study of two ombrotrophic bogs in Latvia, 56-71. In: Mires and peat 7.

106. Lamacraft, R. R. 1979. A method of displaying differences in botanical composition. Australian Journal of Ecology 4, 407-409.

107. Langlais, B., Reckhow, D. A., Brink, D. R. 1991. Ozone in Water Treatment: Application and Engineering. Lewis Publishers, Ann Arbour, MI.

108. Larsen, L. G., Aiken, G. R., Harvey, J. W., Noe, G. B., Crimaldi, J. P. 2010. Using fluorescence spectroscopy to trace seasonal DOM dynamics, disturbance effects, and hydrologic transport in the Florida Everglades. Journal of Geophysical Research 115: G03001.

109. Le Roux, G., de Vleeschouwer, F. (2010) Preparation of peat samples for inorganic geochemistry used as palaeoenvironmental proxies. Mires and Peat 7, 1-9.

110. Li, L., Zhao, Z., Huang, W., Peng, P., Sheng, G., Fu, J. 2004. Characterization of humic acids fractionated by ultrafiltration. Organic Geochemistry 35, 1025-1037.

111. Lindsay, R. 2009. Peatbogs and carbon: a critical synthesis to inform policy development in oceanic peat bog conservation and restoration in the context of climate change. University of East London.

112. Liu, X., Hu, L., Wang, H. 2002. Investigations into the mid-infrared Christiansen effect of the dispersive materials. Infrared Physics and Technology 43(6), 401-405.

113. Lu, X. Q., Childers, D. L., Hanna, J. V., Maie, N., Jaffe, R. 2003. Molecular characterization of dissolved organic matter in freshwater wetlands of the Florida Everglades. Water Resources 37, 2599-2606.

114. Lucas, L. T. 1982. Population dynamics *of Belonolaimus longicaudatus* and *Criconemella ornata* and growth response of bermudagrass and overseeded grasses on golf greens following treatments with nematicides. Journal of Nematology 14, 358-363.

115. Maie, N., Boyer, J. N., Yang, C., Jaffé, R. 2006. Spatial, geomorphological and seasonal variability of CDOM in estuaries of the Florida Coastal Everglades, Hydrobiologia 569, 135-150.

116. Maie, N., Yang, C., Miyoshi, T., Parish, K., Jaffé, R. 2005. Chemical characteristics of dissolved organic matter in an oligotrophic subtropical wetland/estuarine ecosystem Limnology and Oceanography 50, 23-35.

117. Maltby, E., Proctor, M. C. F. 1996. Peatlands: their nature and role in the biosphere, 11-19. In: Global Peat Resources (ed. Lappalainen, E.), International Peat Society, Finland.

118. 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.

119. Markert, B. 1991. Inorganic chemical investigation in the Forest Biosphere Reserve near Kalinin, USSR. Vegetation 95, 127-135.

120. Martin, S., Griswold, W. 2009. Human Health Effects of Heavy Metals. Environmental Science and Technology Briefs for Citizens, Centre for Hazardous Substance Research (CHSR).

121. Martinez-Cortizas, A., Garcia-Rodeja, E., Pontevedra-Pombal, X., Nóvoa-Muňoz, J. C., 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. The Science of the Total Environment 292, 33-44.

122. Mayhew, L. 2004. Humic Substances in Biological Agriculture. Agres 34, 1-2.

123. McBride, M. B. 1994. Environmental chemistry of soils. Oxford University Press, Oxford.

124. McKnight, D. M., Bencala, K. E., Zellweger, G. W., Aiken, G. R., Feder, G. L., Thorn, K. A. 1992. Sorption of dissolved organic carbon by hydrous aluminium and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. Environmental Science Technologies 26, 1388-1396.

125. McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., Andersen, D. T. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnology and Oceanography 46, 38-48.

126. McMorrow, J. M., Cutler, M. E., Evans, M. 2002. Synergy of HyMap and digital elevation data for the analysis of upland peat erosion patterns and composition. Final report to BNSC and NERC.

127. Mitsch, W. J., Gosselink, J. G. 2000. Wetlands. Wiley, New York.

128. Mladenov, N., McKnight, D. M., Wolski, P., Ramberg, L. 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta of Botswana. Wetlands 25(3), 622-638.

129. Mobed, J. J., Hemmingsen, S. L., Autry, J. L., McGown, L. B. 1996. Fluorescence characterization of IHSS humic substances: Total luminescence spectra with absorbance correction. Environmental Science Technologies 30, 3061-3065.

130. Moore, P. D., Webb, J. A. 1978. An Illustrated Guide to Pollen Analysis. Hodder and Stoughton, London.

131. Myllykangas, T., Nissinen, T., Rantakokko, P., Martikainen, P. J., Vartiainen, T. 2002. Molecular size fractions of treated aquatic humus. Water Resources 36(12), 3045-3053.

132. Neto, R., Mead, R. N., Louda, W. J., Jaffe, R. 2006. Organic biogeochemistry of detrital flocculent material (floc) in a subtropical, coastal wetland. Biogeochemistry 77, 283-304.

133. Niemeyer, H. M., Coapaja, S. V., Barría, B. N. 1992. The Triticeae as sources of hydroxamic acids, secondary metabolites in wheat conferring resistance against aphids. Hereditas 116, 295-299.

134. Nikodemus, O., Brumelis, G., Tabors, G., Lapina, L., Pope, S. 2004. Monitoring of air pollution in Latvia between 1990 and 2000 using moss. Journal of Atmospheric Chemistry 49, 521-531.

135. Nomals, P. 1936. Latvijas purvi. Latvijas zeme, daba un tauta. II Latvijas daba. Valtera un Rapas akciju sabiedrības apgāds, 259-320.

136. Nomals, P. 1930. Ūdens, minerālvielu un slāpekļa daudzums un grupējums Latvijas purvos. Doktora darbs. Latvijas Universitāte.

137. Nomals, P. 1937. Kurzemes purvu apskats. Rīgas Latviešu biedrības zinātņu komitejas rakstu krājums. Dabas zinātņu raksti, 161-150.

138. Nomals, P. 1939. Zemgales purvu apskats. LU raksti, Lauksaimniecības fakultātes sērija, IV, 225-428.

139. Nomals, P. 1943. Vidzemes un Latgales purvu apskats. Zemes bagātību pētīšanas institūta raksti.

140. Norton, S. A. 2007. Atmospheric metal pollutants – archives, methods and history. Water, Air and Soil Pollution 7, 93-98.

141. Nriagu, J. O. 1983. Lead and lead poisoning in antiquity. NewYork: John Wiley and Sons.

142. Ohno, T., Bro, R. 2006. Dissolved organic matter characterization using multiway spectral decomposition of fluorescence landscapes. Soil Science of America Journal 70, 2028-2037.

143. Okruszko, H. 1993. Transformation of fen-peat soil under the impact of draining. Polish Academy of Sciences Publication 406, 3-75.

144. Orru, M., Orru, H. 2006. Sources and distribution of trace elements in Estonian peat. Global and planetary change 53, 249-258.

145. Orru, M., Orru, H. 2008. Sustainable use of Estonian peat reserves and environmental challenges. Estonian Journal of Earth Sciences 57(2), 87-93.

146. Overbeck, F. 1975. Botanisch-geologisch Moorkunde. Karl Wacholtz Verlag Neumünster.

147. Overbeck, F., 1947. Studien zur hochmoorentwicklung in niedersachsen und die bestimmung der humifizierung bei stratigraphisch-pollenanalytischen mooruntersuchungen. Planta 35, 1-56.

148. Özkan, E. Y. 2012. A new assessment of heavy metal contaminations in an Eutrophicated Bay (Inner Izmir Bay, Turkey). Turkish Journal of Fisheries and Aquatic Sciences 12, 135-147.

149. Pacyna, J., Pacyna, E., Aas, W. 2009. Changes of emission and atmospheric deposition of mercury, lead and cadmium. Athmospheric Environment 43, 117-127.

150. Pakalne, M., Kalniņa, L. 2000. Mires in Latvia. Suoseura 51(4), 213-226.

151. Paykov, O., Hawley, H. 2013. A novel method for specific surface area determination in swelling clays. Geotechnical Testing Journal 36(4), DOI: 10.1520/GTJ20120197.

152. Peiris, R. H., Hallé, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P. M., Legge, R. L. 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices. Water research 44(1), 185-194.

153. Pekey, H. 2006. The distribution and sources of heavy metals in Izmir Bay surface deposits affected by a polluted stream. Marine Pollution Bulletin 52, 1197-1208.

154. Pernet-Coudrier, B., Croue, J. P., Varrault, G., Dignac, M. F., Saad, M., Mouchel, J. M. 2011. Characterization of dissolved organic matter in Parisian urban aquatic systems: predominance of hydrophilic and proteinaceous structures. Biogeochemistry 106, 89-106.

155. Peuravuori, J., Paaso, N., Pilhaja, K. 2002. Sorption behaviour of some chlorophenols in lake aquatic humic matter. Talanta 56, 523-538.

156. Piotrowska, D. G., Cieslak, M., Królewska, K., Wróblewski, A. E. 2011. Design, synthesis and cytotoxity of a new series of isoxazolidines derived from substituted chalcones. European Journal of Medicinal Chemistry 46, 1382-1389.

157. Potts, P. J. 1987. A handbook of silicate rock analysis. 2nd ed. Blackie.

158. Pujāte, A. 2015. Vides apstākļu izmaiņu un cilvēka darbības pēdas Rīgas līča piekrastes ezeru nogulumos. Promocijas darbs. Latvijas Universitāte.

159. Reimann, C., de Caritat, P. (2005) Distinguishing between natural and anthropogenic sources of element in the environment: regional geochemical surveys versus enrichment factors. Science of the Total Environment 337, 91-107.

160. 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.

161. Rinqvist, L., Holmgren A., Öhorn, I. 2002. Poorly humified peat as an adsorbent for metals in wastewater. Water Resources 36, 2394-2404.

162. Rinqvist, L., Öhorn, I. 2002. Cooper and zinc adsorption onto poorly humified Sphagnum and Carex peat. Water research 36, 2233-2242.

163. Rodríguez, F. J., Núñez, L. A. 2011. Characterization of aquatic humic substances. Water and Environment Journal 25, 163-170.

164. Rustchev, D., Atanasov, O. 1983. Thermal and group analysis of peat. Journal of thermal analysis 27, 439-442.

165. Rydin, H., Jeglum, J. 2008. The Biology of Peatlands. Oxford University Press.

166. Saunders, C. J., Gao, M., Lynch, J. A., Jaffe, R., Childers, D. L. 2006. Using soil profiles of seeds and molecular markers as proxies for sawgrass and wet prairie slough vegetation in Shark Slough, Everglades National Park. Hydrobiologia 569, 475-492.

167. Schoonen, M. A. A. 2004. Mechanisms of sedimentary pyrite formation. Sulfur biogeochemistry – past and present 379, 117-134.

168. Senesi, N. 1990. Molecular and quantitative aspects of the chemistry of fulvic acids and its interactions with metals ions and organic chemicals. Part I. The electron spin resonance approach. Analytica Chimica Acta 232, 51-75.

169. Sheppard, J. D., Forgeron, D. W. 1987. Differential thermogravimetry of peat fractions. Fuel 66, 232-236.

170. Shermer, C. L., Maciorowski, K. G., Bailey, C. A., Byers, F. M., Ricke, S. C. 1998. Caecal metabolites and microbial populations in chickens consuming diets containing a mined humate compound. Journal of the Science of Food and Agriculture 77, 479-486.

171. Shindell, D. T., Schmidt, G. A., Mann, M. E., Faluvegi, G. 2004. Dynamic winter climate response to large tropical volcanic eruptions since 1600. Journal of Geophysical Research 109, D05104.

172. Shotyk, W. 1988. Review of the inorganic geochemistry of peats and peatland waters. Earth Science Reviews 25(2), 95-176.

173. Shotyk, W. 1996. Natural and anthropogenic enrichments of As, Cu, Pb, Sb and Zn in ombrotrophic versus minerotrophic peat bog profiles, Jura Mountains, Switzerland. Water, Air and Soil Pollution 90, 375-405.

174. Shotyk, W., Krachler, M., Martinez-Cortizas, A., Cheburkin, A. K., Emons, H. 2002. A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12 370 14C yr BP, and their variation with Holocene climate change. Earth and Planetary Science Letters 199(1-2), 21-37.

175. Shotyk, W., Le Roux, G. 2005. Biogeochemistry and cycling of lead. Metal Ions in Biological Systems 43, 240-275.

176. Shotyk, W., Steinmann, P. 1994. Porewater indicators of rainwater-dominated versus groundwater-dominated peat bog profiles (Jura Mountains, Switzerland). Chemical Geology 116(1-2), 137-146.

177. Shotyk, W., Weiss, D., Kramers, 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 ^{14}C yr BP. Geochemica et Cosmochimica Acta 65, 2337-2360.

178. Sierra, M. M. D., Giovanela, M., Parlanti, E., Soriano-Sierra, E. J. 2005. Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques. Chemosphere 58, 715-733.

179. Silamiķele, I. 2010. Humifikācijas un ķīmisko elementu akumulācijas raksturs augsto purvu kūdrā atkarībā no tās sastāva un veidošanās. Promocijas darbs. Latvijas Universitāte.

180. Simon, E. C., Thomas, I. 2003. Deposits as archives of industrialization: evidence of atmospheric in coastal wetlands of Southern Sydney, Australia. Water, Air and Soil Pollution 149, 189-210.

181. Spaccini, R., Mbagwu, J. S. C., Conte, P., Piccolo, A. 2006. Changes of humic substances characteristics from forested to cultivated soils in Ethiopia. Geoderma 132, 9-19.

182. Stedmon, C. A., Bro, R. 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnology and Oceanography: Methods 6, 572-579.

183. Stedmon, C. A., Markager, S., Bro, R. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Marine Chemistry 82, 239-254.

184. Stevenson, F. J. 1982. Humus Chemistry – Genesis, Composition, Reactions. N. Y. John Wiley and Sons.

185. Stuart, B. H. 2004. Infrared Spectroscopy: Fundamentals and Applications. John Wiley & Sons, Ltd.

186. Stumm, W., Morgan, J. J. 1996. Aquatic chemistry. 3rd edition. John Willey & Sons, New York.

187. Sun, Q. Y., Lu, P., Yang, L. Z. 2003. The adsorption of lead and copper from aqueous solution on modified peat-resin particles. Environmental Geochemistry and Health 37, 1535-1544.

188. Swietlik, J., Sikorska, E. 2004. Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone. Water Research 38(17), 3791-3799.

189. 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.

190. Tamers, M. A. 2010. Carbon-14 dating with the liquid scintillation counter: total synthesis of the benzene solvent. Science 132, 668-669.

191. Tan, K. H. 2005. Soil sampling, preparation and analysis. 2nd ed. Taylor & Francis Group.

192. Thomas, C. R., Miao, S., Sindhoj, E. 2009. Environmental factors affecting temporal and spatial patterns of soil redox potential in Florida Everglades wetlands, Wetlands 29, 1133-1145.

193. Tipping, E., Smith, E. J., Lawlor, A. J., Hughes, S., Stevens, P. A. 2003. Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. Environmental Pollution 123, 239-253.

194. Tolstoy, V. P., Chernyshova, I. V., Skryshevsky, V. A. 2003. Handbook of infrared spectroscopy 126(47), 15633-15634.

195. Ukonmaanaho, L., Nieminen, T. M., Rausch, N., Shotyk, W. 2004. Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland. Water, Air and Soil Pollution 158, 277-294.

196. van Krevelen, D. W. 1984. Organic geochemistry – old and new. Organical Geochemistry, 65(6), 1-10.

197. Vivian-Smith, G. 1997. Microtopographic heterogeneity and floristic diversity in experimental wetland communities. Journal of Ecology 85, 71-82.

198. von Post, L. 1924. Das Genetische System der Organogenen Bildungen Schwedens. Soil Science 22, 287-304.

199. von Post, L., Granlund, E. 1926. Peat resources in southern Sweden. Stockholm.

200. Walker, M. J. C., Lowe, J. J. 1981. Postglacial environmental history of Rannoch Moor, Scotland III. early-and mid-Flandrian pollen stratigraphic data from sites on western Rannoch Moor and near Fort William. Journal of Biogeography 8(6), 475-491.

201. Weiss, D., Shotyk, W., Rieley, J., Page, S., Gloor, M., Reese, S., Martinez-Cortizas, A. 2002. The geochemistry of major and selected trace elements in a forested peat bog, Kalimantan, SE Asia, and its implications for past atmospheric dust deposition. Geochimica et Cosmochimica Acta 66(13), 2307-2323.

202. Williams, C. J., Yavitt J. B. 2003. Botanical composition of peat and degree of peat decomposition in three temperate peatlands. Ecoscience 10, 85-95.

203. Yavitt, J. B. 1995. Encyclopaedia of environmental biology. London, Academic Press, 345-355.

204. Yeloff, D., Mauquoy, D. 2006. The influence of vegetation composition on peat humification: implications for palaeoclimatic studies. Boreas 35, 662-673.

205. Yu, Z. C., Vitt, D. H., Campbell, I. D., Apps, M. J. 2003. Understanding Holocene peat accumulation pattern of continental fens in western Canada. Canadian Journal of Botany 81, 267-282.

206. Zaccone, C., Cocozza, C., Cheburkin, A. K., Shotyk, W., Miano, T. M. 2007. Enrichment and depletion of major and trace elements, and radionuclides in ombrotrophic raw peat and corresponding humic acids. Geoderma 141, 235-246.
207. 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.
208. Zaccone, C., Santoro, A., Cocozza, C., Terzano, R., Shotyk, W., Miano, T. M. 2009. Comparison of Hg concentrations in ombrotrophic peat and corresponding humic acids, and implications for the use of bogs as archives of atmospheric Hg deposition. Geoderma 148, 399-404.
209. Кац, Н. Я., Кац, С. В., Скобеева, Е. И. 1977. Атлас растительных остатков в торфах. Москва, Недра.
210. Лиштван, И. 1996. Физико-химические свойства торфа. Химическая и термическая его переработка. Химия Твёрдого Топлива Топ 3, 3–23.
211. Тюремнов, С. Н. 1976. Торфяные месторождения. Москва, Недра.

APPENDICES

Appendix 1.   Fen peat elemental composition

Elku mire

Depth, cm	N	C	H	S
10	1.8	44.4	4.5	< 0.5
20	1.4	41.2	3.9	< 0.5
30	1.8	44.4	4.5	< 0.5
70	2.5	43.3	4.7	0.54
105	1.4	44.8	4.8	1.60
110	0.8	48.9	5.1	1.58
145	2.5	46.1	4.9	< 0.5
200	2.0	45.1	5.2	0.54

Svētupes mire

Depth, cm	N	C	H	S
10	2.6	37.8	4.4	< 0.5
30	2.3	38.6	4.3	< 0.5
50	2.1	37.6	3.9	< 0.5
70	1.8	39.2	4.2	< 0.5
80	2.6	34.1	4.3	< 0.5
110	2.7	41.5	4.7	< 0.5
130	2.6	40.0	4.5	< 0.5
150	0.6	33.5	1.2	< 0.5
170	0.5	33.0	1.0	< 0.5
190	1.6	27.6	2.9	< 0.5
210	1.4	39.2	4.3	< 0.5

Vīķu mire

Depth, cm	C	H	N	S
10	38.6	4.5	2.6	< 0.5
30	40.0	4.5	2.4	< 0.5
50	39.4	4.1	2.2	< 0.5
70	40.7	4.4	1.8	< 0.5
90	35.3	4.5	2.6	< 0.5
110	42.2	4.8	2.9	< 0.5
130	40.6	4.6	2.6	< 0.5
150	30.0	3.8	1.9	< 0.5
170	36.2	3.3	1.7	< 0.5
190	31.0	3.3	1.8	< 0.5
210	29.0	3.0	1.5	< 0.5
240	39.8	4.4	1.9	< 0.5
260	28.7	3.8	1.7	6.3

Appendix 2.   Fen peat humic substances emission-excitation matrices

(a)

(b)

(c)

(d)

(e)

a: wood peat; b: grass peat; c: wood-*sphagnum* peat; d: wood-grass peat; e: sedge-*hypnum* peat

Appendix 3. The algorithm used in parallel factor analysis

```
>> DOMFluor
>> OriginalData
>>
PlotEEMby1(1:5,OriginalData,'
R.U.')
>>
PlotEEMby1(5:10,OriginalData,'
R.U.')
>>
[CutData]=EEMCut(Original
Data,20,20,NaN,NaN,'No')
>>
[CutData]=EEMCut(Original
Data,20,20,NaN,NaN,'')
>>
[Test1]=OutlierTest(Cut
Data,2,1,5,'No','No')
>> PlotLoadings(Test1,2)
>> PlotLoadings(Test1,4)
>> PlotLoadings(Test1,5)
>> PlotEEMby1(1:5,CutData,'R.U.')
>>
PlotEEMby1(6:10,CutData,'R.U.')
>> PlotSurfby1(1:5,CutData,'R.U.')
>> PlotSurfby1(6:10,CutData,'R.U.')
>> PlotLL(Test1,2)
>> PlotLL(Test1,3)
>> PlotLL(Test1,4)
>> PlotLL(Test1,5)
>>
[Test2]=OutlierTest(CutData,2,
1,5,'Yes','No')
>> PlotLoadings(Test2,2)
>> PlotLoadings(Test2,3)
>> PlotLoadings(Test2,4)
>> PlotLoadings(Test2,5)
>> PlotLL(Test2,2)
>> PlotLL(Test2,3)
>> PlotLL(Test2,4)
>> PlotLL(Test2,5)
>> EvalModel(Test2,2)
>> EvalModel(Test2,3)
>> EvalModel(Test2,4)
>> EvalModel(Test2,5)
>>
Compare2Models(Test2,3,4)
>> PlotLoadings(Test2,2)
>> CompareSpecSSE(Test2,2,3,4)
>>
[AnalysisData]=SplitData(Test2)
>>
[AnalysisData]=SplitHalfAnaly
sis(AnalysisData,(2:5),'dati.mat')
>>
SplitHalfValidation(Analysis
Data,'1-2',2)
```

```
>>
SplitHalfValidation(Analysis
Data,'3-4',2)
>>
SplitHalfValidation(Analysis
Data,'1-2',3)
>>
SplitHalfValidation(Analysis
Data,'3-4',3)
>>
SplitHalfValidation(Analysis
Data,'1-2',4)
>>
[AnalysisData]=RandInit
Anal(AnalysisData,3,10)
>>
TCC(AnalysisData.Model3,
AnalysisData.Split(1).Fac_3)
Model Split half validated
ans =
   0   1   0
   1   0   0
   0   0   1
>> fingerprint (Test2,3)
>> spectralloadings (Test2,3)
>> comparespectra (Test2,2:5)
>> compcorrplot (Test2,3)
>> specsse (Test2,3)
>> describecomp (Test2,3)
*****************************
*******
Description of PARAFAC
components – Model3
*****************************
*******
Component 1
Ex
 524.0000  0.0010
 518.0000  0.0015
 512.0000  0.0015
 329.0000  0.1850
Em
 445.7790  0.1947
*****************************
*******
Component 2
Ex
 482.0000  0.1744
 470.0000  0.2069
 419.0000  0.1023
 308.0000  0.0345
Em
 578.6900  0.2788
*****************************
*******
Component 3
```

```
Ex
 461.0000  0.1742
 455.0000  0.1739
 428.0000  0.1777
 419.0000  0.1775
 401.0000  0.1463
 395.0000  0.1452
 389.0000  0.1422
 383.0000  0.1409
Em
 498.7890  0.3056
ans =
  [1x2 double]  [1x2 double]
[1x2 double]
  [4x2 double]  [4x2 double]
[8x2 double]
>>
*****************************
*******
Description of PARAFAC
components – Model3
*****************************
*******
Component 1
Ex
 524.0000  0.0010
 518.0000  0.0015
 512.0000  0.0015
 329.0000  0.1850
Em
 445.7790  0.1947
*****************************
*******
Component 2
Ex
 482.0000  0.1744
 470.0000  0.2069
 419.0000  0.1023
 308.0000  0.0345
Em
 578.6900  0.2788
*****************************
*******
Component 3
Ex
 461.0000  0.1742
 455.0000  0.1739
 428.0000  0.1777
 419.0000  0.1775
 401.0000  0.1463
 395.0000  0.1452
 389.0000  0.1422
 383.0000  0.1409
Em
 498.7890  0.3056
```

Appendix 4. Fen peat humic substance four component model

Appendix 5. Differential thermal analysis and thermogravimetry results

Sedge-*sphagnum* fen peat

Sedge fen peat

Wood-sedge fen peat

Wood fen peat

Wood-*sphagnum* fen peat

Wood-grass fen peat

Grass fen peat

Appendix 6.   Associations between fen peat characteristics

Statistically significant correlations (p > 0.05) between peat characteristics in Elku peat profile

	PD	PA	DD	HI	SR	WR	FI	TGI	M	OM	AC	MM	C	N	H	O
PA	0.98															
DD	-0.92	-0.87														
HI	-0.98	-0.97	0.85													
SR	0.70	0.75	-0.78													
WR	-0.96	-0.95	0.79	0.97												
FI	-0.79	-0.77	0.92	0.70	-0.90	0.67										
M	0.84	0.76	-0.93	-0.82		-0.74	-0.78									
OM	-0.68	-0.65		0.76		0.69		0.72	-0.66							
AC	0.68	0.65		-0.76		-0.69		-0.72	0.66	-1.00						
MM	0.66			-0.72		-0.64		-0.87	0.66	-0.97	0.97					
C					0.76	-0.64										
H	0.83	0.86	-0.74	-0.77	0.75	-0.80	-0.65						0.80			
O	-0.64	-0.69	0.63		-0.83		0.67						-0.96		0.91	
N/C														0.99		
H/C	0.84	0.85	-0.64	-0.86		-0.89			-0.77	0.77	0.72				0.86	
O/C		-0.63			-0.80	0.66							-0.98		-0.89	0.99

(PD – peat depth; PA – peat age; DD – decomposition degree; HI – humification index; SR – sedge remains; WR – wood remains; FI – fluorescence index; TGI – thermogravimetric index; M – moisture; OM – organic matter; AC – ash content; MM – mineral matter)

Statistically significant correlations (p > 0.05) between peat characteristics in Svētupes peat profile

	PA	DD	HI	SR	WR	pH	M	OM	AC	CM	MM	C	N	H	O	N/C	H/C	O/C
PD	0.87	-0.78	-0.86		-0.66	0.82	0.61	-0.61	0.61				-0.62			-0.55		
PA		-0.87	-0.76	0.76	-0.92	0.55	0.69				0.59							
DD			0.62		0.76		-0.66											
HI				-0.57	0.57	-0.57	-0.62						0.56			0.59		
SR					-0.86		0.60											
WR							-0.69											
pH								-0.86	0.86	0.83	0.88	-0.61	-0.88	-0.78	0.76	-0.79	-0.71	0.68
FI													0.72		-0.56	0.62		
OM									-1.00	-0.99	-0.97	0.73	0.88	0.96	-0.88	0.77	0.87	-0.79
AC										0.99	0.97	-0.73	-0.88	-0.96	0.88	-0.77	-0.87	0.79
CM											0.92	-0.70	-0.85	-0.94	0.85	-0.75	-0.87	0.76
MM												-0.74	-0.88	-0.94	0.89	-0.76	-0.85	0.79
C														0.66	-0.96			-0.99
N														0.90	-0.73	0.96	0.89	-0.58
H															-0.85	0.82	0.95	-0.71
O																	-0.65	0.97
N/C																		0.90

(PD – peat depth; PA – peat age; DD – decomposition degree; HI – humification index; SR – sedge remains; WR – wood remains; FI – fluorescence index; OM – organic matter; AC – ash content; CM – carbonate matter; MM – mineral matter)

Statistically significant correlations (p > 0.05) between peat characteristics in Vīķu peat profile

	PA	DD	SR	WR	pH	FI	TGI	M	OM	AC	CM	MM	C	N	H	O	N/C	O/C
PD	0.99	-0.55	0.84	-0.68			-0.57	0.90	-0.53			-0.56	-0.60	-0.64	-0.56	0.53		0.60
PA		-0.53	-0.68				-0.57	0.92	0.56	-0.56		-0.60	-0.59	-0.62	-0.58	0.54		0.60
DD			-0.62	0.95		0.54		-0.73	-0.86	0.86	0.79	0.82		0.62				
HI					-0.51													
SR				-0.77		-0.65		0.85	0.69	-0.69		-0.69	-0.58	-0.61		0.62		0.62
WR						0.59		-0.83	-0.90	0.90	0.75	0.87		0.62				
FI														0.53	0.65			
M									0.81	-0.81		-0.84	-0.54	-0.58	-0.51			0.54
OM										-1.00	-0.77	-0.99		0.65	0.79			
AC											0.77	0.99			0.82			
CM												0.65						
C																-0.94		-0.99
N																-0.70	0.76	-0.67
H																-0.88		-0.83
O																		0.97
N/C																		0.64

(PD – peat depth; PA – peat age; DD – decomposition degree; HI – humification index; SR – sedge remains; WR – wood remains; FI – fluorescence index; TGI – thermogravimetric index; M – moisture; OM – organic matter; AC – ash content; CM – carbonate matter; MM – mineral matter)

Appendix 7.   Metallic element concentration

Elku mire (mg/kg), fen peat part of the profile

D., cm	Fe	Mn	Zn	Cu	Mg	Ca	Na	K	Cd	Co	Cr	Ni	Pb
25	748.8	14.0	1.6	1.0	1346.2	25205.3	100.8	17.5	0.07	0.09	1.31	0.23	0.72
30	1100.0	12.7	3.0	0.6	1440.6	27919.6	115.8	20.6	0.07	0.09	0.65	1.35	0.80
35	839.5	8.9	1.9	1.2	1101.0	19863.3	90.0	25.4	0.05	0.25	0.34	0.19	0.15
40	811.2	18.9	2.4	1.4	1221.6	21441.8	79.4	9.5	0.08	0.13	0.49	0.20	0.26
45	1075.7	17.5	4.7	1.3	1198.5	21249.3	107.2	33.0	0.07	0.13	0.47	0.31	0.61
50	1405.5	17.6	0.6	1.0	1352.7	26860.9	68.2	19.3	0.04	0.12	0.29	0.80	0.40
55	2075.8	19.7	1.3	1.2	1362.7	29681.1	71.2	6.3	0.26	0.10	0.33	0.88	0.07
60	1936.3	31.1	0.3	1.3	1265.3	30181.6	79.6	17.1	0.05	0.10	0.41	1.12	0.21
65	2341.3	24.6	2.9	1.3	1204.0	32039.2	79.5	11.6	0.03	0.08	0.40	1.15	0.26
70	2910.1	29.2	0.8	1.1	1311.5	36582.4	75.7	2.2	0.26	0.06	0.41	0.57	0.07
75	2652.5	28.6	0.7	0.7	1069.9	31639.8	71.7	8.0	0.03	0.05	0.32	0.48	0.10
80	3257.5	32.8	0.1	1.3	1247.7	38136.8	73.0	7.8	0.24	0.07	0.36	0.60	0.38
85	2855.5	31.3	1.4	1.5	1064.8	32871.8	91.4	21.6	0.04	0.09	0.52	0.55	0.09
90	3535.6	40.5	0.9	1.4	1296.9	40831.9	92.7	15.0	0.03	0.08	0.41	0.78	0.43
95	2567.6	52.7	5.9	1.4	1229.6	34103.9	101.5	50.4	0.07	0.14	0.59	0.55	3.55
100	3657.1	38.6	0.2	0.6	1081.9	37328.3	78.2	13.2	0.33	0.09	0.33	0.48	0.07
105	3820.1	44.1	0.1	0.7	1067.8	36885.6	77.4	3.6	0.25	0.09	0.30	0.57	0.08
110	3427.8	42.4	4.2	0.8	962.4	33853.6	92.3	16.0	0.29	0.11	0.28	0.44	0.76
115	2957.5	35.1	2.3	0.4	779.5	27635.7	89.0	18.1	0.03	0.11	0.13	0.28	0.14
120	3455.1	36.9	1.5	1.6	1198.5	37472.7	94.5	16.2	0.04	0.08	0.41	0.88	0.13
125	3630.3	39.8	0.1	1.1	1209.5	39229.3	110.9	6.2	0.28	0.08	0.28	0.75	0.07
130	3332.7	38.3	0.4	0.6	1128.1	37208.0	135.9	1.6	0.27	0.09	0.28	0.67	0.07
135	2751.1	30.5	1.8	1.4	1077.9	33598.5	78.5	6.8	0.04	0.07	0.32	0.62	0.35
140	3172.6	54.8	2.8	1.5	1330.1	38959.8	106.6	36.8	0.11	0.05	0.50	0.72	0.76
145	3596.1	41.1	0.1	1.4	1249.7	40759.7	104.0	14.4	0.03	0.07	0.49	1.39	0.23
150	2851.1	39.4	0.4	0.4	850.8	26230.4	62.2	8.2	0.25	0.33	0.25	0.45	0.14
155	3462.0	39.6	0.9	0.7	764.4	27683.8	82.7	18.0	0.04	0.16	0.21	0.19	0.07
160	3747.9	43.1	1.7	1.1	767.4	28646.3	83.6	6.9	0.38	0.14	0.19	0.19	0.64
165	5586.3	32.9	16.8	6.2	698.1	21754.7	103.0	62.7	0.40	1.13	1.43	5.47	0.28
170	2318.3	27.8	2.6	1.8	530.3	16855.4	155.8	23.2	0.06	0.27	0.44	0.82	0.41
175	1948.5	29.0	2.5	4.0	678.5	20354.2	139.0	63.2	0.07	0.56	1.23	2.85	0.46
180	3197.5	23.9	6.4	5.6	559.0	17023.9	115.1	71.2	0.14	0.81	1.33	4.69	0.66
185	4068.9	25.2	17.4	5.2	582.1	17120.1	115.9	39.0	0.13	1.20	1.09	4.84	0.35
190	2672.5	31.4	3.7	0.7	536.9	19372.4	111.9	25.8	0.03	0.18	0.34	0.42	0.07
195	5615.5	31.0	14.7	5.0	942.8	31808.2	117.7	53.8	0.35	0.86	1.43	4.63	0.35

Salas mire (mg/kg)

D., cm	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb
5	54.4	1851.8	68.2	19747.7	13776.7	380.6	1.3	1.7	12.6	5.5	0.26	3.9
10	64.0	1918.7	61.3	19913.6	14489.7	382.2	1.8	1.9	11.9	7.0	0.24	3.1
15	66.6	2050.2	38.8	22234.0	15154.8	417.1	1.6	1.8	14.1	6.0	0.20	< 0.5
20	52.3	1941.3	28.9	21004.8	14348.7	400.7	1.7	2.5	14.2	3.0	0.16	< 0.5
25	60.3	1908.5	32.0	20307.0	13689.9	365.8	2.2	2.8	13.5	3.4	0.18	< 0.5
30	56.4	1901.9	63.4	21698.1	14306.5	398.7	1.4	3.2	14.4	4.7	0.22	1.2
35	65.4	1868.8	101.4	21133.8	12652.4	345.3	1.3	4.4	15.9	6.7	0.24	1.7
40	54.2	1731.3	131.6	19297.0	12284.8	326.4	1.5	4.7	19.8	8.9	0.25	2.2
45	44.1	1518.4	184.2	13538.1	9899.3	197.4	1.2	4.6	15.2	7.3	0.18	4.1
50	54.3	1502.8	217.5	12336.8	10050.0	204.7	1.1	4.4	13.5	7.4	0.13	4.0

Svētupes mire (mg/kg)

D., cm	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb
5	117.7	2204.3	202.4	20498.7	3956.4	54.9	0.53	1.52	7.14	32.11	0.79	43.7
10	125.9	2071.9	106.6	20028.2	2729.9	41.3	0.43	0.93	5.66	14.08	0.35	40.0
15	132.1	2083.3	74.1	18361.0	1710.3	25.8	0.13	0.36	5.16	7.70	0.22	14.1
20	84.1	1570.9	52.3	14895.0	1090.6	15.2	0.20	0.65	5.37	10.60	0.15	8.5
25	90.7	1625.2	38.3	16556.1	971.2	11.6	< 0.12	< 0.16	4.06	13.51	0.22	5.1
30	79.1	1659.7	30.0	18499.4	944.8	15.2	< 0.12	0.54	3.07	7.24	0.13	4.3
35	118.1	2572.9	33.2	29001.2	770.0	21.7	< 0.12	1.47	5.07	3.56	0.17	5.2
40	107.8	2500.1	23.4	28708.3	637.5	23.2	< 0.12	1.25	5.25	4.00	0.15	2.9
45	123.9	3103.4	28.1	36154.3	775.0	84.7	< 0.12	0.95	5.48	0.91	0.24	0.6
50	88.3	2290.0	32.0	26234.6	531.1	16.7	< 0.12	1.08	4.23	2.14	0.08	2.3
55	100.1	2378.3	36.5	26743.0	517.1	17.7	< 0.12	0.43	3.76	2.93	0.16	< 0.5
60	105.9	2422.2	31.1	27100.4	570.2	23.1	< 0.12	0.78	4.62	3.96	0.12	0.6
65	91.0	2220.6	24.5	24484.7	657.5	26.5	0.68	0.67	4.08	2.71	0.10	1.2
70	117.6	2917.6	30.9	33717.8	914.7	43.6	< 0.12	1.01	4.89	1.27	0.18	< 0.5
75	73.5	1864.5	28.5	22346.5	685.7	35.5	< 0.12	1.04	3.77	< 0.2	0.18	< 0.5
80	80.4	2221.3	36.7	28068.2	1227.2	54.0	< 0.12	1.42	5.31	0.65	0.17	< 0.5
85	113.4	2433.7	44.3	31168.0	982.5	60.1	< 0.12	0.83	5.57	1.50	0.19	< 0.5
90	100.8	2507.0	47.4	29761.4	2160.9	62.8	< 0.12	0.71	4.15	12.59	0.18	< 0.5
95	97.3	2381.9	35.7	29846.4	2458.3	58.2	0.12	0.92	4.53	0.29	0.16	< 0.5
100	101.5	2375.8	48.2	23404.6	1482.7	42.6	< 0.12	0.77	1.98	0.26	0.20	< 0.5
105	50.4	1020.1	21.5	10004.0	814.0	18.7	< 0.12	< 0.16	0.89	< 0.2	0.15	< 0.5
110	46.3	1212.9	21.7	14113.5	1319.2	24.5	< 0.12	< 0.16	1.31	0.92	0.13	< 0.5
115	98.7	2062.6	50.5	22613.8	2063.9	47.2	< 0.12	0.69	2.35	2.17	0.15	< 0.5
120	43.3	1246.1	20.8	14711.9	1032.2	24.3	< 0.12	0.15	1.16	< 0.2	0.15	< 0.5
125	91.5	2298.6	47.4	27735.0	1690.8	48.7	< 0.12	0.70	2.24	1.39	0.21	< 0.5
130	50.3	1249.5	31.6	14486.5	812.6	45.4	< 0.12	0.31	1.33	7.28	0.10	< 0.5
135	25.2	616.7	9.0	8602.7	716.5	17.7	0.26	0.52	0.69	0.82	< 0.04	1.0
140	59.4	1357.3	25.0	47779.5	1509.5	34.7	< 0.12	< 0.16	1.09	2.63	0.18	< 0.5
145	64.5	1278.0	23.4	102943.6	1289.4	48.7	1.20	1.17	0.83	2.71	0.11	1.2
150	100.6	1663.6	21.6	152661.1	5760.2	62.2	< 0.12	< 0.16	0.94	2.43	0.15	1.0
155	71.4	1318.6	14.7	123622.5	1409.4	52.6	< 0.12	0.70	0.31	3.95	0.15	1.1
160	76.8	1363.8	11.9	128985.6	1407.8	50.8	< 0.12	0.81	0.37	3.54	0.09	0.5
165	92.8	1666.3	14.3	171262.9	1310.6	49.6	< 0.12	0.78	0.10	1.42	0.13	0.6
170	55.8	1298.3	20.9	60857.1	1777.2	34.1	< 0.12	0.92	0.67	12.15	0.12	< 0.5
175	79.3	1618.8	27.6	63533.5	2064.0	46.4	< 0.12	0.75	1.53	3.75	0.11	< 0.5
180	74.4	1194.6	26.0	45217.2	1286.5	32.6	< 0.12	0.27	0.77	1.69	0.12	< 0.5
185	64.7	1742.8	18.7	49963.7	2925.7	50.2	< 0.12	0.38	1.52	3.21	0.05	< 0.5
190	73.2	1839.6	26.8	63434.4	2896.5	57.4	< 0.12	0.46	1.59	2.48	0.10	< 0.5
195	42.6	1150.7	11.1	32619.8	1644.7	33.4	< 0.12	0.60	1.22	3.21	0.10	< 0.5
200	69.2	2002.9	35.3	77150.9	3839.3	54.0	< 0.12	0.64	1.35	8.01	0.07	1.0
210	79.7	2142.0	32.3	45412.8	5620.5	60.0	< 0.12	0.78	1.29	6.20	0.10	< 0.5
215	90.3	2015.0	35.3	29833.2	6333.2	53.0	< 0.12	0.39	1.09	2.25	0.11	< 0.5

Vīķu mire (mg/kg)

D., cm	Fe	Mn	Zn	Cu	Mg	Ca	Na	K	Cd	Co	Cr	Ni	Pb
5	3681.2	62.9	12.5	6.2	1051.8	18966.4	< 50	180.1	0.26	2.00	1.89	2.78	23.56
10	4728.3	45.8	10.2	6.9	1461.4	30051.0	79.7	157.4	0.24	1.96	2.10	3.25	22.62
20	2600.4	22.9	3.2	5.3	1518.5	30997.1	107.4	88.6	0.13	0.41	0.98	1.95	8.63
25	857.1	5.6	< 2.4	2.9	922.3	19504.7	63.0	35.0	0.11	0.15	0.45	0.97	1.56
30	945.8	16.2	3.4	1.4	1191.1	14243.2	82.2	< 18	0.03	0.07	0.27	0.62	0.37
40	424.1	3.6	4.9	2.3	985.2	16014.1	83.1	19.5	0.03	0.09	0.18	0.60	0.27
45	255.5	3.2	4.2	2.1	861.0	13077.5	86.6	19.9	0.03	0.20	0.17	0.65	0.23
50	597.7	6.2	5.4	2.7	1177.2	21107.7	119.3	22.0	0.05	0.13	0.24	0.65	0.43
55	253.2	2.0	< 2.4	1.6	673.9	10362.9	< 50	< 18	0.17	0.08	< 0.09	0.31	< 0.2
60	216.3	1.8	2.5	1.2	731.1	10327.4	< 50	< 18	0.02	0.05	< 0.09	0.34	< 0.2
70	361.1	3.4	< 2.4	2.5	1127.4	14476.7	< 50	< 18	0.02	0.08	0.09	< 0.3	< 0.2
75	481.6	5.5	< 2.4	3.1	1599.0	20272.5	62.5	< 18	0.02	0.08	0.17	0.47	< 0.2
80	309.6	4.4	< 2.4	2.2	1317.9	15038.9	61.6	< 18	0.02	0.05	< 0.09	0.29	< 0.2
90	378.7	6.1	3.0	2.4	1384.7	17158.8	70.9	< 18	0.02	0.04	0.20	0.48	< 0.2
100	529.1	8.2	2.4	2.2	1630.5	21199.0	64.3	< 18	0.03	0.05	0.13	0.40	< 0.2
105	4362.9	18.9	6.2	4.7	1122.4	7983.3	109.6	220.6	0.07	0.81	2.18	4.36	1.49
110	426.2	4.9	< 2.4	1.4	1627.9	9859.1	60.3	498.6	0.01	0.08	0.20	0.54	< 0.2
115	306.8	5.4	< 2.4	1.1	1312.1	9164.9	62.2	262.8	0.01	0.05	< 0.09	< 0.3	< 0.2
120	341.5	5.8	< 2.4	2.0	1370.2	10248.7	61.5	244.3	0.01	0.05	0.11	< 0.3	< 0.2
125	351.0	6.3	< 2.4	1.3	1303.0	11405.5	85.3	180.4	0.01	0.03	< 0.09	< 0.3	< 0.2
130	364.9	7.6	< 2.4	1.4	1230.1	10440.1	71.8	151.0	0.01	0.03	< 0.09	< 0.3	< 0.2
140	243.3	5.2	< 2.4	0.9	788.2	7085.6	61.0	103.1	0.04	0.03	< 0.09	< 0.3	< 0.2
145	253.0	5.6	2.5	1.0	850.0	7287.0	76.0	110.0	0.02	0.03	0.10	< 0.3	< 0.3
150	288.0	6.0	2.7	1.2	797.5	7470.7	83.6	106.6	0.01	0.04	0.10	< 0.3	< 0.2
155	462.6	10.4	3.0	1.2	862.3	11365.0	< 50	28.4	0.05	0.06	< 0.09	0.27	0.42
160	647.4	12.6	3.2	1.5	1131.6	14930.5	86.7	30.2	0.04	0.08	0.09	< 0.3	< 0.2
170	820.5	14.5	3.2	1.6	1082.0	16650.4	66.2	34.8	0.03	0.08	0.19	0.37	< 0.2
175	723.5	13.5	4.3	1.2	1150.9	15349.4	53.4	< 18	0.03	0.06	0.16	0.40	< 0.2
180	876.3	16.9	4.1	1.5	1201.6	17831.3	57.6	20.8	0.07	0.07	0.19	< 0.3	1.07
185	1024.5	16.7	3.4	1.3	1132.2	16524.1	50.6	< 18	0.22	0.08	0.17	0.26	< 0.2
190	972.8	16.5	4.4	1.3	1179.3	16343.7	50.5	31.3	0.45	0.07	0.17	< 0.3	< 0.2
195	972.7	16.1	2.8	1.7	1308.4	15838.4	62.9	33.9	0.04	0.08	0.17	< 0.3	< 0.2
200	307.3	5.9	< 2.4	0.8	947.2	7993.0	68.4	113.0	0.01	0.04	< 0.09	< 0.3	< 0.2
205	732.4	13.9	3.1	1.3	966.0	11842.4	< 50	23.4	0.03	0.10	0.18	0.33	< 0.2
220	782.7	13.6	< 2.4	1.1	905.8	10593.4	< 50	21.8	0.06	0.05	0.11	0.30	< 0.2
230	1004.3	18.4	4.0	1.5	1054.9	12639.7	< 50	23.2	0.03	0.09	0.15	0.29	0.67
235	1414.4	22.4	2.5	1.6	1355.1	16538.9	53.5	< 18	0.03	0.06	0.15	0.37	< 0.2
240	1695.5	27.0	3.8	1.8	1167.0	20149.4	64.8	26.5	0.04	0.05	0.20	0.43	< 0.2
245	1454.8	22.1	3.3	2.1	1234.2	16072.3	71.4	51.0	0.03	0.13	0.23	0.42	< 0.2
250	1385.8	21.2	4.5	2.1	920.3	12823.1	< 50	37.6	0.07	0.22	0.36	0.79	3.56
255	1140.5	19.0	< 2.4	0.9	961.4	11805.7	115.8	< 18	0.02	0.09	< 0.09	0.30	< 0.2

Appendix 8.   Associations between metallic elements

Wood-grass fen peat, Svētupes mire, depth range: 0.00–0.15 m (n: 4; α: 0.95; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb
Mg	0.91	Mg										
K	0.45	0.77	K									
Ca	0.94	0.99	0.73	Ca								
Fe	0.63	0.88	0.97	0.86	Fe							
Mn	0.69	0.91	0.95	0.90	1.00	Mn						
Co	0.89	0.93	0.59	0.90	0.68	0.71	Co					
Ni	0.48	0.80	0.99	0.75	0.96	0.93	0.66	Ni				
Cu	0.18	0.56	0.96	0.51	0.88	0.84	0.33	0.93	Cu			
Zn	0.23	0.61	0.97	0.56	0.90	0.85	0.41	0.96	0.99	Zn		
Cd	0.44	0.77	1.00	0.72	0.96	0.93	0.62	1.00	0.95	0.97	Cd	
Pb	0.67	0.83	0.86	0.86	0.94	0.96	0.56	0.81	0.77	0.76	0.82	Pb

Wood-sedge fen peat, Svētupes mire, depth range: 0.15–0.50 m (n: 7; α: 0.75; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb
Mg	0.89	Mg										
K	-0.09	-0.33	K									
Ca	0.86	1.00	-0.35	Ca								
Fe	-0.23	-0.54	0.38	-0.57	Fe							
Mn	0.72	0.80	-0.18	0.80	-0.09	Mn						
Co	-0.31	-0.19	-0.56	-0.22	0.03	-0.22	Co					
Ni	0.63	0.73	-0.33	0.75	-0.73	0.21	-0.18	Ni				
Cu	0.82	0.82	-0.44	0.78	-0.46	0.55	0.19	0.59	Cu			
Zn	-0.49	-0.80	0.59	-0.83	0.73	-0.52	-0.11	-0.78	-0.57	Zn		
Cd	0.59	0.29	0.51	0.27	0.42	0.55	-0.66	-0.13	0.17	0.29	Cd	
Pb	-0.47	-0.68	0.12	-0.72	0.46	-0.76	0.53	-0.30	-0.29	0.54	-0.36	Pb

Sedge fen peat, Svētupes mire, depth range: 0.50–2.20 m (n: 43; α: 0.30; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb
Mg	0.88	Mg										
K	0.71	0.74	K									
Ca	0.13	-0.10	-0.34	Ca								
Fe	-0.07	-0.07	0.08	-0.28	Fe							
Mn	0.50	0.60	0.43	0.15	0.36	Mn						
Co	-0.07	-0.11	-0.14	0.17	-0.12	-0.10	Co					
Ni	0.22	0.19	0.12	0.27	-0.49	-0.13	0.28	Ni				
Cu	0.52	0.54	0.51	-0.34	-0.09	-0.04	-0.01	0.48	Cu			
Zn	0.18	0.24	0.23	0.12	0.20	0.38	-0.03	-0.01	0.01	Zn		
Cd	0.41	0.28	0.38	0.09	-0.60	-0.21	-0.06	0.42	0.43	-0.26	Cd	
Pb	-0.11	-0.22	-0.35	0.55	-0.19	-0.08	0.57	0.19	-0.19	0.10	-0.12	Pb

Full peat profile, Svētupes mire, depth range: 0.00–2.20 m (n: 54; α: 0.27; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb
Mg	0.84	Mg										
K	0.51	0.30	K									
Ca	0.02	-0.12	-0.22	Ca								
Fe	-0.15	-0.12	-0.02	-0.22	Fe							
Mn	0.29	0.48	0.12	0.22	0.37	Mn						
Co	0.09	-0.07	0.32	0.10	-0.12	-0.07	Co					
Ni	0.41	0.33	0.36	0.13	-0.46	-0.15	0.32	Ni				
Cu	0.66	0.53	0.55	-0.37	-0.20	-0.19	0.16	0.61	Cu			
Zn	0.34	0.12	0.84	-0.09	0.01	0.01	0.29	0.26	0.45	Zn		
Cd	0.48	0.23	0.88	-0.07	-0.29	-0.03	0.30	0.47	0.57	0.73	Cd	
Pb	0.39	0.09	0.88	-0.14	-0.09	-0.08	0.39	0.36	0.52	0.81	0.80	Pb

Full peat profile, Elku mire, depth range: 0.00–2.00 m (n: 40; α: 0.31; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	-0.10	Mg											
K	-0.12	-0.12	K										
Ca	-0.18	0.56	-0.29	Ca									
Fe	0.00	-0.48	-0.08	0.30	Fe								
Mn	-0.37	0.01	0.91	-0.06	-0.11	Mn							
Co	0.11	-0.55	0.57	-0.55	0.38	-0.55	Co						
Ni	0.22	-0.47	0.32	-0.35	0.52	0.02	0.89	Ni					
Cu	0.23	-0.41	0.47	-0.43	0.36	0.16	0.91	0.93	Cu				
Cr	0.07	-0.11	0.54	-0.36	-0.03	0.33	0.33	0.61	0.76	Cr			
Zn	0.07	-0.33	0.73	-0.40	0.29	0.53	0.88	0.71	0.75	0.59	Zn		
Cd	-0.10	-0.08	0.43	0.11	0.39	0.46	0.39	0.24	0.25	0.19	0.46	Cd	
Pb	-0.32	-0.10	-0.12	-0.18	0.00	0.99	0.32	0.02	0.18	0.37	0.54	0.37	Pb

Transitional wood peat, Elku mire, depth range: 0.00–0.25 m (n: 5; α: 0.88; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.87	Mg											
K	-0.62	-0.90	K										
Ca	0.77	0.95	-0.83	Ca									
Fe	-0.34	-0.72	0.95	-0.65	Fe								
Mn	-0.72	-0.95	0.99	-0.87	0.89	Mn							
Co	-0.72	-0.94	0.99	-0.85	0.90	-0.94	Co						
Ni	-0.68	-0.85	0.95	-0.71	0.89	0.96	0.97	Ni					
Cu	-0.72	-0.71	0.71	-0.47	0.62	0.75	0.78	0.84	Cu				
Cr	-0.76	-0.55	0.23	-0.42	0.00	0.34	0.34	0.28	0.64	Cr			
Zn	-0.52	-0.83	0.98	-0.79	0.95	0.95	0.94	0.92	0.58	0.03	Zn		
Cd	-0.25	-0.70	0.86	-0.75	0.90	0.81	0.80	0.68	0.36	0.00	0.86	Cd	
Pb	-0.69	0.87	-0.62	0.77	-0.34	1.00	1.00	0.97	0.78	0.33	0.95	0.33	Pb

Wood fen peat, Elku mire, depth range: 0.25–0.75 m (n: 10; α: 0.63; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.10	Mg											
K	0.64	-0.30	K										
Ca	-0.39	0.45	-0.70	Ca									
Fe	-0.55	0.14	-0.66	0.91	Fe								
Mn	-0.53	0.04	-0.55	0.74	0.81	Mn							
Co	0.08	-0.66	0.53	-0.74	-0.55	-0.66	Co						
Ni	-0.05	0.51	-0.19	0.62	0.48	0.37	-0.50	Ni					
Cu	-0.47	-0.68	-0.11	-0.21	0.10	0.37	0.15	-0.43	Cu				
Cr	0.54	0.32	0.10	-0.14	-0.43	-0.30	-0.30	-0.26	-0.28	Cr			
Zn	0.68	-0.28	0.54	-0.46	-0.37	-0.39	0.12	-0.15	0.07	0.09	Zn		
Cd	-0.35	0.33	-0.66	0.51	0.58	0.30	-0.32	-0.02	0.03	-0.17	-0.30	Cd	
Pb	0.82	0.10	0.64	-0.39	-0.55	-0.49	-0.17	0.05	-0.54	0.67	0.50	0.67	

Wood-reed fen peat, Elku mire, depth range: 0.75–1.25 m (n: 10; α: 0.63; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.08	Mg											
K	0.77	0.16	K										
Ca	-0.06	0.82	-0.21	Ca									
Fe	-0.21	0.11	-0.59	0.65	Fe								
Mn	0.58	0.29	0.85	0.04	-0.29	Mn							
Co	0.70	-0.30	0.75	-0.33	-0.19	-0.30	Co						
Ni	0.23	0.81	-0.04	0.78	0.34	0.02	-0.39	Ni					
Cu	0.47	0.76	0.35	0.50	-0.11	0.20	-0.13	0.80	Cu				
Cr	0.45	0.72	0.63	0.36	-0.33	0.55	0.55	0.51	0.80	Cr			
Zn	0.76	-0.10	0.84	-0.35	-0.48	0.77	0.83	-0.21	0.10	0.33	Zn		
Cd	-0.42	-0.06	-0.34	0.32	0.61	-0.03	0.07	-0.22	-0.39	-0.24	-0.16	Cd	
Pb	0.57	0.08	0.77	-0.06	-0.21	0.96	0.69	-0.02	0.26	0.60	0.83	0.60	

Reed fen peat, Elku mire, depth range: 1.25–1.50 m (n: 5; α: 0.88; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.15	Mg											
K	-0.17	0.84	K										
Ca	0.44	0.80	0.36	Ca									
Fe	0.58	0.46	-0.09	0.89	Fe								
Mn	0.29	0.93	0.88	0.63	0.28	Mn							
Co	0.57	-0.67	-0.90	-0.17	0.25	-0.67	Co						
Ni	-0.02	0.40	0.11	0.69	0.58	0.12	-0.11	Ni					
Cu	-0.75	0.53	0.71	0.15	-0.21	0.37	-0.93	0.34	Cu				
Cr	-0.22	0.78	0.83	0.53	0.10	0.68	0.68	0.61	0.76	Cr			
Zn	-0.43	0.26	0.73	-0.37	-0.72	0.45	-0.75	-0.45	0.55	0.40	Zn		
Cd	0.75	-0.11	-0.39	0.13	0.43	0.02	0.60	-0.45	-0.78	-0.68	-0.41	Cd	
Pb	-0.38	0.15	-0.17	0.44	0.58	0.67	-0.90	-0.14	0.72	0.69	0.93	0.69	

Sedge fen peat, Elku mire, depth range: 1.50–1.75 m (n: 5; α: 0.88; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd
Mg	-1.00	Mg										
K	0.32	-0.35	K									
Ca	-0.90	0.88	-0.49	Ca								
Fe	-0.21	0.17	0.78	0.13	Fe							
Mn	-0.88	0.87	-0.56	0.99	0.08	Mn						
Co	0.10	-0.11	0.94	-0.36	0.81	-0.11	Co					
Ni	0.17	-0.20	0.97	-0.38	0.84	-0.43	0.99	Ni				
Cu	0.30	-0.33	0.97	-0.45	0.83	-0.49	0.95	0.98	Cu			
Cr	0.26	-0.28	0.98	-0.46	0.80	-0.51	-0.51	1.00	0.99	Cr		
Zn	0.20	-0.22	0.97	-0.36	0.87	-0.41	0.97	0.99	0.99	0.99	Zn	
Cd	-0.38	0.38	0.31	0.28	0.69	0.33	0.53	0.52	0.49	0.46	0.54	Cd
Pb	0.33	-1.00	0.32	-0.90	-0.21	0.03	-0.14	-0.06	0.07	-0.05	0.01	-0.05

Reed fen peat, Elku mire, depth range: 1.75–2.00 m (n: 5; α: 0.88; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd
Mg	0.21	Mg										
K	0.48	0.25	K									
Ca	0.04	0.96	0.07	Ca								
Fe	-0.47	0.70	-0.05	0.70	Fe							
Mn	0.11	0.48	-0.46	0.64	0.09	Mn						
Co	-0.08	0.22	0.29	0.03	0.57	0.22	Co					
Ni	-0.02	0.36	0.58	0.17	0.59	-0.63	0.93	Ni				
Cu	0.14	0.32	0.71	0.10	0.44	-0.67	0.88	0.98	Cu			
Cr	0.36	0.58	0.83	0.37	0.43	-0.40	-0.40	0.88	0.92	Cr		
Zn	-0.40	0.39	-0.17	0.32	0.85	-0.21	0.83	0.69	0.55	0.38	Zn	
Cd	-0.17	0.88	0.29	0.84	0.91	0.14	0.49	0.64	0.55	0.67	0.64	Cd
Pb	0.30	0.21	0.48	0.04	-0.47	-0.73	0.49	0.71	0.82	0.80	-0.01	0.80

Full peat profile, Salas mire, depth range: 0.00–0.50 m (n: 10; α: 0.63; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	Cd
Mg	0.70	Mg									
K	-0.52	-0.96	K								
Ca	0.63	0.96	-0.90	Ca							
Fe	0.62	0.97	-0.95	0.92	Fe						
Mn	0.61	0.97	-0.95	0.96	0.99	Mn					
Co	0.40	0.61	-0.72	0.54	0.60	0.56	Co				
Ni	-0.42	-0.75	0.78	-0.57	-0.82	-0.75	-0.46	Ni			
Cu	-0.20	-0.23	0.30	0.01	-0.30	-0.19	-0.14	0.69	Cu		
Zn	-0.08	-0.55	0.71	-0.46	-0.55	-0.54	-0.49	0.55	0.49	Zn	
Cd	0.28	0.38	-0.33	0.54	0.39	0.47	0.09	-0.20	0.24	0.25	Cd
Pb	-0.48	-0.75	0.74	-0.76	-0.67	-0.69	-0.62	0.29	-0.13	0.61	0.06

Full peat profile, Vīķu mire, depth range: 0.00–2.60 m (n: 52; α: 0.28; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.12	Mg											
K	0.10	0.38	K										
Ca	0.32	0.44	-0.18	Ca									
Fe	0.14	0.63	0.36	0.32	Fe								
Mn	0.01	0.70	0.29	0.26	0.92	Mn							
Co	0.06	0.24	0.34	0.30	0.74	0.59	Co						
Ni	0.19	0.41	0.43	0.20	0.87	0.65	0.81	Ni					
Cu	0.26	0.47	0.29	0.61	0.76	0.56	0.81	0.84	Cu				
Cr	0.16	0.44	0.44	0.25	0.91	0.72	0.86	0.98	0.87	Cr			
Zn	0.05	0.52	0.33	0.20	0.87	0.85	0.77	0.80	0.70	0.85	Zn		
Cd	-0.07	0.17	0.05	0.39	0.45	0.41	0.50	0.39	0.47	0.47	0.48	Cd	
Pb	0.12	0.11	0.22	0.54	0.50	0.39	0.81	0.49	0.73	0.60	0.53	0.52	

Wood fen peat, Vīķu mire, depth range: 0.00–0.20 m (n: 4; α: 0.95; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.92	Mg											
K	-0.95	-0.80	K										
Ca	0.87	0.98	-0.77	Ca									
Fe	-0.49	-0.13	0.70	-0.09	Fe								
Mn	-0.99	-0.88	0.97	-0.82	0.57	Mn							
Co	-0.87	-0.67	0.98	-0.65	0.81	0.91	Co						
Ni	-0.61	-0.27	0.79	-0.22	0.99	0.68	0.88	Ni					
Cu	-0.58	-0.26	0.79	-0.24	0.98	0.65	0.89	0.98	Cu				
Cr	-0.77	-0.52	0.92	-0.51	0.90	0.82	0.98	0.93	0.96	Cr			
Zn	-0.94	-0.80	1.00	-0.79	0.68	0.96	0.98	0.77	0.78	0.93	Zn		
Cd	-0.90	-0.76	0.98	-0.76	0.71	0.93	0.99	0.78	0.81	0.95	1.00	Cd	
Pb	-0.87	-0.70	0.97	-0.71	0.76	0.90	0.99	0.82	0.85	0.97	0.99	1.00	

Grass fen peat, Vīķu mire, depth range: 0.20–0.40 m (n: 5; α: 0.88; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.82	Mg											
K	0.27	0.42	K										
Ca	0.51	0.67	0.92	Ca									
Fe	0.27	0.76	0.60	0.67	Fe								
Mn	0.39	0.78	0.09	0.25	0.81	Mn							
Co	0.47	0.15	0.59	0.44	-0.03	-0.22	Co						
Ni	0.42	0.56	0.98	0.94	0.66	0.22	0.62	Ni					
Cu	0.30	0.23	0.90	0.85	0.24	-0.28	0.65	0.85	Cu				
Cr	0.16	0.50	0.93	0.86	0.82	0.38	0.36	0.93	0.68	Cr			
Zn	0.91	0.61	0.08	0.37	-0.03	0.09	0.31	0.19	0.28	-0.12	Zn		
Cd	-0.04	0.23	0.94	0.79	0.62	0.08	0.41	0.89	0.78	0.95	-0.24	Cd	
Pb	-0.18	0.12	0.89	0.71	0.59	0.04	0.31	0.81	0.71	0.91	-0.37	0.99	

Wood-*sphagnum* fen peat, Vīķu mire, depth range: 0.40–0.60 m (n: 4; α: 0.95; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.64	Mg											
K	1.00	0.62	K										
Ca	0.95	0.85	0.94	Ca									
Fe	0.96	0.80	0.96	0.99	Fe								
Mn	0.99	0.74	0.98	0.98	0.99	Mn							
Co	0.88	0.77	0.87	0.93	0.96	0.93	Co						
Ni	0.75	0.99	0.74	0.93	0.89	0.84	0.85	Ni					
Cu	0.90	0.85	0.89	0.97	0.98	0.95	0.99	0.91	Cu				
Cr	1.00	0.62	1.00	0.94	0.96	0.98	0.87	0.74	0.89	Cr			
Zn	1.00	0.61	1.00	0.93	0.95	0.98	0.85	0.73	0.87	1.00	Zn		
Cd	-0.13	-0.56	-0.12	-0.29	-0.19	-0.19	0.02	-0.50	-0.14	-0.12	-0.14	Cd	
Pb	1.00	0.62	1.00	0.94	0.96	0.98	0.87	0.74	0.89	1.00	1.00	-0.12	

Wood-grass fen peat, Vīķu mire, depth range: 0.65–1.05 m (n: 7; α: 0.75; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	-0.34	Mg											
K	0.95	-0.44	K										
Ca	-0.64	0.93	-0.72	Ca									
Fe	0.95	-0.37	1.00	-0.67	Fe								
Mn	0.93	-0.21	0.96	-0.52	0.97	Mn							
Co	0.95	-0.41	1.00	-0.70	1.00	0.96	Co						
Ni	0.95	-0.41	1.00	-0.69	1.00	0.96	1.00	Ni					
Cu	0.73	0.12	0.78	-0.21	0.82	0.83	0.80	0.80	Cu				
Cr	0.96	-0.41	1.00	-0.70	1.00	0.96	1.00	1.00	0.80	Cr			
Zn	0.90	-0.58	0.97	-0.80	0.96	0.90	0.96	0.97	0.69	0.97	Zn		
Cd	0.41	0.41	0.48	0.13	0.55	0.63	0.50	0.52	0.85	0.51	0.39	Cd	
Pb	0.95	-0.44	1.00	-0.72	1.00	0.96	1.00	1.00	0.78	1.00	0.97	0.48	

Wood-grass fen peat, Vīķu mire, depth range: 1.20–1.60 m (n: 9; α: 0.67; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd	Pb
Mg	0.17	Mg											
K	0.15	0.45	K										
Ca	0.03	0.59	-0.43	Ca									
Fe	0.04	0.32	-0.66	0.95	Fe								
Mn	-0.10	0.25	-0.73	0.92	0.98	Mn							
Co	-0.04	0.12	-0.80	0.87	0.96	0.97	Co						
Ni	0.19	0.06	-0.29	0.46	0.58	0.44	0.49	Ni					
Cu	0.12	0.78	-0.08	0.89	0.77	0.72	0.63	0.38	Cu				
Cr	0.07	-0.07	-0.44	0.46	0.62	0.51	0.56	0.97	0.32	Cr			
Zn	0.08	-0.10	-0.79	0.67	0.86	0.82	0.86	0.77	0.43	0.86	Zn		
Cd	-0.27	-0.45	-0.90	0.35	0.55	0.60	0.67	0.28	-0.08	0.42	0.70	Cd	
Pb	-0.46	-0.40	-0.62	0.16	0.30	0.39	0.37	0.14	-0.14	0.38	0.51	0.63	

Wood-grass fen peat, Vīķu mire, depth range: 1.60–1.80 m (n: 4; α: 0.95; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd
Mg	-0,48	Mg										
K	0,96	-0,70	K									
Ca	0,30	0,40	0,18	Ca								
Fe	-0,36	0,03	-0,21	0,46	Fe							
Mn	-0,28	0,47	-0,29	0,79	0,85	Mn						
Co	0,11	-0,55	0,34	0,28	0,81	0,48	Co					
Ni	0,42	-0,29	0,35	-0,59	-0,96	-0,95	-0,64	Ni				
Cu	0,84	-0,33	0,83	0,69	0,17	0,27	0,48	-0,13	Cu			
Cr	0,79	-0,06	0,70	0,82	0,11	0,36	0,29	-0,15	0,96	Cr		
Zn	-0,43	0,78	-0,65	-0,17	-0,52	-0,18	-0,93	0,31	-0,64	-0,40	Zn	
Cd	-0,61	0,00	-0,43	0,13	0,93	0,67	0,71	-0,87	-0,16	-0,25	-0,40	Cd
Pb	0,06	0,81	-0,17	0,82	0,08	0,60	-0,30	-0,32	0,28	0,54	0,43	-0,16

Sedge-*hypnum* fen peat, Vīķu mire, depth range: 1.80–2.00 m (n: 4; α: 0.95; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd
Mg	-0.02	Mg										
K	0.81	-0.50	K									
Ca	-0.50	0.87	-0.80	Ca								
Fe	-0.59	0.82	-0.89	0.98	Fe							
Mn	-0.68	0.73	-0.95	0.95	0.99	Mn						
Co	-0.67	0.29	-0.91	0.53	0.67	0.76	Co					
Ni	-0.17	-0.52	-0.17	-0.42	-0.25	-0.13	0.55	Ni				
Cu	-0.41	0.80	-0.87	0.86	0.92	0.91	0.81	0.03	Cu			
Cr	-0.81	0.50	-1.00	0.81	0.90	0.95	0.90	0.15	0.86	Cr		
Zn	-0.78	0.33	-0.59	0.70	0.66	0.67	0.23	-0.49	0.32	0.61	Zn	
Cd	-0.56	0.35	-0.36	0.62	0.53	0.51	-0.05	-0.71	0.15	0.38	0.96	Cd
Pb	0.58	0.51	0.43	0.20	0.03	-0.11	-0.67	-0.90	-0.10	-0.42	0.06	0.32

Sedge fen peat, Vīķu mire, depth range: 2.00–2.20 m (n: 4; α: 0.95; p < 0.05)

	Na	Mg	K	Ca	Fe	Mn	Co	Ni	Cu	Cr	Zn	Cd
Mg	0.62	Mg										
K	0.22	0.14	K									
Ca	0.54	0.99	0.22	Ca								
Fe	0.58	0.95	0.45	0.97	Fe							
Mn	0.56	0.95	0.43	0.97	1.00	Mn						
Co	0.85	0.87	-0.10	0.80	0.72	0.72	Co					
Ni	0.89	0.21	0.34	0.13	0.23	0.20	0.51	Ni				
Cu	0.32	0.52	-0.76	0.43	0.21	0.23	0.70	-0.02	Cu			
Cr	-0.86	-0.75	0.24	-0.65	-0.55	-0.55	-0.98	-0.57	-0.76	Cr		
Zn	1.00	0.62	0.22	0.54	0.58	0.56	0.85	0.89	0.32	-0.86	Zn	
Cd	-0.52	-0.90	0.30	-0.85	-0.71	-0.72	-0.89	-0.07	-0.84	0.83	-0.52	Cd
Pb	0.25	0.91	0.06	0.94	0.87	0.88	0.63	-0.21	0.47	-0.47	0.25	-0.84

Appendix 9. Associations between metallic elements and peat characteristics

Statistically significant correlation coefficients (p < 0.05) among Vīķu Mire peat characteristics and metallic element content

Metal	PD	PA	DD	SR	WR	M	OM	AC	CM	MM	C	N	H	O	O/C
Fe			0.62		0.66	-0.58	-0.87	0.87	0.56	0.89					
Mn							-0.74	0.74		0.78					
Zn			0.54	-0.56	0.68	-0.66	-0.85	0.85		0.89					
Cu		-0.54	0.71	-0.71	0.82	-0.76	-0.93	0.93	0.67	0.93					
Mg	-0.57	-0.55	0.57	-0.58	0.60	-0.57					0.72	0.84	0.67	-0.68	-0.72
Ca		-0.49		-0.57	0.56	-0.66	-0.66	0.66		0.70					
Na	-0.57	-0.57													
K			0.52									0.63			
Cd															
Co			0.56		0.60	-0.81		0.81	0.57	0.81					
Cr			0.72	-0.55	0.77	-0.66	-0.93	0.93	0.64	0.94					
Ni			0.62	-0.51	0.68	-0.55	-0.86	0.86	0.56	0.88					
Pb			0.81	-0.60	0.86	-0.76	-0.98	0.98	0.72	0.97					

(PD – peat depth; PA – peat age; DD – decomposition degree; SR – sedge remains; WR – wood remains; M – moisture; OM – organic matter; AC – ash content; CM – carbonate matter; MM – mineral matter)

Statistically significant correlation coefficients (p < 0.05) among Svētupes Mire peat characteristics and metallic element content

Metal	PD	PA	DD	HI	SR	WR	pH	FI	TGI	OM	AC	CM	MM	C	N	H	O	N/C	H/C	O/C
Fe	0.57						0.74								-0.58			-0.55		
Mn	0.60																			
Zn						0.62														
Cu	-0.80	-0.70	0.66	0.76			-0.71			0.59	-0.59	-0.62						0.57	0.55	
Mg								0.56												
Ca							0.74				0.69	0.72		-0.55	-0.80	-0.82	0.71	-0.73	-0.77	0.59
Na		-0.58	0.56																	
K	-0.55	-0.83	0.68	0.58	-0.71	0.75														
Cd	-0.56	-0.78		0.60	-0.79	0.70														
Co		-0.81	0.63		-0.76	0.76														
Cr																				
Ni																				
Pb	-0.55	-0.86	0.69	0.55	-0.79	0.81														

(PD – peat depth; PA – peat age; DD – decomposition degree; HI – humification index; SR – sedge remains; WR – wood remains; FI – fluorescence index; TGI – thermogravimetric index; M – moisture; OM – organic matter; AC – ash content; CM – carbonate matter; MM – mineral matter)

Statistically significant correlation coefficients (p < 0.05) among Elku Mire peat characteristics and metallic element content

Metal	PD	PA	DD	HI	SR	WR	pH	FI	TGI	M	OM	AC	CM	MM	C	N	H	O	N/C	H/C	O/C
Fe	0.97	0.98	-0.85	-0.97	0.73	-0.95		-0.72		0.76	-0.74	0.74		0.68			0.87	-0.66		0.91	
Mn							0.90														
Zn									-0.89		-0.83	0.83		0.93							
Cu									-0.81	0.65	-0.82	0.82		0.88							
Mg	-0.77	-0.79	0.82	0.73	-0.81	0.66		0.72		-0.66	0.64	-0.64			-0.63		-0.77	0.70		-0.64	0.66
Ca		0.68		0.71		-0.71									0.65			-0.65			
Na																					
K									-0.66												
Cd											-0.76	0.76		0.67			0.65			0.71	
Co									-0.86	0.68	-0.87	0.87		0.94							
Cr																					
Ni	0.73	0.64		-0.67					-0.89	0.74	-0.81	0.81		0.91						0.72	
Pb						0.85															

(PD – peat depth; PA – peat age; DD – decomposition degree; HI – humification index; SR – sedge remains; WR – wood remains; FI – fluorescence index; TGI – thermogravimetric index; M – moisture; OM – organic matter; AC – ash content; CM – carbonate matter; MM – mineral matter)