The impact of environmental factors on metal accumulation and peat properties

Inese Silamikele, Maris Klavins, Laimdota Kalnina, Eliza Kuske and Olgerts Nikodemus

University of Latvia, Faculty of Geographical and Earth Sciences, Alberta 10, LV- 1010, Riga, Latvia
Phone: +371 67334096, e-mail: Inese.Silamikele@lu.lv, Maris.Klavins@lu.lv, Laimdota.Kalnina@lu.lv, Eliza.Kuske@gmail.com, Olgerts.Nikodemus@lu.lv

Summary

Interdisciplinary peat studies were carried out in 6 bogs in central and north eastern part of Latvia. Coring and peat sampling has been done by peat sampler, but the obtained monoliths was subdivided into slices and the peat samples were analyzed for their botanical composition, presence of palinological indicators, elemental composition (C, H, N, and S), ash content, metal content; they were dated (^{14}C) and humic acids (HA) were extracted. In addition, isolated humic acids were analyzed using Fourier transform infrared spectroscopy (FT-IR) and UV–Vis spectroscopy (E_4/E_6 ratio). Metal accumulation character indicate recent accumulation of trace elements of dominantly anthropogenic origin, however elements such as Fe, Zn, Mn are at higher values in deeper layers.

Key index words: raised bogs, peat properties, Latvia

Introduction

Peat is a dark coloured organic deposit (<25% by weight mineral matter) formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees. The structure of peat ranges from fibric to sapric, and the relative proportions of C, H, and O vary, depending upon the botanical composition and degree of decomposition. Typical abundances of major elements are in the range 50–60% C, and 5–6% H. These elements tend generally to increase with the increasing degree of decomposition, while the O content (30– 40%) decreases indicating increasing aromaticity and decreasing number of O containing structures and functional groups in the structure of peat forming organic matter. Peatlands are waterlogged areas where the rate of biomass production is greater than the rate of decomposition. An ombrotrophic peat bog is a domed peatland in which the surface layers are hydrologically isolated from the influence of local ground waters and surface waters, and are supplied only by atmospheric deposition. The acidic, anaerobic waters retard the rate of decomposition of organic materials. For this reason, organic matter (plants and animals) remains preserved in peat profiles for millennia, and these ecosystems continue to represent a sink for carbon. In addition, ombrotrophic bogs constitute an authentic record of information on environmental and paleo-environmental evolution and are thus used as references in studies of past and present patterns in global climatic change and of the impact of historical human activity in causing heavy metal contamination (Kalnina, 2003).

In the present study raw peat and HA isolated from the different layers of peat section from several bogs in Latvia has been characterized and compared with the aim to study development and decomposition of the organic matter depending on its origin along the peat profile and to investigate the character of accumulation of trace elements depending on the peat age, botanical composition and decomposition degree.

Material and methods

Site location

Study area include six small ombrotrophic bogs located in the central (Riga District: Eipurs, Kronu-Dzelves and Bullu) and north eastern part (Limbazi District: Keru, Kalnu and Zilais) of Latvia (Fig.1). These bogs are located in the lowlands (Coastal and Middle Latvia Lowlands); however, they are of different origin. Eipurs, Kronu-Dzelves, and Bullu bogs have been developed due to ground paludification, while Keru, Kalna and Zilais Bogs have been formed in the result of shallow basin fill-in. All studied bogs nowadays are typical raised bogs with a number of bog lakes and pools; however they are influenced by drainage or peat cutting.

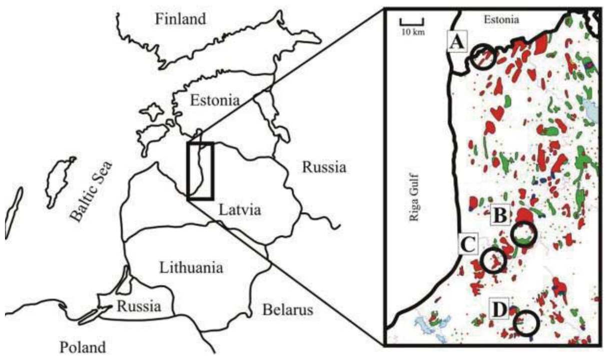

Figure 1. Sampling sites; A – Keru, Kalna and Zilais Bog; B – Eipurs Bog; C-Kronu-Dzelves Bog; D- Bullu Bog

Sampling

Coring and peat sampling has been done by peat sampler in the cupola area of each bog, where the surface peat layers are clearly elevated up to 2-4 m beyond the edge of the bog and has not been influenced by peat sliding. The peat samples (50 cm long monolithes) were put in special cartridge and wrapped in polythene film to preserve field moisture, brought to the lab and sliced into 3 cm sections using a stainless steel knife. The outside edges were systematically discarded, as those could have been contaminated during the sampling. The first slice (+3 to 0 cm) corresponds to the living plant material on the bog surface.

Sample preparation and analysis of physical and chemical properties

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

Carbon, hydrogen, nitrogen, and sulphur concentrations were determined using a combustion gas chromatography technique. The measured data were corrected for moisture and ash. The elemental compositions of all peat samples and HA respectively were determined as the mean value of 3 measurements. The FT-IR spectra were acquired in transmittance mode using a Thermo Nicolet FT-IR spectrophotometer. Potassium bromide pellets were obtained by pressing, under vacuum, a homogenized mixture of 400 mg of infrared-grade KBr and 1 mg of sample (dried, milled peat and HA, respectively). Spectra were recorded in the range 4000–400 cm^{-1}. The UV–Vis absorption spectra of HA were recorded with a UV–Vis spectrophotometer (Perkin Elmer, model γ Helios): 3 mg of HA were dissolved in 10 ml of 0.05 M $NaHCO_3$ solution, which was used as the blank. The E_4/E_6 ratios were calculated as the ratio of absorbance at 465 and 665 nm.

Humic acids extraction and isolation

HA are the dark-coloured part of organic material that can be extracted from soils by dilute alkali and other reagents and that are insoluble in dilute acid. HA were extracted from all the samples of the core. Briefly, peat samples were extracted with NaOH 0.5 M at room temperature. After agitation (for 24 h), centrifugation, and filtration, the alkaline extract was acidified with HCl to pH 1.5 and allowed to precipitate for 24 h. Those operations (extraction) were repeated by keeping the same volume of base solution in each cycle. The coagulate (humic fraction) was separated from the supernatant (fulvic fraction) by centrifugation. The supernatant was then acidified with HCl to pH 1.5 in order to coagulate the HA, and centrifuged; and the partly purified HA was washed with a solution of bi-distilled water + HCl (pH 3), manually shaken, and centrifuged. Finally, the HA were transferred to a dialysis membrane (Spectra/Por membrane, MWCO 6–8000) and dialyzed against distilled water that was changed at frequent intervals (6–7 h) in order to remove Cl^-. Following these treatments, the HA were dried.

Peat botanical composition and pollen analysis

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

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

Results and discussion

The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate both differences and similarities of the studied bog development and peat properties. Kroņu-Dzelve Bog has been formed due to paludification of sandy ground in the result of groundwater level increase and wet conditions in the small depression. Raised bog cotton grass peat layer covers sandy bottom, which overlays by pine-cotton grass peat. The upper part of peat section is represented by 3.2 m thick *Sphagnum fuscum* peat layer with decomposition level 9 to 17 %. Botanical composition is not very changeable: *Sphagnum fuscum* (60-75%), *Eriophorum vaginatum* 10-15%, *Sphagnum rubellum* 10-15% and dwarf shrubs 10-15%. Completely different is botanical composition of Eipurs Bog, though it origin is similar. The lowest part of Eipurs is formed by fen wood-grass peat, hypnum and sedge-hypnum peat (Fig. 2) which is covered by transition type wood peat. The upper part is represented by 3.45 m thick raised bog peat of different types and decomposition degree. For example, well decomposed (40-48%) pine-cotton grass peat occur at the depth interval 1.18-1.39 m (Fig. 2). Maybe it can be explained by its accumulation, possibly during the Second Climatic Optimum. Although these bogs are located comparatively close together, their local conditions for peat formation have been different. The gyttja in the bottom of the Keru, Zilais and Kalna bog depressions indicates their origin as fill-in of shallow water basins. Pollen data indicate that they started their development during late Atlantic or Sub-boreal time.

The ash contents range between 0.30 ± 0.05 % and 6.10 ± 0.05 %, with an average content of 1.8 ± 0.05. The C concentration ranges from 42 % to 57 %, H from 5 % to 7 %, N from 0.5 % to 2.5 %, and S from 0 % to 1.7 %. The O content was determined by mass balance and it ranged from 32 % to 50 %. In general, C, N and H concentrations increase with depth, however high variability is common and the changes of the N content can be directly associated with the changes in decomposition degree. The S concentration is very variable along the profile; on the other hand O concentration decreases with depth and it is indirectly correlated with C concentration. C/N ratio is an index of the humification process at first due to specific microbial activity in anaerobic, acidic environment. This ratio can be efficiently used as a measure of peat degradation. The decreasing C/N ratios indicate an increasing peat decomposition and vice versa. H/C ratio is an index of molecular complexity and it

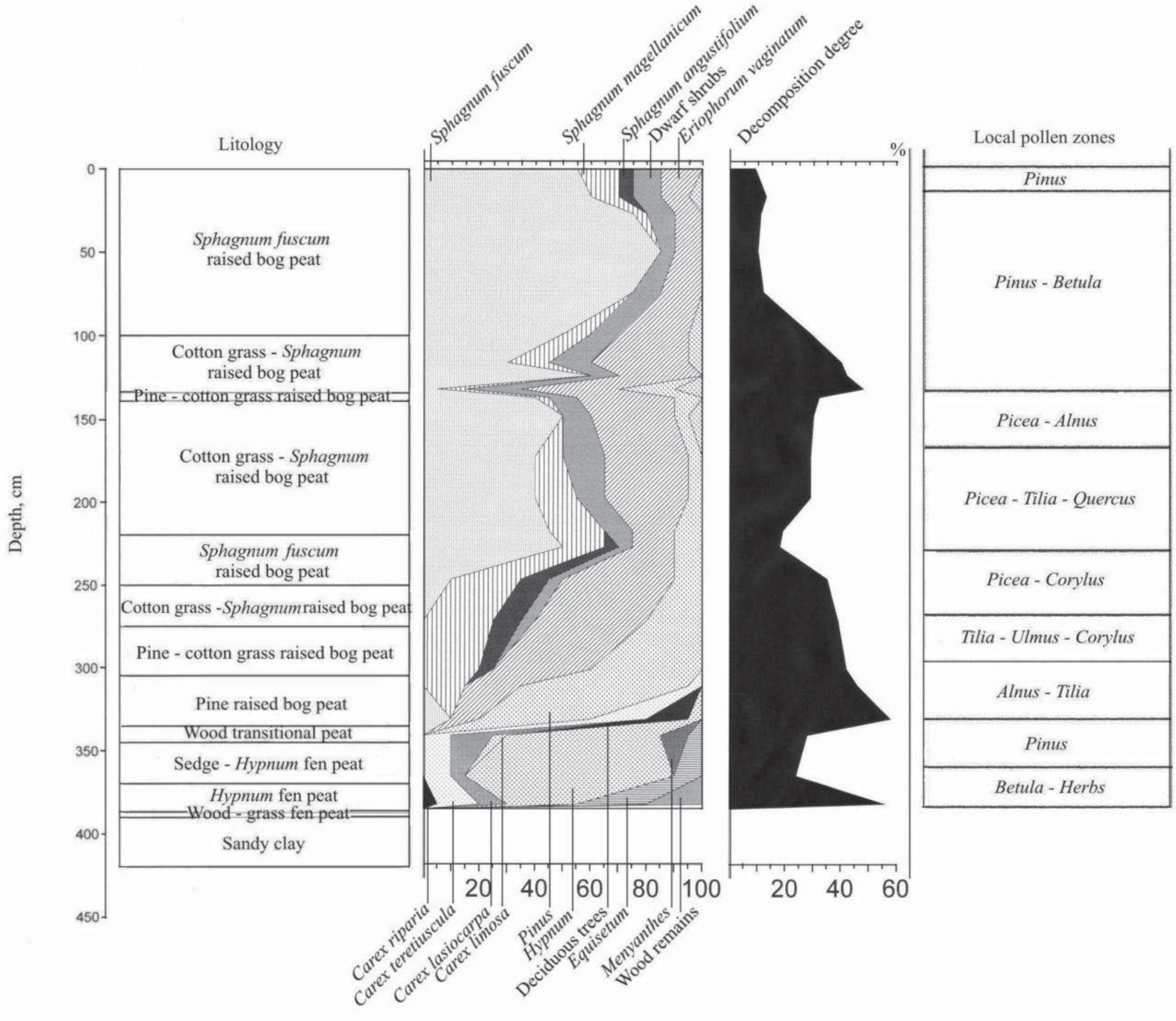

Figure 2. Peat stratigraphy and composition in Eipurs Bog

ranges from 1.6 to 1.2. It is relatively constant with depth; below 50 cm, it decreases. On the other hand, the O/C ratio is considered an indicator of carbohydrate and carboxylic contents and can be directly related to aromatization of the organic mater forming peat. The O/C ratio decreases with depth, however in layers with higher decomposition degree also values of this indicator are high.

If botanical composition indicates high variability of the peat composition, then physical and chemical properties suggest that this core may be divided into several sections: (a) a superficial zone, oxygenated, in which less complex (low H/C ratio) and slowly degradable (high N/C ratio) molecules are probably abundant, (b) a deep zone, anoxic or scarcely oxygenated because of the water table presence; this section shows a low N/C ratio and an high H/C ratio, indicating a possible increase in system aromaticity (i.e., humification), (c) a transitional zone in which C, H, N, S and ash contents increase and N/C and H/C ratios decrease. Such character of changes of peat composition indicates that microbial activities probably can be considered as the major factor influencing properties of peat as a substrate.

Peat columns serve as an archive storing profiles of trace elements. However, the trace element accumulation capacity depends on the peat properties. In this respect, trace element concentrations (Cu, Cd, Co, Ni, Pb, Fe, Mn, Zn, Cr) have been estimated in the full profile of the peat column. Metal accumulation character in the studied peat columns indicate accumulation of dominantly anthropogenic trace elements (for example, Pb, Co, Ni, Cu) in the upper layers of the peat column as well as accumulation in deeper layers of elements possibly due to feeding way with groundwater.

For characterization of the humification process the FT-IR, fluorescence spectroscopy and ^{1}H-NMR spectroscopy of solid organic phases, as well as humic extracts provides information about the nature, reactivity, and structural arrangement of structure pf peat forming organic matter, especially considering the changes in organic materials with depth. Results of spectral analysis are consistent with the presence along the peat profile of cellulosic, hemi-cellulosic, lignocellulosic, lignin-derived structures and other byproducts derived from plant materials at various stages of decomposition. Generally, the FT-IR spectra change along the profile, suggesting significant variations of the molecular composition and chemical structures of the peat samples. Obtained spectra demonstrate that the anoxic conditions of peatlands favor the preservation of lipids. These results are consistent with oxidative processes and decomposition phenomena of plant tissues and residues continuously occurring in the top horizons of the peat, leading to the release of variable amounts of organic acids and small molecular mass compounds. At the same time a decreasing trend of polysaccharide and polysaccharide- like substances with depth (determined as aliphatic/polysaccharide ratio) is common.

UV, FT-IR, fluorescence and ^{1}H NMR spectra show a possible distinction of the studied peat core in 3 sections: (1) a superficial layer (from the living layer to approximately 24 cm), poorly decomposed, where oxidative processes take place and rather heterogeneous organic materials at various stages of decomposition occur; (2) a deep zone (under 39 cm depth), more homogeneous, typical of reducing environmental conditions and possibly due to the permanent presence of the water table; here, an obligate anaerobic microbial community can carry out only a partial and slow decomposition of the organic matter.

Acknowledgements

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