Genesis of Peat Humic Acid Structure and Properties Within Bog Profiles

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Abstract Studies of living organic matter humification process are essential for understanding of carbon biogeochemical cycle, and considering this, the aim of this study is to analyse relations between properties of the peat, peat humic acids (HAs) and humification degree on example of analysis of two bog profiles in ombrotrophic bogs to identify the links between peat age, decomposition and humification degree, botanical composition and properties of peat humic acids (elemental, functional composition). The found variability of peat properties is much less than the significant differences in properties of peat-forming living matter, thus stressing the dominant impact of humification process on peat properties. Correspondingly composition of peat humic acids are little affected by the differences in properties of precursor living organic material and indicators as decomposition degree, humification degree, humic acid elemental ratio and concentrations of acidic functional groups are best descriptors of changes of organic matter during humification process.

Keywords Peat • Humic substances • Humic acids • Structure • Humification

Introduction

In the carbon biogeochemical cycle of key importance is the transformation of living organic matter into refractory part of organic matter – humic substances – humification, playing an important role in the diagenesis of fossil carbon deposits. In the same time character of transformation of living organic matter is very complex object of study, considering the high variability of the environmental

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conditions under which the living organic matter is decaying, slow pace of the humification reactions and the large number and structural differences in organic molecules composing living organic matter. From this perspective it is important to study humification processes in the conditions where the transformation of living organic matter could be studied in relatively homogeneous and stable environment in the bogs, identifying as the study object peat and its diagenesis. In form of peat are stored significant amounts of organic carbon and thus peat reserves play major role in the carbon biogeochemical cycling and are of especial role considering the ongoing climate change process (Borgmark 2005). Industrial and agricultural uses of peat are growing, and significant amounts of peat are mined industrially. The humification in the peat take place in very much differing conditions both at spatial scale (from tropical regions to Arctic environment), both under temporally changing conditions (historically peat development can last for many thousands years). During peat development even at one special site major changes in vegetation, temperature, amount of precipitations and correspondingly of the bog hydrological conditions, land use changes in the basin of wetland can take place (Chapman et al. 2001); thus, it might be expected to find corresponding changes in properties of peat humic substances, identifying molecular descriptors of organic matter diagenesis process. However, relations between peat properties (especially in full peat profiles) and properties of peat humic substances have been an object of very few studies (Zaccone et al. 2007).

The aim of this study is to analyse relations between the peat and peat humic acid (HA) properties and organic matter humification degree on example of analysis of peat profiles in ombrotrophic bogs.

Materials and Methods

In-depth study of peat composition, humification degree and properties of peat humic acids has been done on two ombrotrophic bogs located in the central part of Latvia. Full peat profiles were obtained cut into 5-cm layers for analysis of peat properties and isolation of humic acids. HAs were extracted and purified using procedures recommended by the International Humic Substances Society (Tan 2005). The ^{14}C dating was done at the Institute of Geology of the Tallinn Technical University (Estonia). Carbon, hydrogen, nitrogen and sulphur concentrations in peat and humic acid samples (elemental analysis of C, H, N, S) were carried out using an Elemental Analyzer Model EA-1108. UV/Vis spectra were recorded on a Thermo Spectronic Helios γ UV spectrophotometer. Humification degree was estimated as suggested by (Borgmark 2005). An automatic titrator TitroLine easy was used to measure carboxylic and phenolic acidity of each HA. The known Ca-acetate method (Tan 2005) based on the formation of acetic acid was used for determination of the total amount of carboxylic groups. Hydrophobicity of humic substances has been characterized by their distribution between water and polyethylene phases (Zavarzina et al. 2002) as distribution coefficient K_{PEGW}. Infrared (IR) spectra were recorded, in the 4,000–500 cm^{-1} range using a Perkin Elmer 400 IR spectrophotometer. Electron spin resonance (ESR) measurements were carried out with a RE-1306 spectrometer, operated at X-band frequencies with 100-kHz magnetic field modulation. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.47 MHz, respectively, with a Bruker DRX300 NMR.

Results and Discussion

A study of living organic material transformation (humification) is of utmost importance for better understanding of carbon biogeochemical cycling. Such study can help to describe humification process at molecular level, supporting development of new understanding of chemical and biochemical processes behind the humification and structure of humic substances. Following this approach in this study, we selected two ombrotrophic bogs of similar age, located spatially closely, but with very much differing peat column stratigraphy and bog profile botanical composition as well as decomposition degree. The selected study objects thus support the analysis of the relations between peat development conditions and peat properties as well as identification of the humification indicators at best describing living organic material transformation process. The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate both differences and similarities of the studied bog development and peat properties. 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 after Ice Age. Completely different is botanical composition of Eipurs Bog, though its origin is similar. Basic peat properties was analysed using peat elemental (C, H, N, O, S) composition. Parameter describing peat composition (atomic ratio H/C) is well correlated with the peat decomposition degree, thus indicating molecular mechanisms behind peat humification – dehydrogenation (hydrogen removal from organic molecules) during humification process. Other indicators of peat organic matter generally well describing peat transformation process includes HA/FA, D_{540}, E_4/E_6 and I_{460}/I_{510} not so much describing peat but rather humic matter properties.

Studies of elemental composition of peat HAs extracted from a peat column can give information about ongoing humification reactions during peat development. Humification has been mostly studied with the aim to analyse composting and soil formation processes. However, the humification process in peat is much different from that in composts and soils, which have a quite rapid decomposition of organic matter in early humification stages. However, in waterlogged environments, under the impact of anaerobic and acidic conditions, the humification process of the saturated peat layers is very much retarded. Nevertheless, in peat it is possible to follow the humification process for very long periods (more than several thousand years).

The changes of H/C ratio in humic acids from Dzelve bog show importance of peat accumulation speed. Bottom to middle layers of bog show increasing H/C ratio.

Upper layers of humic acids from Dzelve bog show relative stable H/C ratio, relatively high amount of carbon and hydrogen but decreasing oxygen percentage. Changes of H/C ratio in humic acids from Eipurs bog show differences between fen peat at the 3.5–4.62-m depth and other layers of bog, and these values are lower for fen peat. Lower C, H percentage and ratio H/C and higher ratio O/C are common for peat which fully or partly is formed from wood (generally – pine); these effects indicate presence of lignin.

The relation between H/C and O/C atomic ratio of HAs (van Krevelen graphs as frequently applied for studies of HSs and the C biogeochemical cycle) reveals changes in the elemental composition of humic acids and thus is useful in identification of structural changes and the degree of maturity of HAs. Van Krevelen graph is a graphical representation of the humification process, indicating the degree of maturity and intensity of degradation processes such as dehydrogenation (reduction of H/C ratio), decarboxylation (reduction of O/C ratio), demethylation, occurring during the genesis of humic acids. From the point of view of chemistry, peat elemental ratio of peat HAs demonstrate the changes of HA composition during peat diagenesis, considering it as a process in which more labile structures (carbohydrates, amino acids, etc.) are destroyed, but thermodynamically more stable aromatic and polyaromatic structures emerge. Comparatively, the studied peat HAs are at the start of the transformation process of living organic matter.

To provide reliable and quantitative information about the diagenesis of HAs, we carried out further studies of the dependence of the elemental composition of the peat and its humic acids on the peat age (depth and decomposition degree). The trends of dependence between H/C values and the depth of the peat samples were mostly negatively related, demonstrating that dehydrogenation is amongst the dominant processes during ageing of peat HAs. Further methods such as FTIR, ESR and ^{1}H and ^{13}C NMR were used to get an insight in the structure of humic acids.

A study of correlations between properties of humic acids isolated from corresponding peat layers and peat decomposition degree proves the concept about major processes behind the humification and illustrates the diagenesis of peat organic matter. At first the increased peat decomposition degree might be associated with dehydrogenation of peat humic acids probably leading towards development of aromatic structures. Another evidently ongoing process is development of acidity – genesis of carboxylic groups in peat humic substances during peat organic matter decomposition and humification.

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