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CHANGES OF PEAT HUMIC ACID PROPERTIES DURING PEAT GENESIS PROCESS

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SUMMARY

Comparative and complex characterization of peat humic acids (HAs) isolated from peat profiles of different origin in Latvia was done. Elemental and functional analysis of the isolated HAs was done, their acidity and molecular weights estimated. Properties of HAs isolated from the Latvian peat were compared with HA from other sources (soil, water, coal and synthetic humic substances). Major properties of peat HAs depended on their origin, indicating the importance of humification processes.

KEYWORDS: humic acid, peat, Latvia, humification degree

INTRODUCTION

Humic substances (HSs) are a general category of naturally occurring, biogenic, heterogeneous organic substances that can be generally characterized as yellow to black in color, of high molecular weight, and refractory (Stevenson, 1994). HSs form most of the organic component of peat forming up to 60–85% of the organic matter in peat.

Peat can be a source of up to 500 Gt of C as HAs of industrial value (Markov et al., 1998). There have been few studies aimed at understanding of C biogeochemical cycling, structure and properties of peat HSs in relation to peat properties, especially considering the high potential for industrial production (Fong and Murtedza, 2007).

The interest about peat properties is growing as far as peat as substance supports and influences bog and wetland ecosystems, but peat profiles can serve as an archive indicating conditions in past environments. In form of peat is stored significant amounts of organic carbon and thus peat reserves play major role in the carbon biogeochemical cycling and is of especial role considering the ongoing climate change process. Industrial and agricultural uses of peat are growing and significant amounts of peat are mined industrially. Considering this, there is an increasing interest into studies of peat properties diagenesis of their properties. 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, 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.

The aim of the present paper is to analyze the properties of peat HAs isolated from peat profiles and to evaluate the impact of the character of humification processes.

MATERIALS AND METHODS

From profiles of 8 high-type bogs of industrial importance in Latvia, peat samples were collected and after peat dating (¹⁴C) and characterization, humic acids were isolated. The analysis of peat botanical composition was performed microscopically decomposition degree was determined. HAs were extracted and purified using procedures recommended by the International Humic Substances Society (Tan, 2005). Industrially-produced HA (Aldrich) and IHSS reference HA isolated from Pahokee (USA) peat were used for comparison.

Elemental analysis (C, H, N, S and O) was carried out using an Elemental Analyzer Model EA-1108 and the found values were normalized in respect to ash content. UV/Vis, fluorescence, FTIR spectra were recorded and the ratio E₄/E₆ were calculated. Titration was used to measure acidity of each HA (Tan, 2003).

RESULTS AND DISCUSSION

Peat HSs can be considered especially appropriate for studies to understand the C biogeochemical cycle because links can be made between HS properties and the decomposition degree of the original organic matter. In addition, studies of peat humification are of definite applied and theoretical interest, considering the growing need for industrially-produced HA.

In this study the peat samples were from different depths in eight raised bogs in Latvia, representing bogs of industrial importance, and reflecting bog development conditions in Northern Europe. The botanical composition of the deepest peat layer was mostly high-type cotton-grass-sphagnum peat and high-type fuscum peat, but in the upper layer it was high-type fuscum peat. The age range of samples was 200–9000 years, and their decomposition varied from 8 to 70 %. The age and decomposition degree of peat gradually increased with increased depth.

There was significant variation in elemental composition of HAs within the peat profiles.

Depending on the bog and the intervals of changes, the elemental compositions of the studied peat HAs were highly variable: C was 49–57%; H was 4.6–5.7%, N was 1.6–2.8%, S was 0.5–1.5% and ash was 0.1–1.2%. The O content, with range 32–42%, was determined by mass balance. In general, C and H concentrations increased with depth. N concentrations decreased with depth, but S concentration was very variable down the profile. The elemental composition of

HAs from peat in Latvia is of similar magnitude to those for peat HA's from other regions of the world.

The most dominant functional groups in the structure of HAs were carboxyl and phenolic hydroxyl groups, giving a sum of total acidity of HAs. The range of total acidity was 6.67–8.36 meq/g and was usually higher for HAs from upper peat layers.

The peat HAs were analyzed using van Krevelen graphs as frequently applied for studies of HSs and the C biogeochemical cycle. According to Orlov (1990), the index of atomic ratios O/C, H/C and N/C is useful in identification of structural changes and the degree of maturity of HSs obtained from different environments. The relation between H/C atomic ratio and O/C atomic ratio of HAs of differing decomposition degree – beginning with bog plants up to brown coal, lignite and coal – reveals changes in the associated elemental composition (Fig. 1). Figure 1 could be considered 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 decay of peat-forming plants, and peat humus maturation continuing up to coal. These changes are especially evident if atomic ratios of peat-forming plants (Sector 3 in Fig. 1) are compared to the atomic ratio of organic matter of a high decomposition degree (low moor peat, coal) (Sector 3 in Fig. 1). From the point of view of chemistry, peat HAs have an intermediate position (Sector 5 in Fig. 1) between the living organic matter and coal organic matter and their structure is formed in 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 samples on their age. 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. O/C *vs.* N/C atomic ratios indicates that the decarboxylation processes were in line with the reduction of N concentration relative to C content in HSs.

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 analyze 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 results demonstrate that it is possible to study the stage of humification of organic matter in peat according to its age and apply the methods of analysis to the estimation of peat humification. Humification degree is suggested as a good measure of peat decomposition.

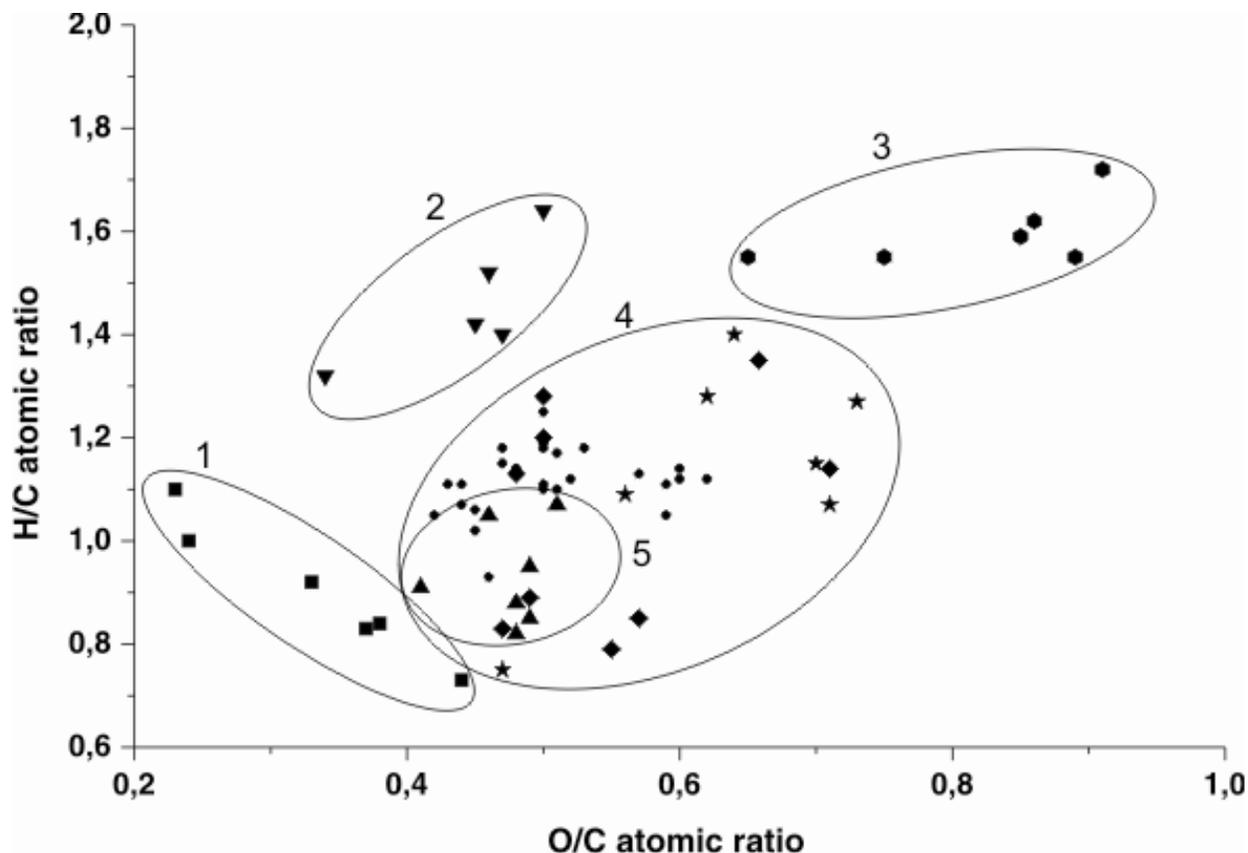


Fig. 1. Van Krevelen (H/C vs. O/C atomic ratio) graph of bog plants (●); HAs isolated from peat samples from bogs in Latvia (◐); reference peat HA (IHSS 2008) and peat HA (★); soil HA (◆); HA from different coals and lignite (■), sedimentary HA (▼) and aquatic HA (▲).

UV–Vis absorption ratios were measured to provide information about the humification state of peat samples. The ratio E_4/E_6 is often used to describe the extent of condensation of the aromatic C-containing structures; low ratios reflect high degrees of condensation of aromatics, while high ratios mean the presence of large quantities of aliphatic structures and low amounts of condensed aromatics. This ratio is also inversely related to the degree of aromaticity, particle size, molecular weight and acidity.

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

CONCLUSIONS

The elemental, functional, mass-molecular characterization of peat HA's stress the role of their origin on HS properties. The present study showed that the dominant peat mass was relatively homogeneous unless there was high variability in peat HAs properties. The source of changes in peat HAs properties extracted from industrially important bogs could be at first natural variability of bog biological material (mosses, reeds, shrubs etc) and structural changes of bog biological material during the humification process.

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