Humification indicators of peat

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Summary

An important parameter of organic matter in soils, peat, and fossil carbon-containing deposits is their decomposition degree that describes their transformation intensity –the humification degree of original living organic matter. In this article approaches to the analysis of humification degree of thoroughly described and ^{14}C dated peat columns extracted from several bogs in Latvia have been investigated and compared. A new humification indicator is suggested: a ratio of the total amount of organic matter in peat in respect to the amount of humic substances.

Key index words: Peat; Humification degree; Decomposition degree

Introduction

Major part of peat organic matter is composed from humic substances. Historically, the term "humus" has been applied to the dark-coloured, organic matter in soils, and the terms "humic acid", "fulvic acid", and "humin" have been used to designate different portions of humus. To characterize humification process, the development of humification indexes that link the rate of transformation of living organic matter and the development of humic substances with parameters describing the properties of the formed materials can be an important indicator (Lu *et al.*, 2001). Several humification indexes have been suggested to study humification process during composting in order to evaluate maturity of compost (Jerzykiewicz *et al.*, 1999) and study soil formation processes (Corvasce *et al.*, 2006). Usually humification process is evaluated by making indirect measurements that describe structural changes that occur during the humification process. Several methods have been suggested for description of humification, such as the measurement of E_4/E_6 ratio that indicates development of condensed macromolecules and the amount of organic /aliphatic carbon estimated by ^{13}C CP MAS NMR. A significant amount of organic matter is stored as the organic matter of peat. However, few studies on humification processes of peat have been done (Schnitzer and Levesque, 1979; Francioso *et al.*, 2003), although bogs and wetlands form one of the largest sources of refractory organic matter.

The aim of this article is to study the humification process of peat and to identify links between peat age (its decomposition degree) and the basic properties of peat and the organic matter of peat.

Materials and Methods

Sampling. 28 peat samples were collected from the profiles of five high type bogs of industrial importance in Latvia. The profiles were obtained in varying depths from 0 to 145 cm. The peat samples were dried in laboratory conditions at a temperature of 105°C. The samples were then homogenized and sieved trough a 1 mm sieve.

Peat characterization. The analysis of botanical composition of the peat was performed using Carl-Zeiss binocular microscope, but the decomposition degree was determined using known methods. The ^{14}C dating was done at the Institute of Geology of the Tallinn Technical University (Estonia). Elemental analysis (C, H, N, S, and O) was carried out using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). Ash content was measured after heating 50 mg of each peat sample at 750°C for 8 h. UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co) spectrophotometer in a 1-cm quartz cuvette. The ratios E_2/E_6, E_2/E_3, E_3/E_4, E_4/E_6: ratio of absorbance at 280, 340, 465 and 665 nm was determined for the solution of 5 mg of the humic or fulvic acid in 10 ml of 0.05 M $NaHCO_3$. Organic carbon concentration of peat extracts was determined Shimadzu TOC – VCSN. For carbohydrate analysis, humic samples (10 mg) were suspended in 10 ml of 6 M HCl and heated at 100 C for 3 hrs. In the hydrolysates, the concentration of carbohydrates was determined with the help of phenol-sulphuric acid assay following the method described by Chaplin and Kennedy (1994). Cation exchange capacity (ammonium acetate method) and concentration of phosphates were determined using methods suggested for soil analysis (Tan, 2005).

To study humification process following indicators has been used:

1. Humification index (HI) (Cavani *et al.*, 2003)
2. Pyrophosphate index (PyI) (Schnitzer and Levesque, 1979)
3. Humus quality K value (Hargitai 1994)

We suggested to use:

- Peat humification index (PHI)

1.00 g of peat sample was shaken for 24 hrs with 50 ml of deionised water, filtered, and in the filtrate the total organic carbon of the aquatic extract (C_w) was determined. Another 1.00 g portion of the same peat sample was extracted shaking for 24 hrs with 50 ml of 0.1 M NaOH, filtered, and in the filtrate the total organic carbon of the alkaline extract (C_{NaOH}) was determined. The peat humification index was calculated as:

$$PHI = \frac{C_w}{C_{NaOH}} \times 100$$

Humification degree (HD)

1.00 g of peat sample was shaken for 24 hrs with 50 ml of 1.0 M NaOH, filtered, and in the filtrate the total organic carbon of the alkaline extract, containing humic substances (C_{HS}), was determined (mg C/g). The peat humification degree was calculated as:

$$HD = \frac{C_{HS}}{C_{peat}} \times 100$$

, where C is the carbon in the sample (mg/g).

Results and Discussion

Although the transformation process of living organic matter (humification) is of importance in understanding of carbon biogeochemical cycle, the number of studies dedicated to this topic is rather small. Peat can be considered an especially appropriate subject of studies of humification because it is possible to establish links between peat's properties and the decomposition degree of original organic matter. In addition, the studies of peat humification are of a definite applied and theoretical interest.

In this study peat from 5 raised bogs in Latvia has been used and samples from different depths have been obtained, representing bogs of industrial importance, as well as reflecting bog development conditions in Northern Europe. The botanical composition of the deepest layer of peat is mostly high type cotton-grass-sphagnum peat and high type fuscum peat, but in the upper layer it is high type fuscum peat. The age of the samples varies from 400 to 2260 years, and their decomposition degree (van Post scale) varies from H2 to H6.

However, the basic parameters of peat do not display a similar increasing trend for all the studied samples. Carbon and nitrogen content of peat samples from the bog Mazais Veiķenieks increases with increasing age (the depth and decomposition degree), but the content of sulphur is decreasing with increasing age. However, for the rest of the studied bogs, the variability of elemental composition is not so random and most probably depends on the botanical composition and the specific peat formation conditions (first, the hydrological regime in the corresponding bog).

The peat humification process has been analysed using van Krevelen graphs frequently applied for the analysis of carbon biogeochemical cycle and genesis of fossil fuel. The index of atomic ratios O/C, H/C, and N/C is useful in the identification of structural changes and the degree of maturity of peat in different depositional environments. The graph of H/C atomic ratio against O/C atomic ratio reveals changes in the properties associated with coalification reactions.

Figure 1 shows the relation between H/C atomic ratio and O/C atomic ratio of organic material of a differing decomposition degree – beginning with bog plants up to brown coal, lignite, and coal. The graph in Fig. 1 could be considered as a graphical statistical representation of 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 maturation continuing up to coal. These changes are especially evident if atomic ratios of peat forming plants are compared to the atomic ratio of organic matter of a high decomposition degree (low moor peat, coal). From the point of view of chemistry, humification can be considered as a process in which more labile structures (carbohydrates, amino acids, etc) are destroyed, but thermodynamically more stable aromatic and polyaromatic structures emerge. It follows that the analysis of atomic ratios confirms the background of processes during peat humification. As shown in Figure 1, H/C ratio decreases with increasing decomposition degree of the original living matter, starting with peat forming plants, cellulose, and proteins, and up to bituminous coal. Comparatively, the studied peats are at the start of the transformation process of living organic matter. The van Krevelen graph (Fig. 1) also indicates a decrease in O/C ratio illustrating the decrease in the amount of oxygen-containing functional groups, such as methoxyl, carboxylic, and carbonyl functional groups, in the fossil material with increasing humification degree. In order to provide reliable and quantity information about the early diagenesis, we carried out further studies of the dependence of the elemental composition of the peat samples on their age (depth and decomposition degree). The trends of dependence between H/C values and the depth of the peat samples mostly show negative relation; Kaigu and Mazais Veiķenieks peat bogs have the highest negative correlations, while Dižais Veiķenieks bog shows a strong positive relation indicating the general trends of peat transformation, however, at the same time demonstrating that atomic ratio cannot be correctly used to study the humification process due to the significant impact of the original plant composition and peat formation conditions.

Changes of carbohydrate concentration in peat correlate more strongly with peat depth and, evidently, peat age. The concentration of carbohydrates in peat reduces with increasing depth of the studied peat layers, clearly indicating that carbohydrate degradation is amongst major processes describing peat formation and humification.

Variability of the 25 parameters, describing peat properties, their decomposition degree, age, and peat humification process, has been analysed with the help of the principal component analysis. The first five components extracted from the data on the basic peat properties and the studied humification coefficients explained 84 % of the total variance. The first component involved parameters surely describing the development of peat – its elemental composition (C, N and O) and correlated well with the suggested humification degree HD. The second component characterized the correlation between peat type, hydrogen, and nitrogen; these parameters are correlated with peat humification index PHI. The third component characterized the humification processes because it included most of the humification coefficients used in our study; their correlation with peat age and type is comparatively high. It is supposed that all the used humification coefficients can be applied

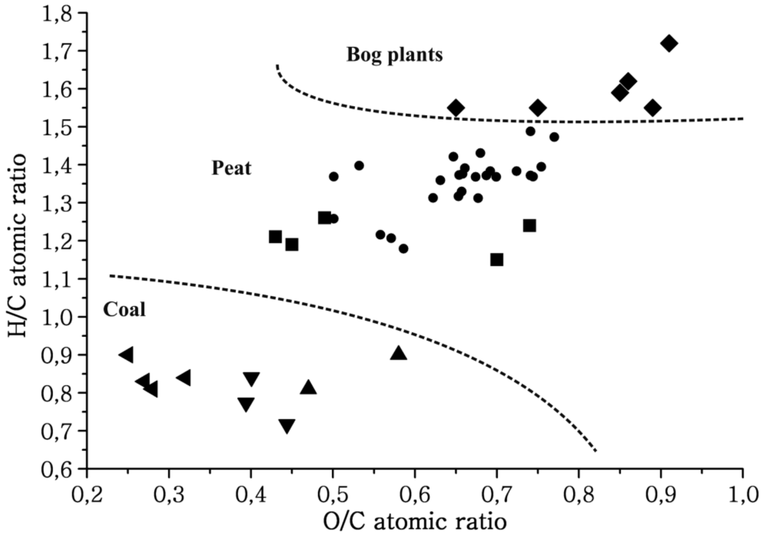

Figure 1. Van Krevelen (H/C vs. O/C atomic ratio) graph of bog plants (◆) peat samples from studied bogs in Latvia (●), reference peat samples (IHSS) and peat samples from common peat bogs (■), brown coal (▲), coal (◀), lignite (▼).

for analysis of peat humification process since each of them describes differing aspects of humification process. The fourth component was characterized by a close relation between the extinction ratios of humic extracts; it rather described the properties of peat humic matter than the transformation degree of peat organic matter. However, the very simple parameter – extinction ratio E_4/E_6 is well correlated with the depth of the location of the peat samples and peat age; it can also be efficiently used to analyze the humification process. The fifth component can be designated as the "age component" since it presents a very good correlation between peat depth, age and such humification indicators as E_4/E_6, H/C, K, PyI, and HD. Therefore these humification indicators can be recommended for characterization of peat humification process. The first question to be resolved includes the definition of the concepts "decomposition degree" and "humification degree". The decomposition degree describes the extent to which original (living) organic matter is transformed. Decomposition process thus includes: a) transformation processes of living organisms and their tissues; b) degradation of molecules forming a living organism; c) mineralization (transformation of organic carbon compounds containing organic nitrogen, phosphorous, and sulphur compounds into their inorganic species); d) formation of refractory organic substances – humic substances. Decomposition can also be described as the breakdown of plant material accomplished by microorganisms that use decaying organic matter as a source of energy and a building material. Besides the chemical decomposition, an important indicator of decomposition is mechanical friction. In case the decomposition degree is one of the key parameters describing possibilities to use peat for agricultural purposes, several schemes of the characterization of decomposition are suggested, such as von Post scale, r value, and the peat classification of International Peat Society. The estimation of the humification degree is often based on the monitoring of humic substances (HS), humic acids (HA), and fulvic acids (FA), isolated by extraction in alkaline solution (Stevenson, 1994). Among the proposed indexes of maturity, those most representative of the evolution of the maturity of the compost were presented, particularly the indexes measuring the evolution of humic acids (HA) compared to fulvic fraction (FF) or fulvic acids (FA). Humification is a narrower concept, describing the development of humus (humic substances). As humification degree we suggest to use the ratio of the total amount of organic matter to the amount of formed humic substances:

$$HD = \frac{C_{HS}}{C_{peat}}$$

As the results of our study show, this parameter corresponds well to the peat depth and age, so it can also be used to study the transformation processes of organic matter.

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