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EFFECT OF PH ON THE RELEASE OF ORGANIC MATTER FROM MUCKS

Изучена роль pH в высвобождении органического вещества (ОВ) из торфяников. Исследования проводились для H – моноионных форм семи торфяников (Terric Histosols). Концентрацию растворенного органического вещества (РОВ) определяли колориметрически (465 нм). На основании полученных спектров поглощения были рассчитаны параметры $Q_{2/6}$ и $Q_{4/6}$. Растворенность ОВ существенно зависит от величины pH. Зависимость может быть описана следующим уравнением: РОВ = 0.01 exp(b_1*pH). Полученные результаты подтверждают зависимость между параметрами W_1, Q и b_1.

Ключевые слова: *растворенное органическое вещество (РОВ), pH, степень вторичной трансформации.*

Introduction

Peatlands are large sources of dissolved organic matter. Peat represents a highly organic material, which in nature contains typically 80–90 %. The importance of humic substances in water management of peat is suggested by the fact that peat contains about 25–30 % humic acids (HA) on a dry weight basic [1]. The melioration of peatlands led to the biotic and abiotic changes, which implicated the degradation of organic matter and organic compounds. Kalbitz et al. [2] showed that the land use of peatlands effects on fulvic acids (FA) properties, which account for the major fraction of dissolved organic matter. The above mentioned authors suggested that long-term intensive land use (from 50 to above 200 years) resulted in larger proportion of the aromatic structures and a larger degree of polycondensation of FA [2]. However it is unknown what changes in the units of the structure of FA they cause. Leinweber et al. [3] reported that in water-soluble FA, which are the main component (about 60 %) of dissolved organic matter, the proportion of carbohydrates and phenols together with lignin monomers increased with increasing intensity of soil tillage, aeration and peat degradation.

Most of the peatlands in Poland have been drained and subjected to agricultural use. Draining melioration changes natural peat soil evolution characterized by processes among which mineralization and secondary humification are of the greatest importance. The above processes lead to the changes in the morphological, chemical, biological and physical properties of peat soils. Taking into account the degree of the peat transformation, the muck mass can be divided into three categories: Z_1 – peaty muck, Z_2 – humic muck and Z_3 – proper muck [4]. In the peat-muck soil, the muck constitutes the upper part and primary peat the lower part of the profile. The thickness of the muck layer depends on the intensity of drainage. Based on the thickness of this layer, peat-muck soils are next divided into three groups, weakly transformed (MtI), medium transformed (MtII) and strongly transformed (MtIII) [4].

While water conditions change, soil mass loses its sorption abilities and gains more hydrophobic character. The mechanism of the above changes is called secondary transformation. It causes a decrease in the humus content and changes its quality and release of ash elements. As the consequence of the secondary transformation, soil degradation and lost of fertility occurs. One of important factor of these phenomena can be release of organic matter which can affect not only the soil but the quality of groundwater and surface water. To improve agricultural properties of muck soils and protect of groundwater and surface water from pollution and rapid degradation, knowledge of the influence of pH, temperature, ionic content of soil solution on mobility of organic matter is necessary. In particular, pH of organic soil is very important for coagulation and peptization processes of organic matter. Changes in pH affect the electrostatic charge that induces attraction – repulsion of negatively charged surfaces of humic acids to other soil components.

Important characteristics of organic matter is its ability to form water-soluble and water insoluble complexes with metal ions and hydrous oxides and to interact with organic compounds such as alkanes, fatty acids, dialkyl phthalates, pesticides etc. Of special concern is the formation of water-soluble complexes of FA with toxic metals and organics.

The effect of pH on organic matter release from mineral and organic-mineral soils has been the subject of many investigations [5]. However, there is still to little of studies connecting results of optical measurements (concentrations, Q-factors) with kinetic investigations of alkalization processes.

The purpose of studies was to carry out the model investigations to look for effect of the degree of the secondary transformations on the DOM release at various pH in peat-muck soils. In that studies, spectrophotometric measurements of the concentration of released total dissolved organic carbon and indexes calculated on its basis ($Q_{2/6}$, $Q_{4/6}$) were supported by mathematical formula of organic carbon dynamics, which was established in order to improve of method sensitivity.

Matherials and methods

The study was conducted on 7 meadow muck samples (Terric Histosols) at different states of secondary

to the degree of mucking and to the secondary transformation of the soil mass. The lowest density (0.21–0.28 $g \cdot cm^{-3}$) is observed in mucks, which posses the lowest soil water adsorptivity index ($0.41<W_1<0.48$). In the strongly transformed mucks, the values of W_1 range from 0.60 to 0.74, the bulk density is higher (from 0.24 to 0.34 $g \cdot cm^{-3}$). Most of the soils are acidic (samples 1, 3, 4, 5), one is slightly acidic (sample 6) and one – very acidic (samples 2).

Very similar spectra were observed for the DOM extracted at various pH values. These absorption spectra had neither maximum nor minima and the optical density usually decrease as the wavelength increased. The composition of organic matter is frequently characterized by the ratio of absorbances at λ=465nm (Q_4) and at λ=665 nm (Q_6) [8] and also by 280/665nm ratio. As the absorbance at λ=465 nm is due to smaller molecules, and at λ=665 nm to larger molecules, the $Q_{4/6}$ ratio is expected to be larger for FA of low molecular weight and smaller for humic acids of greater molecular weight studies. The $Q_{4/6}$ ratio is <6 for HA and 6–18.5 for FA [9]. Kononova [9] believes that the magnitude of the $Q_{4/6}$ is related to the degree of condensation of the aromatic C network, with a low ratio indicative of a relatively high degree of condensation of aromatic condensation and infers the presence of relatively large proportions of aliphatic structures. Conversely, a high $Q_{4/6}$ ratio reflects a low degree of aromatic condensation and infers the presence of relatively large proportions of aliphatic structures. $Q_{2/6}$ index characterizes content of compounds of lignin types. Those ratios have been reported to vary for humic materials extracted from different soil types and to be independent on concentrations of humic materials [9–10]. The $Q_{4/6}$ and $Q_{2/6}$ ratios for the organic matter released from the studied soils at pH=8 and in relation to secondary transformation index are shown in Fig. 2.

The $Q_{4/6}$ values ranging between 5.3 to 8 show that in the studied mucks the relative content of FA and HA is very similar and that the FA is prevailed.

The amounts of DOM measured in the extracts at different pH are shown in Fig. 3. The dissolution of soil organic matter was significantly affected by pH. The

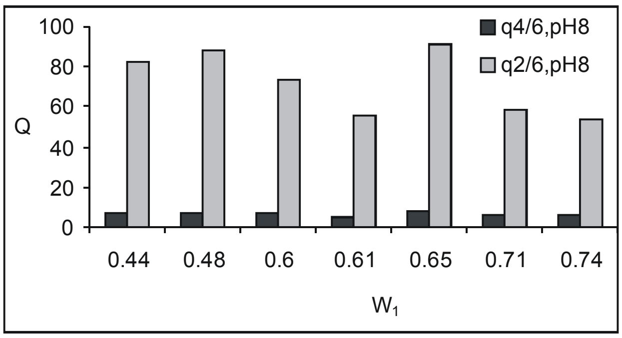

Fig. 2. Relationship between $Q_{2/6}$, $Q_{4/6}$ of extracted organic matter and secondary transformation degree

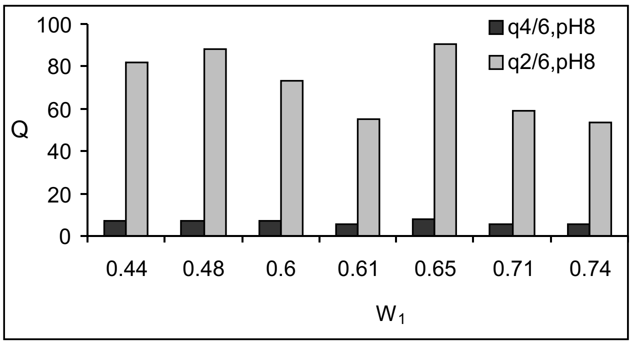

Fig. 3. Concentration of dissolved organic matter released at different pH from extracts vs secondary transformation index of studied mucks

results of [11] suggest that the key factor in humic release is the net electrical charge which is governed principally by pH. Data in Fig. 3 show the dissolved organic matter concentration was small that at low pH values. Generally the dissolution of organic matter increases with an increase in pH. An increase in pH leads to an increase in the negative surface charge of organic substances that causes their repulsion by each other and the other negatively charged soil components. Also the organic-organic and organic-mineral bonds by multivalent cations may be broken by cations neutralization, e. g. aluminum or precipitation, e.g. magnesium. The above processes cause migration of organic particles from the solid to the liquid phase. Low $Q_{4/6}$ ratio reflects high proportion of strongly colored humus substances. So, it can be stated that muck formation process enriched the investigated soils with humic acids. Low molecular weight organic substances could be leached out from the soils during the transformation process. The contents of fulvic acids were higher in less transformed samples.

Previous researches of the authors showed, that the organic matter dissolution process during alkalization could be satisfactory described with the following equation [12]:

$$DOM(pH) = 0.01 \exp(b_1 \cdot pH),$$

where b_1 was parameter which could be considered as quantitative index of OM release process under the experimental conditions applied.

It was proved, that index of equation – b_1 increases with secondary transformation degree. The highest concentration of DOM was obtained for the strongly secondary transformed sample (W_1=0.74). The opposite was obtained for the weakly secondary transformed sample (W_1=0.48). The tendency of increasing of DOM with the state of secondary transformation could indicate that the partial disruption of humus aggregates took place during the secondary humification. As a consequence of the above different substances of lower molecular weight, e. g. FA acids were formed. Qualitative index – Q are also correlated with b_1 and W_1 indexes what was presented in previous investigations [12].

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