Empirical equation to describe the effect of pH on organic matter release from mucks

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A b s t r a c t. The effect of high pH values on release of organic matter from mucks was investigated. This study was conducted on homoionic hydrogen forms of 13 meadow muck samples (Terric Histosols). States of secondary transformation were estimated using the water holding capacity index, W_1 which is the ratio of the centrifuge moisture equivalent measured after predrying at 105°C and one week rewetting to the centrifuge moisture equivalent of fresh sample. Concentrations of dissolved organic matter (DOM) released were determined colorimetrically at 465 nm. The dissolution of soil organic matter was significantly affected by pH. The relationship could be satisfactorily described by the equation: $DOM = 0.01 \exp(b_1\ pH)$. The b_1 parameter quantified the DOM release process in relation to the changes in soil pH.

K e y w o r d s: muck, humic and fulvic acids, dissolved organic matter (DOM), pH, state of secondary transformation

INTRODUCTION

Peatlands are large sources of dissolved organic matter (DOM). DOM is involved in a number of biogeochemical processes, including pH buffering, nutrient cycling, ionic balance, mineral weathering, metal leaching, pollutant toxicity, mobility and bioavailability.

When peatland is drained, accumulated peat mass is transformed into a different formation called muck. The above process is called the secondary transformation or mucking process (Okruszko, 1993). The secondary transformation can cause a decrease in the humus content, changes in its quality, release of ash elements and organic matter occurs. Some of organic substances (humus) are sorbed by soil solid particles and tend to accumulate at or near the soil surface. Some of the material is transported through unsaturated zone into the saturated zone, where can remain dissolved and move with the groundwater that could became organically polluted (Kaiser and Zech, 2000). So, dissolved organic matter (DOM) is an important component of soil and aquatic environments. The nature and the amount of DOM in soil solution can influence the quality of groundwater and surface waters. Knowledge of the factors influencing the release of DOM is necessary to protect the groundwater and the surface water from pollution and rapid degradation.

The availability of organic matter and its mobility in the soil is a consequence of many factors, including properties of the soil (Hajnos *et al*., 2002), as well as changes in climate, especially temperature and rainfall patterns (McDowell and Wood, 1984; Nambu and Yonebayshi, 2000). In particular, pH is very important for adsorption of organic matter on soil particles and its release to soil solution. Changes in pH affect the electrostatic charge that induces attraction – repulsion of negatively charged surfaces of humic acids to other soil components.

The effect of pH on organic matter release from mineral and organic-mineral soils has been the subject of many investigations (Kalbitz *et al*., 2000). There is still a lack of studies on the kinetics of organic matter release in organic soils especially mucks. Colorimetry is one the most researched and widely applied methods to determine the concentration of DOM in soil solution as well as to perform its qualitative characteristic (Ghosh and Schnitzer, 1979; MacCarthy and Rice, 1985).

The objective of this study was to investigate the effect of high pH on release of organic matter from mucks and to look for a mathematical formula of organic carbon dynamics. The degree of the secondary transformation into investigated mucks was taken into account. It is expected that the experimental approach contribute to a better understanding of the dynamic of organic matter release under laboratory conditions.

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MATERIALS AND METHODS

The study was conducted on 13 meadow muck samples (Terric Histosols) at different states of secondary transformation. The samples were collected at the depth of 5-20 cm from sites located in a low moor area of the Wieprz-Krzna Canal and Biebrza River. The state of transformation of the studied soils was estimated using water holding capacity index, W_1, determined according to Gawlik (1992). This index is determined by dividing the water capacity of a sample that has been previously dried at 105°C by its water capacity in the natural state. Values of W_1 less than 0.36 characterize non-transformed peat fraction. Values of W_1 ranging from 0.36 to 0.61 are characteristic for weakly and medium transformed peats. W_1 between 0.61 and 0.82 are found in strongly transformed peats and W_1 larger than 0.82 are typical for degraded hydrogenic soils. Recently, Gawlik (2000) has proposed a modified classification scheme of the muck formations, which takes into account also the content of mineral fraction. However, the soils studied in this work were formed from proper peats and contain more or less uniform amounts of mineral components. Therefore, we decided to use the W_1 index as the degree of secondary transformation. Table 1 shows W_1 values for the studied soil materials and their selected physical properties.

Because of the conditions of genesis, the muck formations differ in their surface ionic composition and pH. The chemical heterogeneity of investigated mucks could masked these properties which depend on the stage of secondary transformation and have an affect on DOM release process. So, it was decided to carry the experimental approach on monoionic forms. Homoionic hydrogen forms of the studied soils were obtained by three-time leaching with 0.1 M HCl at the w/w ratio of solid to liquid equal to 1:100, following by four-time leaching with distilled water and

centrifuging. Next, the wet homoionic hydrogen forms of samples corresponding to 0.4 g of dry organic matter were diluted with distilled water and treated with NaOH solutions to arrive at pH values around 5, 6, 7 and 8. Finally the ratio of solid to liquid in the suspensions was adjusted to 1:100 w/w. Values of pH were measured with Radiometer Copenhagen model pH 240 pH/Ion meter. The suspensions were equilibrated during 48 h and their pH values were recorded. Next, the DOM extracts were taken by 45 μm mambrane filtering.

Concentrations of DOM in the extracts were determined colorimetrically via the light absorption at 465 nm using Jasco V-500 UV/VIS spectrophotometer. Next the absorption spectra in the UV and VIS regions for a few mucks (1,5,12) and sodium humate (Aldrich H1, 675-2) solutions were measured. Generally, humic substances extracted from studied mucks yield uncharacteristic spectra in the UV and VIS regions (Fig. 1) (Brown, 1980). Because the absorption spectra for organic matter extracted from the studied mucks were the same to that for sodium humate (Aldrich H1, 675-2) solutions, the calibration curve was based on a series of 10 various concentrations (from 0.005 to 0.15 mg ml^{-1}) of the Aldrich reagent. Also the ratio of absorbances at 465 and 665 nm was determined in the extracts obtained at pH 8.

RESULTS AND DISCUSSION

All of soil samples are characterized by low (< 25%) ash content (Table 1). Soils examined greatly differ for volumetric densities, which are undoubtedly related to the degree of mucking and to the secondary transformation of the soil mass. The lowest density (0.21-0.28 g cm^{-3}) is observed in mucks, which posses the lowest soil water adsorptivity index (0.41<W_1<0.55). In the strongly transformed mucks, the values of W_1 range from 0.6 to 0.82, the bulk density is higher (from 0.28 to 0.39 g cm^{-3}). Most of the soils

T a b l e 1. Selected physical properties of investigated samples

No. sample	W_1*	pH in H_2O	pH in KCl	Ash content d.m. (%)	Bulk density (g cm^{-3})	Total porosity (% vol.)
1	0.44	5.1	4.5	22.7	0.21	88.5
2	0.48	4.7	4.2	20.5	0.28	84.7
3	0.55	5.5	5.2	17.6	0.25	84.6
4	0.60	5.4	5.0	21.2	0.34	81.4
5	0.61	5.8	5.3	15.1	0.24	85.2
6	0.65	5.4	4.9	20.5	0.32	82.5
7	0.65	5.5	5.0	18.9	0.31	80.9
8	0.67	4.8	4.2	16.3	0.28	82.7
9	0.71	5.7	5.3	15.8	0.31	80.9
10	0.71	6.2	5.8	22.8	0.30	83.6
11	0.72	5.0	4.5	18.0	0.36	77.8
12	0.74	5.8	5.3	21.5	0.29	84.1
13	0.82	5.5	5.0	22.3	0.39	78.7

W_1 – index of the secondary transformation, according to Gawlik (2000).
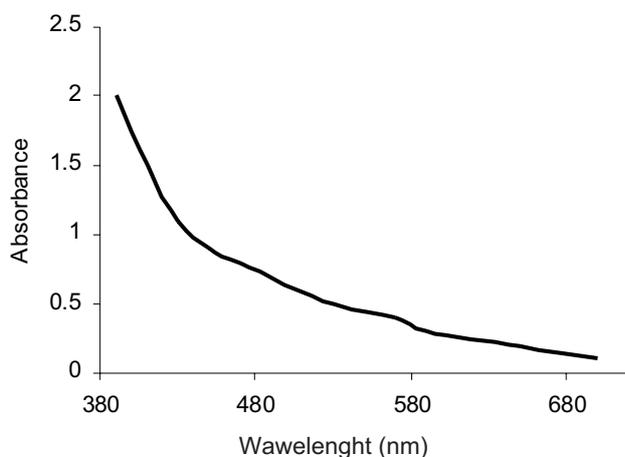
Fig. 1. Typical absorption spectrum of humic substances.

are acidic (samples 1, 3-7, 9, 11-13), one is slightly acidic (sample 10) and two - very acidic (samples 2 and 8).

A typical absorption spectrum of the organic matter extracted from the studied soils is presented in Fig. 1.

Very similar spectra were observed for the DOM extracted at various pH values. These absorption spectra had neither maxima 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 465nm (E_4) and at 665 nm (E_6) (Baes and Bloom, 1990). As the absorbance at 465 nm is due to smaller molecules, and at 665 nm to larger molecules, the E_4/E_6 ratio is expected to be larger for fulvic acids of low molecular weight and smaller for humic acids of greater molecular weight. The E_4/E_6 ratio is <6 for humic acid and 6-18.5 for fulvic acid (Kononova, 1966). This ratio has been reported

to vary for humic materials extracted from different soil types and to be independent on concentrations of humic materials (Kononova, 1966; Ghosh and Schnitzer, 1979). The E_4/E_6 ratio for the organic matter released from the studied soils is shown in Table 2.

The E_4/E_6 values ranging between 5.3 to 8 show that in the studied mucks the relative content of fulvic and humic acids is very similar and that the fulvic acids prevail (for eight samples E_4/E_6 is above 6).

The amounts of DOM measured in the extracts are shown in Fig. 2.

The dissolution of soil organic matter was significantly affected by pH. The results of Tipping and Woof (1990) suggest that the key factor in humic release is the net electrical charge which is governed principally by pH. Data in Fig. 2 show the dissolved organic matter concentration was small that at low pH values. Generally the dissolution of organic matter increases with the 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, *eg* aluminum or precipitation, *eg* magnesium. The above processes cause migration of organic particles from the solid to the liquid phase.

The concentration of the DOM increases exponentially with the pH (Fig. 1). This dependence could be described with the equation:

$$DOM(pH) = a \exp(b \, pH), \qquad (1)$$

where DOM(pH) is the amount of dissolved organic carbon (kg m^{-3}) and the coefficients a (kg m^{-3}) and b (dimensionless) are fitting parameters. The coefficient a shows the

T a b l e 2. Parameters obtained from colorimetric measurements and regression analysis

No. sample	E_4/E_6	a	b	b_1	R^2
1	7.0	0.0116	0.511	0.532	0.99
2	7.4	0.0096	0.522	0.516	0.97
3	6.9	0.0216	0.523	0.643	0.94
4	6.7	0.0138	0.530	0.579	0.97
5	5.3	0.0176	0.500	0.589	0.96
6	5.5	0.0101	0.656	0.658	0.96
7	8.0	0.0057	0.621	0.537	0.98
8	7.6	0.0075	0.600	0.558	0.98
9	7.2	0.0109	0.584	0.597	0.99
10	5.9	0.0156	0.590	0.661	0.97
11	5.6	0.0461	0.463	0.706	0.71
12	5.7	0.0307	0.527	0.715	0.85
13	6.3	0.0208	0.556	0.673	0.94

E_4/E_6 – ratio of absorbance at 465 nm to absorbance at 660 nm; a, b – coefficients from Eq. (1); b_1 – coefficient from Eq. (2); R^2 – correlation coefficient.

DOM(pH)=$a \cdot$exp($b \cdot$pH)
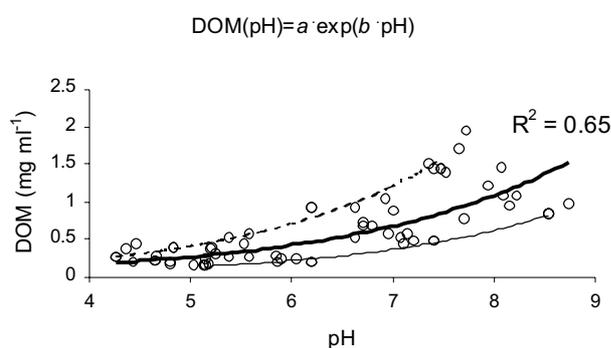
Fig. 2. Dependence of dissolved organic matter (DOM) on pH. Thick line – average, dashed line – sample of $W_1 = 0.74$, solid line – sample of $W_1 = 0.48$.
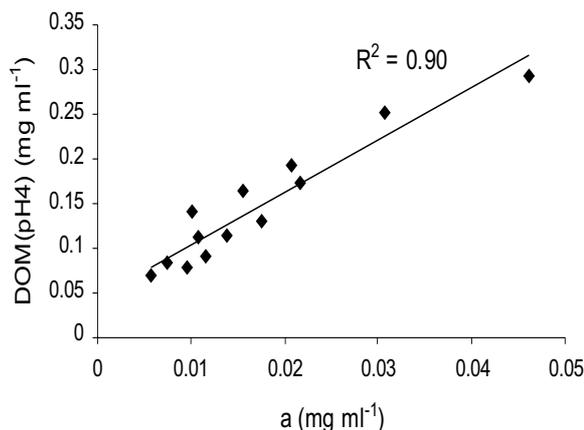
Fig. 3. Concentration of dissolved organic matter (DOM) released at pH 4 versus concentration of dissolved organic matter (a) presented in the solution before alkalization process.

theoretical amount of organic matter released at pH=0. If we assume that at low pH values the dissolution of organic matter is practically not influenced by the pH, the coefficient a reflects the overall ability of the given soil to release organic substances. The values of a coefficient are low ranged between 0.0057 mg ml^{-1} for soil number 9 and 0.0461 mg ml^{-1} for soil number 6.

Table 2 shows coefficients a and b for the studied mucks. Figure 3 shows the dependence between the coefficient a and the amount of organic matter released at the beginning of the experiment (at pH=4). The high correlation coefficient between the above data (0.90) indicates that the coefficient a may describe the amount of organic substances present in the solution before alkalization process, indeed.

The organic matter dissolution process during alkalization coud be satisfactory described with the equation:

$$DOM(pH) = 0.01 \exp(b_1 pH). \qquad (2)$$

In this case the value of 0.01 was matched empirically. Values of b_1 coefficient termed 'b_1 index' together with R^2 are collected in Table 2. The Eq. (2) provided high correlation between the experimental data ($R^2 > 0.94$ in most cases). After introduction of a single a=0.01 value for all samples, the single b_1 parameter can be considered as quantitative index of OM release process under the experimental conditions applied.

In the studied mucks the organic matter composition is a consequence of the state of secondary transformation expressed in this paper by the water holding capacity index, W_1. This index correlated with values of E_4/E_6 as shown in Fig. 4.

Low E_4/E_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. The investigated samples could be divided into two groups for which individual linear regression lines can be plotted. The first group consisted of samples of W_1 below 0.63 (circles in Fig. 4) and the second one of mucks of W_1 above 0.63 (squares in Fig. 4). One of the studied samples (degraded muck No. 13) did not belong to either of the groups. As it was stated (Fig. 4) more secondarily transformed mucks had higher relative contents of humic acids.

As it is seen in Fig. 2 the value of b_1 index appeared to depend on the state of the secondary transformation. 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, eg fulvic acids were formed. Figure 5 illustrates the dependence of b_1 coefficient on the water holding capacity index W_1.
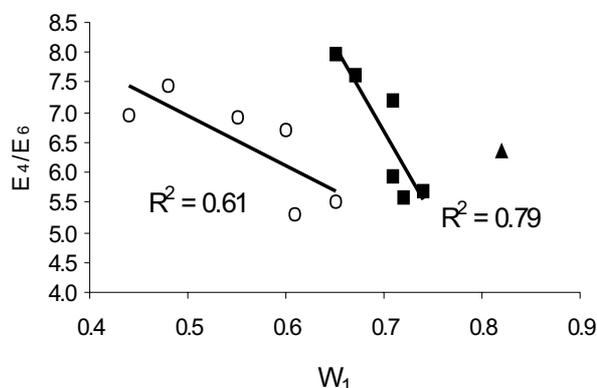
Fig. 4. Relation between the ratio of absorbances, E_4/E_6 and water holding capacity index, W_1 (circles – mucks at W_1 below 0.63; squares-mucks at W_1 above 0.63).
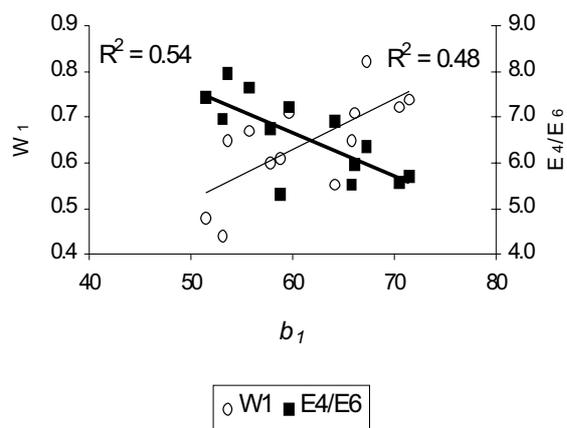
Fig. 5. Water holding capacity index, W_1 and ratio of absorbances, E_4/E_6 versus b_1 coefficient.

One can see that the b_1 index increases with the W_1 index (R^2=0.48). Moreover in Fig. 5 the relationship between b_1 coefficient and E_4/E_6 ratio is shown (R^2=0.54). The correlations were not high and showed only the presence of a general trend. The decrease in relative content of fulvic acids in investigated soils (E_4/E_6) resulted in increase in b_1 values. That indicated that humic acid fraction were easier dissolved. The opposite relationship was expected as fulvic acids have lower molecular weight and contain more chargeable carboxylic groups per unit mass (Sposito, 1989). In general the greater (more negative) the charge on the humic substances, the greater should be the extent of their release. Non-transformed peats (low W_1) had high E_4/E_6 (Fig. 4). However, one can expect that during the secondary transformation process, together with intensive mineralization and oxidation, humic acids do not remain intact and their molecular mass decreases. So strongly coloured organic matter belonging previously to humic part became fragmented and released to the solution. The UV/VIS absorption and the E_4/E_6 ratio is due to absorbance of photons only by chromophoric groups. Also at low pH values the fulvic acid predominantly dissolves and this might have been removed during samples pretreatment.

Humic substances (humus) are formed during humification process. Various interpretations have been proposed to elucidate the mechanisms of humification process which leads to humus formation. In general, humification can be defined as a conversion of degradation products of soil organic residues by series of polymerization reactions into new types of polymeric species that are different from the precursor ones (Schnitzer and Khan, 1978; Wershaw, 1994). The chemical structures of humus constituents are still controversial. There is an evidence that humic substances are mixtures of polymers of different molecular weights and charge densities (Stevenson, 1982). Increase of pH can cause decomposition of polymers and that induces solubility of lower molecular weight components.

CONCLUSIONS

1. Two empiric equations $DOM(pH) = a \exp(b\ pH)$ and $DOM(pH) = 0.01 \exp(b_1\ pH)$ were derived to describe the release of DOM from muck soils at laboratory conditions. The next step should be the experiments under field conditions to verify the proposed equations. These equations may be used for a prediction of the future trends in the chemical behaviour of muck.

2. The coefficient a describes intrinsic (independent on the environment) ability of the soil to release DOM.

3. The b_1 index could be used to quantify the DOM release process in relation to the increase in soil pH. So, this index may be useful in quantitative explanation of surface water organic pollution.

4. The release of the DOM depended on the degree of the secondary transformation of the studied soils.

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