

Effect of phosphates on dissolved organic matter release from peat-muck soils

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A b s t r a c t. The impact of phosphates on organic matter release from peat-muck soils was shown. Peat-muck samples were described among others by water adsorption index, content of amino acids, bulk density, pH, and ash. On the base of obtained data, studied samples were characterized in terms of variable surface charge and possible changes in surface properties of humic acids which might have been under phosphates influence. Nature of studied humic acids were defined by elemental analysis.

The release of dissolved organic matter from calcium forms of the humic acids was significantly affected by concentration of added salt. Generally, an increase in concentration of phosphates resulted in increasing of humic substances released to the solution up to 0.025 mol dm⁻³ of the added salt. At very low, initial phosphate concentration, the secondary coagulation of dissolved organic matter was observed. Potentiometric titration curves of humic acid solutions without addition of phosphate ions showed that studied organic matter was differentiated in relation to variable surface charge. However, titration curves of humic acids with additions of different phosphates concentrations were identical what could indicate that under experiment conditions, phosphates did not influence on structure of humic acid surface.

K e y w o r d s: humic acids, phosphates, mucks, dissolved organic matter

INTRODUCTION

The evolution of hydrogenic peat soils is closely related to the genesis of peat and to the changes in water relations. The chemical composition of peats depends mostly on the geobotanical conditions of their formation and on the depth of sampling (Hertkorn *et al.*, 2002). Due to a number of factors including oscillation of ground water level, changes of aerobic conditions, different plant communities, root exudates and products of degradation of plant remains, peat-muck soils may undergo a process of secondary transformation (Szajdak, 2002).

The peat-muck soils are a very rich in natural organic matter, which consists of a mixture of plant and animal products at various stages of decomposition, and substances synthesized after breakdown of these compounds. Changes and release of organic matter accompany the process of secondary transformation of peat. In particular, decomposition of plant biomass, transamination of ketoacids, root exudates and autolysis of microorganisms release amino acids, which are the main source of soil nitrogen (Friedel and Scheller, 2002; Kögel-Knabner, 2002). Amino acids can subsequently undergo mineralization, migration down the soil profile, adsorption, and humification (Kuzyakov, 1997). The mucks belong to group of soils containing a lot of organic matter. That matter is subject to a number of processes also it is released to soil solution. Released organic substances including humic substances can get through to ground water or water reservoirs and may contaminate water environment.

The main factors which have influence on making mobile organic matter are temperature, pH of soil and its ion composition (Sokołowska and Matyka-Sarzyńska, 2002; 2006; Sokołowska *et al.*, 2006). Presence of mineral compounds such as phosphates, creates potential possibility for release organic matters to soil solution. The most important anthropogenic sources of phosphates in the soils are detergents, water softening, food and drinks (Karageorgiou *et al.*, 2007). But the most significant contribution in distribution of phosphates to soils have artificial fertilizers (Chantigny, 2003). Organic matter released to soil solution can be much differentiated in respect of particle mass, structure (relation between aliphatic chains and aromatic rings) and surface functional groups. Additionally, presence of phosphates can cause structural changes of released organic matter, especially when metal ions (Fe³⁺, Al³⁺) would be presence,

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because these ions can easily chelate phosphates as also other groups to organic matter (Sposito, 1989). In connection with the above it is possible that humic substances could change its properties.

Most of studies about phosphates were related to influence of phosphate ions on environment and living organisms, issues of sorption or migration in soil, usability as a plant nutrient and problem of eutrophication (Kiryluk, 2003; Said-Al Ahl and Abdou, 2009). There are also studies about chemical interactions of phosphates ions on inorganic cations and anions (Lucci *et al.*, 2010). Whereas not much information can be found about subject of influence of free phosphate ions on organic matter included in soils.

The main purpose of these studies was to investigate the influence of different concentrations of phosphate ions on the release processes of dissolved organic matter (DOM) from undissolved form of humic acids (HA). The aim of this study was also to determine the potential structural changes of DOM, which could take place under an influence of phosphates ions.

MATERIALS AND METHODS

The study was conducted on five peat-muck soils. Samples were collected in various phases of the mucking process at the depth of 5–20 cm. The sites were located in the low moor area of the Wieprz-Krzna canal (Polesie Lubelskie) and in the Biebrza river valley on the Kuwasy and Modzelówka peat bogs in Poland. Selected physical properties of samples were determined according to Myślińska (2001). Water adsorption index for studied soils were determined by Gawlik method (1992). This parameter is related to secondary transformation of soils. Type of muck samples was determined according to Okruszko method (1993). Determination of the bound amino acids has been carried out on a T 339 amino acid analyzer (Mikrotechna-Prague). All the measurements have been performed in triplicate with the deviation not exceeding 5%, and results have been averaged. Humic acids (HA) were extracted from soils by modified Schnitzer method (Gonet, 1990). Elementary composition: C, H and N contents of each HA were determined with a Perkin–Elmer CHN 2400 analyzer. The ratios of C/N and H/C were also calculated.

From obtained humic acids, five input suspensions were prepared with the same concentration. From input HA suspensions five identical solutions were prepared and placed into separated containers. Solutions were taken using syringes with 0.45 μm filters. At next step, crystallic hexahydrate of calcium chloride was added to all containers in order to obtain final concentration of calcium in the solution 0.05 M (that concentration of calcium cations, did not cause precipitation of HA from solution – what was found during preliminary studies. After equilibrium stabilization, concentration of HAs remained in solution and over calcium humate sediment, were determined for all samples.

In the second step, calcium forms of HAs were treated by NaH_2PO_4 solutions at increasing concentration (0.01; 0.015; 0.025; 0.035 and 0.05M) (solution obtained from pure for analysis reagent, POCH) Samples were vigorously shaken and left closed on 24 h to obtain equilibrium state. Concentration of the DOM released after phosphates addition were determined at 465 nm using Jasco V-530 spectrophotometer. Addition of phosphates in different concentration could change pH of solution, so influence of solution pH on HA releasing in relate to phosphates concentration was also measured by UV-VIS method as humic acid measurement at 465 nm.

From the input suspension of HAs, solutions of humic acids (400 mg kg^{-1}) with different concentrations of phosphate ions and on the basis of 1M NaCl were prepared. Concentration of phosphates in HA solutions was established on 0, 200, 400 and 600 mg kg^{-1} by addition of pure for analysis NaH_2PO_4 . Simultaneously, equilibrium solutions (phosphate ions on the basis of 1M NaCl and without HAs) were prepared.

All solutions were adjusted to pH = 3.00 with concentrated HCl. Both suspensions (400 mg kg^{-1} of HAs with phosphate addition and in the solution of 1M NaCl) and their equilibrium solutions (phosphate ions in the 1M solution of NaCl, without HAs) were equilibrated and then titrated with 0.1N NaOH in 1N NaCl solutions using Titrimo 702 SM apparatus. The titration was stopped at pH = 10. During the addition of the titrant, suspension was stirred vigorously under nitrogen atmosphere. Experimental points were automatically recorded for both equilibrium solution (phosphates in the 1M NaCl) and the suspension (HA with phosphates in 1M NaCl) with the step of 0.1 pH unit. Elaboration of obtained data, surface variable charge (Q) and normalization of curve of surface charge (N) and distribution function of surface dissociation constants were carried out according to Józefaciuk and Shin (1996).

RESULTS AND DISCUSSION

Basic description of studied peat-muck soils was displayed in Tables 1 and 2. The samples were characterized by low ash content (< 25%). Soils greatly differed by bulk densities, what was probably the result of different degree of mucking and different stage of secondary transformation of the soil mass. The lowest bulk density ($0.21, 0.25 \text{ g cm}^{-3}$) was observed for peaty mucks (Z_1), which also possessed the lowest soil water adsorptivity index ($W_1 = 0.44$ and 0.55). For the proper mucks (Z_3), the bulk density was higher (from 0.31 to 0.39 g cm^{-3}), and the values of W_1 ranged from 0.65 to 0.82 . All samples of the soils possessed high porosity (from 77.8 to 88.5%) and acidic character what was typical for soils rich in organic matter.

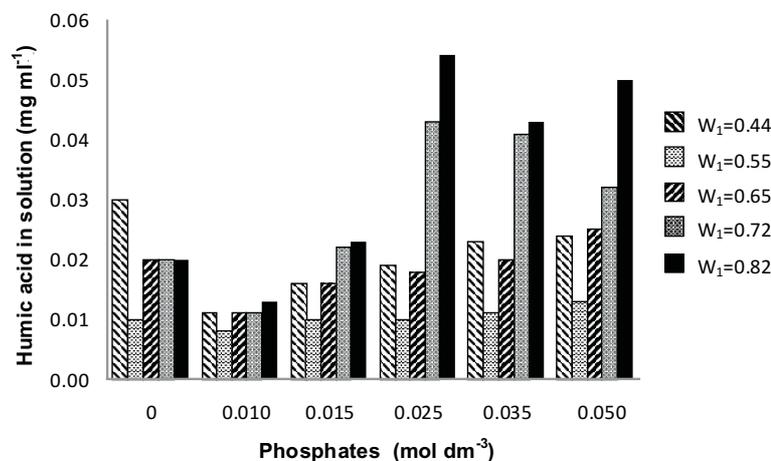


Fig. 1. Release of humic acid from calcium humates under influence of phosphate ions. Humic acids were extracted from five muck soils described by different stage of secondary transformation W_1 .

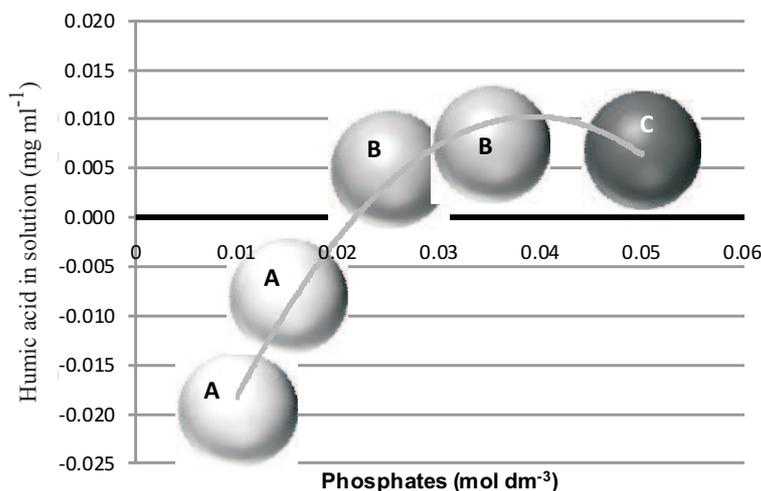


Fig. 2. Relationship between the average concentration of humic acids released to solution and concentration of added salt Na_2HPO_4 ; A – coagulation of HA, B – releasing of HA, C – secondary coagulation of HA.

create bridges linking phosphates ions and HAs, so the inconsiderable coagulation process could occur. This initial coagulation of DOM decreased with an increase in phosphates concentration. Next, peptization process took place. Humic acid No. 1 showed only coagulation without peptization (in all range of phosphates ions). In this case the lowest secondary transformation index W_1 could be a decisive factor. For the rest of samples, an increase of DOM concentration released to solutions (DOM peptization) could be the result of washing out calcium cations from solid phase, because Na_2HPO_4 solution is a good extractant of organic matter. There is also some probability of creating of soluble, mobile and organophosphorus complexes. Additional, secondary coagulation of DOM occurred after maximum of peptization ($> 0.025\text{M}$ of phosphates) for samples Nos 4 and 5. It might be due to decrease of pH after increasing addition of

NaH_2PO_4 solution as well due to increase of ionic strength. Figure 2 shows three areas of processes occurring in studied systems for average concentration of DOM.

Relationship between pH of the reaction medium, concentrations of added salt and DOM releasing from calcium humates was presented on Fig. 3. It could be concluded that pH of the solution had significant influence on interaction between phosphates ions and HAs. Increase in pH caused increase in DOM releasing at the same phosphates concentration. Generally, peptization processes of HAs started above pH 7 (HA peptization started above pH 6 only at two the highest phosphates concentrations).

Influence of phosphates ions on DOM releasing was also investigated using potentiometric titration method. Comparison of of variable surface charge (Q) of 5 humic acids solutions without phosphates ions showed that small

Release of humic acid to the solution under phosphate adding influence	0%	<20%	20-50%	>50%	
	pH of studied suspension	11			
	10				
	9				
	8				
	7				
	6				
	0.33	0.66	1.0	2.0	6.0

Adding of phosphates as fraction of total cation exchange capacity of calcium humates at different pH

Fig. 3. Influence of pH of the reaction medium and concentrations of added salt on humic acid peptization.

differences appeared between studied humic acids. Relationship between variable surface charge and apparent surface dissociation constants is presented on Fig. 4.

These differences might result from different properties of the peat-muck soils, such as, for example, humification degree, porosity or content of mineral components in the soil. Generally, with increase in stage of secondary transformation, W_1 , the surface charge, Q , decreased. Lower amount of surface charge could be result of lower amount of acidic surface functional groups such as carboxylic or phenolic.

Also some information about surface functional groups of HAs could be found from comparison of the apparent surface dissociation constants distribution function for each HAs isolated from peat-muck soils (Fig. 5).

According to the literature, the most significant functional groups of HAs are: carboxyl and phenol groups, but also hydroxyl, carbonyl, methoxyl and chinone groups (Martin *et al.*, 1963). The values of pK for carboxyl groups (pK_{-COOH}) are of the order 10^{-2} - 10^{-5} and for hydroxyl groups: 10^{-9} - 10^{-11} , what indicates that under acidic and neutral conditions these groups occur mainly as negative colloids, whereas under alkaline conditions these groups are dissociated. In our studies differences between HAs Nos 1-5 could be noticed in the position of peaks at $pK_{app} \sim 9.5$ and especially at $pH \sim 4.5$. HAs possessed higher peaks at $pK_{app} \sim 4.5$ suggested presence of bigger content of carboxyl groups. On the other hand, presence of higher peaks at $pK_{app} \sim 9.5$ could suggest higher content of phenol groups for HAs.

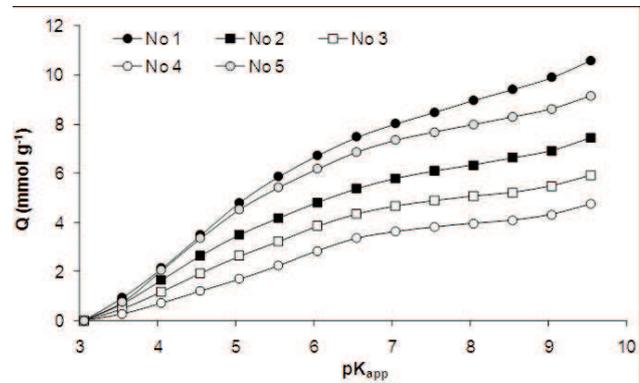


Fig. 4. Curves of variable surface charge (Q) vs. apparent surface dissociation constants for humic acids Nos 1-5.

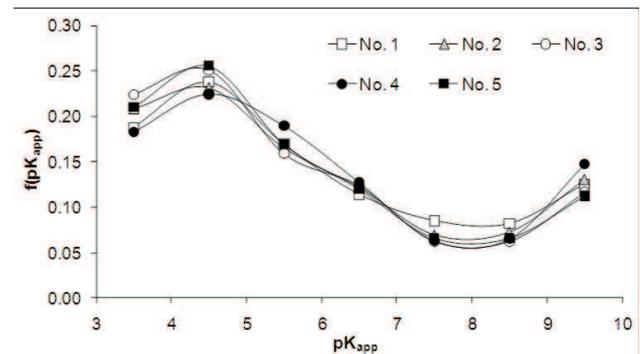


Fig. 5. Distribution function of surface dissociation constants of investigated humic acids.

The factor which could disturb titration processes was sorption of carbon dioxide (CO_2). In spite of nitrogen atmosphere usage, long time necessary to perform the titration could cause insignificant absorption of CO_2 by the solution (slightly higher curve at $pK_{app} \sim 6$ came from $pK_{HCO_3^-} = 6.37$ and $pK_{CO_3^{2-}} = 10.25$ – second value was out of the studied range).

Titration of HAs Nos 1-5 (HA concentration = 400 mg kg^{-1}) with addition of different concentration of phosphates ($200, 400, 600$ and 800 mg kg^{-1}) showed that the presence of this salt did not cause any visible change in the surface structure of studied HAs. It was displayed on the normalized curves of variable surface charge (N) versus apparent surface dissociation constants (pK_{app}) of humic acid No. 4 (400 mg kg^{-1}) with exemplary concentration of phosphates (Fig. 6). Curves N vs. pK_{app} practically overlapped for HA and for HAs with phosphates ions.

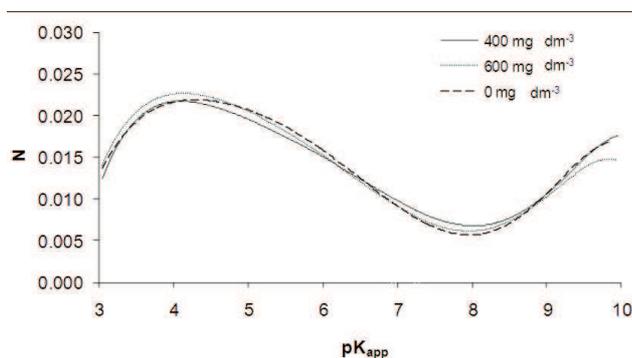


Fig. 6. Normalized curve of variable surface charge vs. apparent surface dissociation constants of humic acid No. 4 (400 mg dm^{-3}) with exemplary concentration of phosphates.

Lack of visible influence of phosphates ions on DOM surface structure could be caused by washing out (during the extraction) the majority of Al, Mn and Fe ions, which under natural conditions form complexes with HA and can bind compounds of phosphorus through metal bridges. Orthophosphoric acid is tribasic. It dissociates in three stages, but the first one is the highest in comparison with the second and third stage. The dissociation constants for three stages are: $\text{pK}_{a1} = 2.12$, $\text{pK}_{a2} = 7.21$, $\text{pK}_{a3} = 12.67$, respectively. The proportion of the three orthophosphate forms depends on the pH of the solution. According to Bohn *et al.* (1979) the H_2PO_4^- and HPO_4^{2-} ions are predominant in acid and basic soil solutions, respectively. Phosphate ions combine also with many divalent and trivalent cations to form ionic pairs and complexes. In acid soils, the most solid phase of phosphates is associated with Fe and Al. In basic soils, phosphates are associated with Ca or Mg.

Trace amounts of the cations listed above could be responsible for secondary coagulation of HA from solution. This hypothesis was confirmed in these studies using spectrophotometric measurements (Fig. 2). However, the amount of these cations could be too low to register visible changes on titration curves of HA with phosphates (the signal might be lower than interferences from the apparatus). It was also possible that the phosphates concentration used in potentiometric measurements were too small to cause visible changes of the surface functional groups. According to literature, average content of phosphates in soils ranges between $40\text{--}1000 \text{ mg kg}^{-1}$ (Bohn *et al.*, 1979). Laboratory level of experiment was connected with shorter time of interaction between DOM and phosphates ions than it occurs in natural conditions in soils. From these reasons, applied phosphates concentrations could not cause significant effect for interactions between DOM and phosphates ions. Potentiometric titration process in the presence of higher concentration of phosphate ions was difficult for realization. Phosphates exhibit ability for creating buffering systems. It is especially im-

portant during titration at medium values of pH because phosphate buffer contains hydrogenorthophosphates (Na_2HPO_4 , NaH_2PO_4) and buffer works in the pH range 5.5–8. In this range neutralization of OH^- ions, coming from added sodium hydroxide solution, requires a long time (indeed, pH value was constant within a long period of titration). This is a direct consequence of buffer properties of phosphates and significantly depends on pH of phosphates forms (Bera *et al.*, 2006; Petrusatti and Prado, 2007). Obviously, this behavior increases the time of titration in this pH range, perturbs the equilibrium state establishment and induces interferences on the titration curves. Consequently, titration in the presence of phosphate ions with concentrations higher than 600 mg kg^{-1} is very difficult to conduct. Therefore, phosphates concentrations used in that experiment were a compromise between inducing the greatest effect of phosphates on humic acids and minimize buffer properties of phosphates.

Bounded amino acids belong to the principal organic components of organic nitrogen in soils. These compounds are present in the form of proteins and peptides, which are connected to humic substances by hydrogen-bonding. Proteins and peptides react also via amine groups with phenolic products of lignin degradation or phenols created from the metabolic reaction of microorganisms (Szajdak, 2002; Szajdak and Sokolov, 1997). During separation of total amino acids the following groups were discriminated: acidic, neutral, basic and sulfur amino acids. Data collected in Table 2 indicate that neutral amino acids predominate in all soils, and their content ranges from 2.28 to 8.45 mg kg^{-1} . The content of acidic amino acids with positive net charge at neutral pH and acidic amino acids with negative net charge is similar. The amount of basic amino acids ranges from 0.95 to 4.27 mg kg^{-1} . The highest amount of these amino acids has been found in peat-muck soil belonging to very strongly and secondarily transformed class (soils Nos 4 and 5), in which water adsorptivity index was 0.72 and 0.82 , respectively. Strong correlations were found for the content of different kinds of amino acids and the parameters, which describe humic substances in soils. One of them is the correlation between water adsorptivity index W_1 and the amount of amino acids in the investigated soil samples. For different kinds of amino acids their content increases with increasing W_1 index (Fig. 7).

These correlations are probably preserved not only for soil materials, but also for clear HAs. Nitrogen contained in the Schnitzer's extracts of HAs (Table 3) may have its origin in amino acids. Especially, the presence of amino acids, which can yield charge is probable and the potentiometric titration method can confirm that. The charge of humic substances mainly originates from carboxylic and phenolic groups. The functional groups of amino acids can also produce some charge. This is indicated as increasing base consumption during the titration and by the distribution

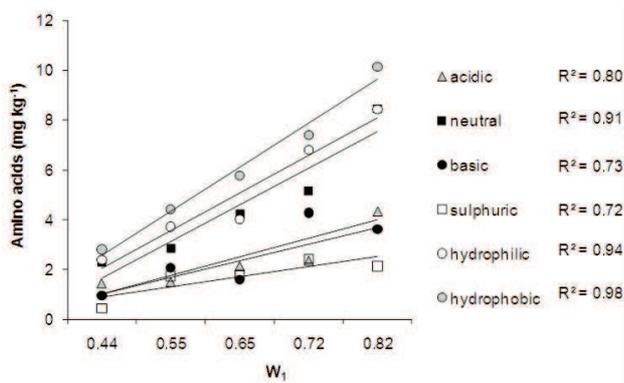


Fig. 7. Relationship between amount of amino acids and water adsorptivity index W_1 of studied mucks.

function of surface dissociation constants of investigated HA. The influence of strong acidic group such as carboxylic are seen at low pK_{app} values, whereas weak acidic groups at higher pH, and basic functional groups at pH about 8-11.

CONCLUSIONS

1. Maximum of peptizing activity of phosphates anions depends on the index of secondary transformation of soil. The amount of humic acid released from calcium humates increases with increasing index of the secondary transformation of mucks.

2. Phosphates at range $0.02-0.03 \text{ mol dm}^{-3}$ can cause peptization of organic matter by removal of polycations from solid phase. Decrease of pH (addition of phosphates) and increase of ionic strength all can cause secondary coagulation of humic acid from solution.

3. Released organic matter does not change under the influence of phosphates addition at experiment conditions.

4. Titration curves and apparent surface charge values of individual mucks differ. They are correlated with water adsorption index. Comparison of apparent surface dissociation constants distribution function permits for qualitative characterization of humic acids surface.

5. Strong correlations between water adsorption index and the amount of different kind of amino acids are found. It could be evidence on dependence of transformation processes of nitrogen compounds in soil on transformation processes of humic acids. The presence of functional groups of amino acids may be observed by using potentiometric titration method.

6. Surface charge observed at high pH values can result from presence of amino acids in structure of humic acids.

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