

## Influence of phosphate ions on buffer capacity of soil humic acids

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**Abstract.** The object of this study was to determine change of natural buffer capacity of humic acids by strong buffering agents, which were phosphate ions. Studies were carried out on the humic acids extracted from peat soils. Additional information was obtained by determination of water holding capacity, density, ash and pH for peats and optical parameter  $Q_{4/6}$  for humic acids. Humic acid suspensions exhibited the highest buffer properties at low pH and reached maximum at  $\text{pH} \sim 4$ . Phosphates possessed buffer properties in the pH range from 4.5 to 8.0. The maximum of buffering was at  $\text{pH} \sim 6.8$  and increased proportionally with an increase in the concentration of phosphate ions. The study indicated that the presence of phosphate ions may strongly change natural buffer capacity of humic acids by shifting buffering maximum toward higher pH values. Significant correlations were found for the degree of the secondary transformation with both the buffer capacity and the titrant volume used during titration.

**Keywords:** wetlands, phosphates, agriculture, water holding capacity, buffer capacity

### INTRODUCTION

Humic acids (designed as HAs) play essential biological, chemical and physical role in soils and improve soil conditions for plant growth. They influence several processes such as sorption and transport of hydrophobic organic compounds, stabilization of aggregates and bioavailability and complexation of metal cations (Khaled and Fawy, 2011; Kim *et al.*, 2005). Among many methods for obtaining information about physico-chemical properties of HAs (and organic soils in general), potentiometric titration is frequently used. In particular, the back titration method is applied for qualitative and quantitative analysis of the dependence of variable surface charge ( $Q$ ) on pH, as well as for evaluation of the distribution functions of apparent surface dissociation constants and the amount of particular functional groups (Campitelli *et al.*, 2006; Gondar *et al.*, 2005; Janos *et al.*,

2008). Electrochemical measurements can be also used to perform the analysis of buffer properties of soils and soil components (Lavelle and Spain, 2002; Garcia-Gil *et al.*, 2004; Pertusatti and Prado, 2007; Prado *et al.*, 2006).

Buffer properties of soils can be defined as ability of a soil to resist to sudden pH changes under the influence of acids or bases. Buffering is connected with maintenance of an equilibrium state between soil solution and hydrogen ions (and aluminum) contained in the soil sorption complex. When alkaline agents appear in a soil, hydrogen ions are removed from the soil solution (due to neutralization) and supplemented from the soil sorption complex. On the other hand, when hydrogen ions are introduced to the soil solution, they are transferred to the sorption complex. In both cases soil pH does not change significantly until saturation of the sorption complex by those ions. Buffer properties of soils are strongly positively correlated with their sorption capacity. HAs contained in soils exhibit high cation-exchange capacities. Consequently, the buffer capacity of these compounds and HA-rich soils is also high (Lavelle and Spain, 2002). However, excessive amounts of strongly alkalified or acidified agents in the environment and over-saturation of the soil complex with ions, can exceed the natural buffer capacity of the soil system, resulting in a soil pH change, or changing the natural buffer capacity into a buffer capacity characteristic for newly introduced components.

Buffer capacity,  $\beta$ , is expressed as the number of moles of a strong acid or base which, when introduced to  $1 \text{ dm}^3$  of a buffer solution, changes its pH by one unit:

$$\beta = dc / dpH \approx \Delta c / \Delta pH, \quad (1)$$

where:  $\Delta c$  is the number of strong acid or base moles added to the buffer solution and  $\Delta \text{pH}$  is the change in the pH value.

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Buffer capacity in the range of soils rich in humic acids can also change in relation to secondary transformation degree. One of the indexes of secondary transformation is a parameter proposed by Gawlik (1992) called: water holding capacity ( $W_1$ ). This index is a quantitative description of water holding by organic soils. The water holding capacity index appeared to be very useful in the analysis of several specific properties of peats (Sokołowska *et al.*, 2005).

Studies of buffer properties of systems involving soil organic matter and phosphates have substantial value for the environmental research. These studies focus attention on an important problem and consequences of peat degradation by phosphates enrichment in environment, due to former agricultural activities. HAs and their salts play the role of natural soil buffers. However, phosphates also possess strong buffer properties, but most of phosphates are in unavailable forms and their natural ionic content in soils is low, ranging between 40 and 1000 mg dm<sup>-3</sup>, whereas in case of weakly fertile soils, phosphates content in the soil solution can decrease below 0.1 µg ml<sup>-1</sup> and is rarely greater than 1 µg ml<sup>-1</sup> (Bohn *et al.*, 1979; Mussa *et al.*, 2009). Higher presence of phosphates in soils results from human intervention and is mainly connected with fertilization, as well with a widespread use of detergents (Köhler, 2006).

The amount of phosphorus available for plants in natural soil is usually insufficient (Wei *et al.*, 2009), which necessitates fertilization by artificial phosphorus compounds. The optimal soil conditions for plants to assimilate phosphates are in the pH range 6.5-7.0. Too low pH (e.g. in organic soils, or due to soil acidification) or too high pH (e.g. due to liming can additionally decrease phosphates availability to plants (Lavelle and Spain, 2002). Phosphorous belongs to the group of macroelements that take part in cell respiration processes. This element also has a great influence on the growth of the generative parts of plants. It is present both as a constituent of such compounds as nucleic acids, phospholipids and ATP, and as a metabolite involved in energy transfer, the activation of proteins and the regulation of metabolic processes (Smith *et al.*, 2003).

The aim of study is to determine the natural buffer capacity of five samples of humic acids, as well as to determine the change of natural buffer capacity of HAs by strong buffering agents, which are phosphates ions.

## MATERIAL AND METHODS

For HAs isolation, five peat soils characterized by different degrees of secondary transformation (assessed by the water absorption index,  $W_1$ ) were collected from the depth of 5-20 cm, from 5 sites used as meadows. 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. Several basic physico-chemical characteristics of peat samples were evaluated, they are collected in Table 1. pH was measured in KCl and H<sub>2</sub>O solutions using electrochemical method. Ash content was determined by combustion of peat at 550°C and weighting the residue. Bulk density was measured as a ratio of mass of oven dry peat to the volume of peat before drying.

The so-called water holding capacity index ( $W_1$ ) was used to characterize the degree of secondary transformation of the peat soils Gawlik (1992).

HAs were extracted from peat soils using alkaline extraction proposed by International Humic Substances Society (Swift, 1996).

The  $Q_{4/6}$  index was determined using the spectrophotometric method measuring of the absorbance ratio at wavelengths 472 and 664 nm. The  $Q_{4/6}$  index is specific for humic materials extracted from different soil types and was reported to be independent of the concentrations of humic materials. All UV-VIS measurements were carried out using a Jasco V-500 spectrophotometer. The calculated values of the  $Q_{4/6}$  index are also presented in Table 1.

In the next step, suspensions containing 400 mg dm<sup>-3</sup> of the extracted HAs and different concentrations of phosphate (V) ions (0, 400, 600 mg dm<sup>-3</sup>) were prepared on the basis of 1 M sodium chloride solution. Phosphates solution was prepared from sodium dihydrogen phosphate pure for analysis. The selected phosphate concentrations are related to the concentrations of these ions in environment.

All titrations were carried out using the Titrino 702 (Metrohm) apparatus. Due to the fact that potentiometric titration of buffer substances is difficult, optimization of the method (Boguta and Sokołowska, 2010) by selection of an appropriate dose step, titrant concentration, rate of titrant supply, potential drift value and sample concentration was carried out before measurements. pH of all the suspensions

**Table 1.** Selected properties of the investigated peat soils

| No. | $W_1$ | $Q_{4/6}$ | Ash<br>(% d.m.) | Bulk density<br>(g cm <sup>-3</sup> ) | pH <sub>H<sub>2</sub>O</sub> | pH <sub>KCl</sub> |
|-----|-------|-----------|-----------------|---------------------------------------|------------------------------|-------------------|
| 1   | 0.44  | 6.8       | 22.7            | 0.21                                  | 5.1                          | 4.5               |
| 2   | 0.55  | 5.2       | 17.6            | 0.25                                  | 5.5                          | 5.2               |
| 3   | 0.65  | 5.6       | 18.9            | 0.31                                  | 5.5                          | 5.0               |
| 4   | 0.72  | 5.3       | 18.0            | 0.36                                  | 5.0                          | 4.5               |
| 5   | 0.82  | 7.7       | 22.3            | 0.39                                  | 5.5                          | 5.0               |

$W_1$  – water holding capacity,  $Q_{4/6}$  – optical parameter of humic acid structure, humification degree.

was adjusted to 3 by a diluted HCl solution. Then, the suspensions were titrated from pH=3 to 10 using a 0.1 mol dm<sup>-3</sup> NaOH solution based on a 1 mol dm<sup>-3</sup> sodium chloride solution. The concentration of sodium chloride in the titrant solution, as well as in the suspensions was established to be 1 mol dm<sup>-3</sup> for the ionic strength maintenance. The speed of titration was varied during the measurement. It depended on the time needed to obtain the equilibrium state in the suspension after each titrant drop added. Buffer capacities of HAs with different hydrogen phosphate additions were calculated from the potentiometric titration curves (pH<sub>sol.</sub> vs. V<sub>titrant</sub>) using Eq. (1). All the measurements were conducted in three replicates and then averaged.

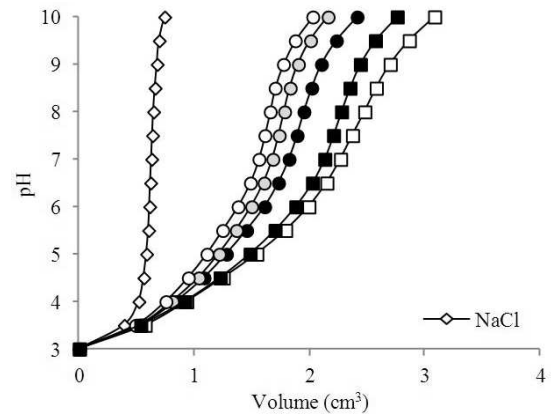
### RESULTS AND DISCUSSION

Peats samples are characterized by wide spectrum of secondary transformation index measured as water holding capacity – the values of W<sub>1</sub> range from 0.44 to 0.82. Ash content is high, in range of 17.6-22.7. Bulk density is from 0.21 to 0.39 g cm<sup>-3</sup>. The soils under study possess pH typical for organic soils, ranging from 5.0 to 5.5 for measurements in H<sub>2</sub>O and from 4.5 to 5.2 for measurements in KCl. The results obtained from spectrophotometric analyses show that HAs extracted from peat soils Nos 2, 3 and 4 (see Table 1 for the sample code) has low Q<sub>4/6</sub> index (the average value is 5.4). This value can indicate high-molecular and strongly condensed aromatic structure of the HAs. The extract 5 exhibits the highest value of the Q<sub>4/6</sub> index (7.7), while the HA 1 displays a medium value of the Q<sub>4/6</sub> index (Q<sub>4/6</sub>=6.8). These values suggest lower molecular mass and lower degree of aromatic ring condensation. According to literature, Q<sub>4/6</sub> parameter correlates with particle molecular mass and can be appropriate index for it expressing (Senesi and Sipos, 1985). Selected potentiometric titration curves of the HAs, evaluated for bare HAs and for humic HAs with different additions of phosphate ions are presented in Figs 1 and 2, respectively.

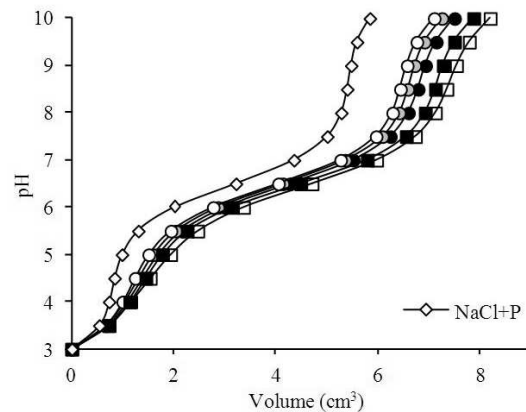
Consumption of the titrant by HA suspensions without phosphates is about 2-3 cm<sup>3</sup> for different HAs. Phosphate addition to HAs results in higher consumption of the titrant, in some cases even higher than 8 cm<sup>3</sup>. In the case of the samples without phosphates, the rate of titration is the highest in the pH range of 6-8, whereas for the samples with phosphates it is the highest within the pH ranges 3.5-6.0 and 7.5-9.5. For increasing phosphate concentration, the plateau of the titration curve is shifted towards higher values; into the pH range of 6-7.

Buffer capacities ( $\beta$ ) of the suspensions were plotted as functions of pH. Examples of the curves are shown in Figs 3-5.

Buffer capacity curves calculated for particular HA suspensions without addition of phosphates differed each from other (Fig. 3). Pronounced differences are seen within the range of pH corresponding to dissociation of strong acidic carboxylic groups (Janos *et al.*, 2008). Buffer capacities within that pH range are the highest and reach maxima at pH ~ 4 (the



**Fig. 1.** Potentiometric titration curves of HAs without phosphates addition. The samples abbreviated NaCl denoted the reference solution of 1M NaCl, all the remaining sample codes are given in Table 1: □ – 1, ● – 2, ● – 3, ○ – 4, ■ – 5.

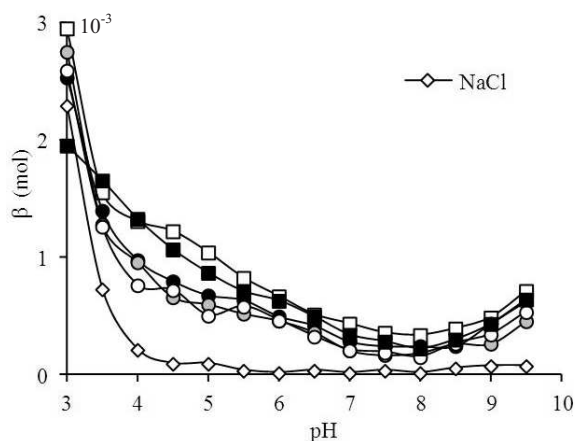


**Fig. 2.** Potentiometric titration curves of HAs with addition of 600 mg dm<sup>-3</sup> of phosphates. Explanations as in Fig. 1.

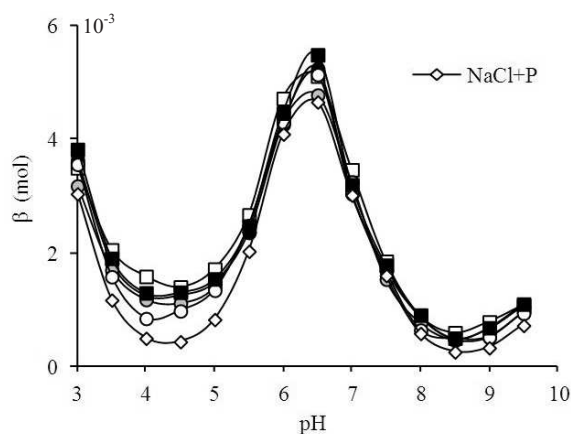
curve originating from NaCl solution is regarded as a background, so the difference between the curve for a HA sample and the curve for NaCl is the highest at pH ~ 4). Minimum buffer capacities for the suspensions of HAs without phosphates are reached at pH ~ 8. However, for pH > 8, a secondary, small increase in the buffer capacity is noticed.

The presence of phosphates leads to an increase of the buffer capacity. This is reflected by the growth of  $\beta$  values in the pH range 5-8. The phosphate buffering range overlaps in part with the buffering range originating from HAs.

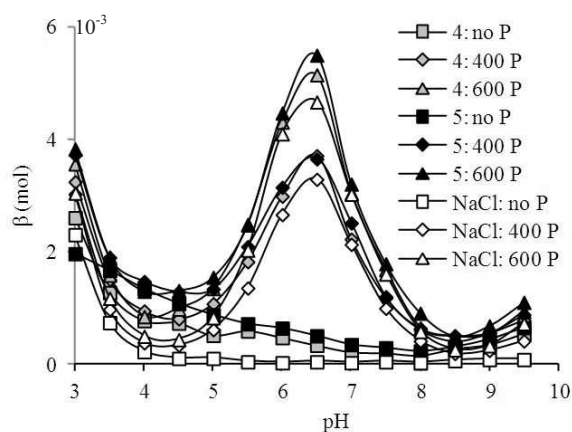
All the titration curves of HAs without phosphate ions possess similar, S-like shape, though they indicate different consumption of the titrant by different samples. The differences in the titrant consumption are caused by qualitative and quantitative differences in the composition of the HAs. That supposition is confirmed by the values of the Q<sub>4/6</sub> index calculated from spectrometric data. Q<sub>4/6</sub> parameter shows that humification index of humic acids varies. Low Q<sub>4/6</sub> ratios indicate high degree of aromatic condensation and



**Fig. 3.** Curves of  $\beta$  vs. pH for humic acids without addition of phosphate (V) ions. Explanations as in Fig. 1.



**Fig. 4.** Curves of  $\beta$  vs. pH for humic acids with addition of phosphate (V) ions ( $600 \text{ mg dm}^{-3}$ ). Explanations as in Fig. 1.



**Fig. 5.** Buffer capacity of humic acids 4 and 5 with different phosphate concentration in  $\text{mg dm}^{-3}$ . Additionally, the concentration of phosphate ions is given and 'no P' denotes the results obtained without addition of phosphates.

higher level of organic material humification. Higher values of  $Q_{4/6}$  index correspond to lower humification level and to lower molecular mass.

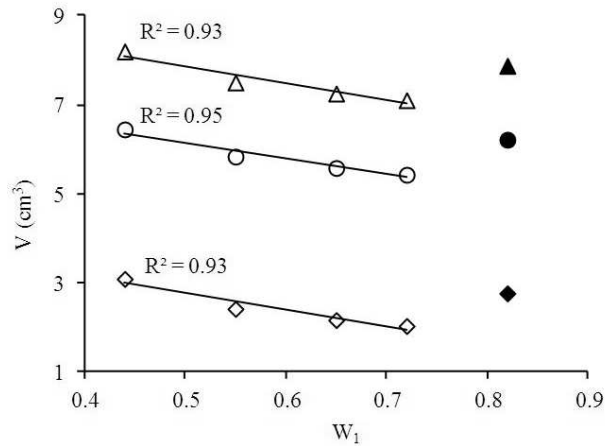
The increasing consumption of the titrant provides also evidence of the presence of a greater amount of surface acidic and weakly acidic functional groups, mainly carboxylic and phenolic. In the case under study, the volume of the titrant consumed should be proportional to the amount of the surface functional groups of the HA, or more precisely, to the amount of the protons bonded to the functional groups of HA and titrated during addition of titrant. The rate of HAs titration is the highest at pH 6-8. It suggests low content of functional groups in this pH range. On the other hand, the rate of titration decreases below and above that range, probably due to the titration of carboxylic (low pH) and phenolic groups (higher pH).

The shape of the titration curves obtained for HAs with phosphates differs from the shape of the curves for HAs without phosphate ions. The former curves exhibit two steps (Fig. 2). Titrant volume needed for titration of HAs together with phosphates is much higher than the titrant volume necessary for the titration of HAs without phosphates. Higher consumption of the titrant results, of course, from the presence of phosphates, which are titrated together with HAs.

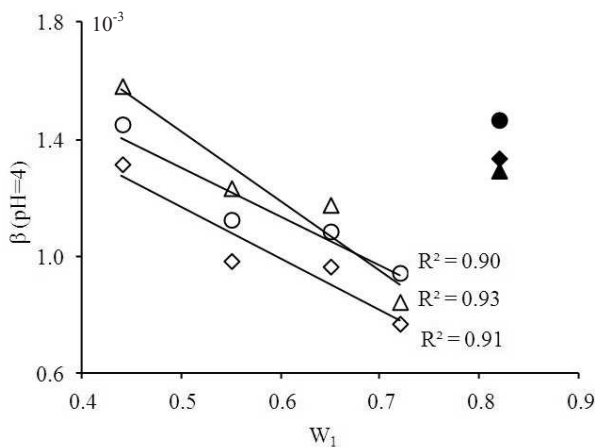
The highest titrant consumption is within the plateau region (pH 6-7), where the changes of pH during titrant addition are the slowest. The pH range within which the pH changes are the slowest indicates buffering by the phosphates ions. Simultaneously, significant difference between titrant volume used for the titration of the suspension of HAs with phosphates and without phosphates, points to bigger role of the phosphates (at concentrations of  $400$  and  $600 \text{ mg dm}^{-3}$ ) on the buffering processes than of bare HAs.

The titrant consumptions by the solutions of HAs without, as well as with phosphates at concentrations of  $400$  and  $600 \text{ mg dm}^{-3}$  correlate negatively with the water holding capacity index  $W_1$  (Fig. 6). Correlations have been found for the pH range of 3.0-9.5.

The correlation in Fig. 6 become significant, if the result for the extract 5 will be discarded. Such treatment is justified, since spectrophotometric investigations shows that HA no 5 differs from all the remaining samples (Table 1). This sample displays considerably higher optical  $Q_{4/6}$  index than all the remaining HAs, which suggests the presence of the lightest fraction of HAs, or the heaviest fraction of fulvic acids (the borderline between humic and fulvic acids is not well defined). On the other hand, HAs 1-4 are characterized by rather low  $Q_{4/6}$  values and thus they can be regarded as samples with predominance of particles of greater molecular mass (corresponding to low  $Q_{4/6}$  values). Next argument supporting excluding HA 5 is the value of the  $W_1$  index. According to Gawlik classification of secondary transformation index, appropriate ranges of  $W_1$  values correspond to different stages of secondary transformation:  $0.36 < W_1 < 0.45$  – to the



**Fig. 6.** Correlation between the titrant volume  $V$  (used in the titration process of HA with phosphates and NaCl) and the secondary transformation index  $W_1$ ,  $\diamond$  HA+0P,  $\circ$  HA+400P,  $\triangle$  HA+600P (black marked points are not included in relationship, they belong to sample No. 5).



**Fig. 7.** Correlation between buffer capacity  $\beta$  of humic acids mixed with phosphates (on the base of sodium chloride) and the secondary transformation index  $W_1$ . Explanations as in Fig. 6.

initial stage,  $0.46 < W_1 < 0.60$  – to a weak stage,  $0.61 < W_1 < 0.75$  – to a medium stage,  $0.76 < W_1 < 0.90$  – to a strongly degraded stage and  $W_1 > 0.90$  – to the totally degraded stage. Samples 1-4 belong to the initial, weak and medium secondary transformed stages. Sample No. 5 possesses high value of  $W_1$  index (0.82). This value is close to that characteristic for totally degraded soil. Therefore, the sample No. 5 can be considered as having chemical properties different from remaining samples.

The curves of the buffering capacity calculated from potentiometric titration illustrate buffering ability of HAs, phosphates ions, as well as the influence of phosphates ions on the buffer capacity of HAs. The buffer capacities of different HAs without phosphates differ significantly in the range of  $3.3 < \text{pH} < 5.0$  (Fig. 3). The differences between  $\beta$  va-

lues that are observed at low ( $\text{pH} < 4$ ) can be assigned to dissociation of carboxylic groups with different acidic strength (Bergelin *et al.*, 2000) and indicate a great diversity between amounts of those surface functional groups.

The differences between  $\beta$  values for different samples at low pH can be also attributed to different degrees of secondary transformation of organic matter in the samples. The HAs obtained from the samples with high  $W_1$  index exhibit lower buffer capacity at low pH than the samples characterized by low  $W_1$  index.

The correlation of buffer capacity at  $\text{pH} = 4$  ie at the value of pH close to the buffer capacity maximum and  $W_1$  index is presented in Fig. 7. Similarly as in Fig. 6, the linear regression is determined discarding the data for the sample No. 5.

Summing up: the index of secondary transformation  $W_1$  increases with a decrease of  $\beta$ . Since  $\beta$  increases with an increase of the amount of  $-\text{COOH}$  groups, one can conclude that the HAs extracted from weakly transformed soils possess higher amount of carboxylic groups.

All  $\beta$  curves of the HAs samples exhibit broad minima at  $\text{pH} \approx 8$ . Above that value, buffer capacity increases slightly up to  $\text{pH} = 10$ . The shape of the buffering curves is similar to the shape of buffer capacity curves of HAs reported in the literature (Garcia-Gil, 2004), but the magnitude of  $\beta$  evaluated by us and in the above cited work is different. According to Campitelli (Campitelli *et al.*, 2003) the peaks in Fig. 3 for the  $\text{pH} > 8$  can be attributed to phenolic groups or, possibly, to secondary or tertiary amines. The latter groups are titrated together with phenols and their content can be related to the total amount of nitrogen in the material. It should be stressed, however, that the differences between  $\beta$  values for different HAs for  $\text{pH} > 8$  are rather small and, in general, the content of those functional groups is smaller than content of functional groups at low pH.

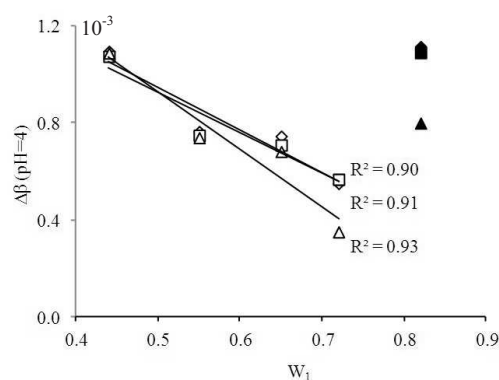
According to the literature (Campitelli *et al.*, 2006), carboxylic groups dissociate in the range of low and medium pH, ordinarily from 3 to 6, with respect to group acidity. Being weakly acidic, phenolic groups dissociate at higher pH ( $\text{pH} \sim 9$ ). Therefore, in the case of the HAs under study, the high buffer capacity at  $\text{pH} = 4$  indicates the presence of strong acid carboxylic groups that play buffer role, whereas the high buffer capacity in the high pH range can indicate the presence of phenolic, amino or other functional groups with similar acidity. The presence of phenolic and carboxylic groups in the structure of humic substances can be also confirmed by studies of the distribution function of the apparent surface dissociation constant,  $\text{pK}_{\text{app}}$  (Kohler *et al.*, 2002).

Our investigations show that addition of different concentration of phosphate ions (400 and 600  $\text{mg dm}^{-3}$ ) to HAs, causes significant increase of buffer capacity of all systems. Moreover, the influence of phosphates depends strongly on the pH of the medium. It results from chemical properties of the phosphates ions, especially from possibility of three-step dissociation. The phosphate ions can appear in different ionic forms, depending on pH (Bohn *et al.*, 1979).

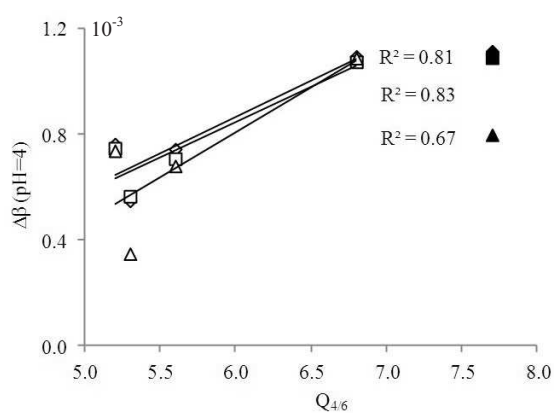
The form of phosphates has an obvious impact on the changes of the natural buffer capacity of HAs. The titration of HA suspensions with phosphates is quick in the pH range from 3 to 6 (Fig. 3), because, according to Bohn *et al.* (1979), the phosphates are (almost in 100%) in the  $\text{H}_2\text{PO}_4^-$  form. Above pH = 6, the amount of  $\text{HPO}_4^{2-}$  anions in the solution increases and at pH ~ 7 both  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  forms occur at equimolar concentration. The equimolar mixture of these two forms of phosphates ions is known as a strong inorganic buffer, with maximum of buffering at pH ~7. Our studies confirm that the buffer maximum of the system containing HAs and phosphates is reached close to that pH (Fig. 4). The HAs with phosphates buffer strongly in the range of pH of 5-8, with maximum at pH=6.5 (Fig. 4). The influence of phosphates on the buffering system is also illustrated in Fig. 5, where the results obtained for HAs extracted from peats are compared with the results for the HA suspensions involving 400 and 600  $\text{mg dm}^{-3}$  of phosphates. It can be seen that the height of the maximum of (at pH=6.5) increases with an increase of the phosphate concentration. Outside the region of the maximum ( $5 < \text{pH} < 8$ ), the values of  $\Delta\beta$  are practically unchanged if the concentration of the phosphates changes from 0 to 600  $\text{mg dm}^{-3}$ . Such behaviour indicates the lack of chemical interactions of phosphates ions with HAs in range of the presence of strong carboxylic and phenolic groups under experiment conditions. That supposition is confirmed by calculation of buffer capacities of clear HAs from following formula:  $\Delta\beta(\text{pH}4) = \beta(\text{HA}, \text{P}, \text{NaCl}) - \beta(\text{P}, \text{NaCl})$ . pH 4 is applied as a maximum of HA's buffering. Buffer capacities of clear HAs calculated from systems contained HA, different amount of phosphates ions and sodium chloride are almost identical in given pH and are depended only on properties of studied HAs, what was presented through relationships  $\Delta\beta$  vs.  $W_1$  (Fig. 8) and  $\Delta\beta$  vs.  $Q_{4/6}$  (Fig. 9). Simultaneously plots 8 and 9 showed that secondary transformation index and  $Q_{4/6}$  index strongly influence the buffer properties of HAs, what is expressed by high determination  $R^2$  indexes. Buffer capacities of clear HAs calculated from difference  $\beta(\text{HA}, \text{P}, \text{NaCl}) - \beta(\text{P}, \text{NaCl})$  prove also in clear way that humic acids have great importance in buffering possibilities of entire system, especially at low pH. Presence of the relationship between  $\Delta\beta$  of HAs and  $Q_{4/6}$  proves that low molecular fraction of humic substances have significant influence on the growth of the buffer capacity of the entire system. The lower  $Q_{4/6}$  index, the higher molecular mass and as experiment showed: the lower buffer capacity of humic acids.

Addition of phosphates causes partial overlapping the buffering ranges of phosphate ions and HAs extracted from peat soils (at pH from 3.5 to 8.0). The presence of phosphates clearly increases the buffer capacity of natural HAs within the range of pH ~ 4.5-8.0. In this range of pH, the functional groups of HAs are the most significant, because they are completely ionized and determine the natural soil buffer

capacity  $\beta$ . Therefore, an increase in the content of phosphates in soil can have a considerable impact on the acid – base equilibrium and homeostasis state existing in soils; especially organic soils, like peats. Such soils are rich in organic matter, so the maximum buffer capacity is placed in low pH range, similarly to humic acids. High content of phosphates ions in those soils system can disturb their natural buffering properties by shifting maximum buffer capacity towards the maximum typical for phosphates ions (pH=7). This can have serious consequences on the environment, organic matter state and peatland protection, because soils are exposed on pH increasing involving such negative processes like peptization and releasing of humic acids to ground water, as shown in previous investigations (Matyka-Sarzyńska and Sokołowska, 2005; 2006). It should be stressed that the addition of phosphates into soils rich in organic matter can also change the cation exchange capacity of soil. This parameter depends mainly on the presence of acidic and weakly acidic carboxyl and phenolic groups of humic substances.



**Fig. 8.** Correlation between the secondary transformation index and buffer capacity of clear humic acids (expressed as  $\Delta\beta(\text{pH}4) = \beta(\text{HA}, \text{P}, \text{NaCl}) - \beta(\text{P}, \text{NaCl})$ ). Explanations as in Fig. 6.



**Fig. 9.** Correlation between the  $Q_{4/6}$  and buffer capacity of clear humic acids (expressed as  $\Delta\beta(\text{pH}4) = \beta(\text{HA}, \text{P}, \text{NaCl}) - \beta(\text{P}, \text{NaCl})$ ). Explanations as in Fig. 6.

In organic soils, phosphate ions are often bonded with iron and aluminum cations. However, in a basic medium, they accompany calcium compounds. In turn, metal cations are easily sorbed by soil organic matter; thus they can play a role of bridges between organic matter and phosphate compounds, creating complex macromolecules. The methodology of the above described investigations, connected with receiving pure HAs extracts by IHSS method, assumes washing out exchangeable cations from humic acids. So, purified humic acids probably do not show structural changes after phosphates addition, because the lack of cations makes creation of bridges linking humic acids with phosphates ions impossible. This assumption agrees with the results obtained in previous works. In particular, it was proven that the distribution functions of apparent dissociation constants of pure humic acids and humic acids with phosphates ions overlapped in the entire pH range, so the surface structure of humic acids was not changed by the phosphates (Sokołowska *et al.*, 2011). However, it should be remembered that in the natural environment, aluminum and iron ions are commonly connected with soil organic matter, and chemical links between phosphates, cations and HAs can take place, affecting the state of the natural environment.

#### CONCLUSIONS

1. It has been proved that higher amount of phosphates can adversely affect natural buffer capacity of organic soils. Phosphate ions possess buffer properties in the pH range of 4.5-8.0 with maximum at pH~6.8, which increases directly proportionally with the increase of the phosphate concentration. Humic acids exhibit the highest buffer properties at low pH and their buffer capacities reach maximum for pH ~ 4.

2. The presence of phosphates disturbs the acid – base equilibrium and homeostasis state existing in organic soils, by shifting the maximum buffering capacity toward higher pH ranges, typical for phosphates ions.

3. The studies indicated that secondary transformation index (in paper measured as water holding capacity) has significant influence on the buffer capacity, both humic acids and humic acids together with phosphate ions. At low pH the differences between  $\beta$  for consecutive samples can be associated with the degree of secondary transformation of organic matter. At low pH values  $\beta$  decreases with increasing  $W_1$  what is proved by high value of the correlation coefficient. This also provided evidence of a great diversity between the amounts of surface carboxylic groups which dissociate at low pH range.

4. Buffer capacity of humic acids decreases with the decrease in optical parameter  $Q_{4/6}$ . It is evidence that low molecular fraction of humic substances have significant influence on the growth of the buffer capacity of the entire system.

5. There are no interactions between phosphates and humic acids at maximum of humic acids buffering (pH=4). It is confirmed by the same values of buffer capacities coming from only humic acids but measured in systems of humic acids with different concentrations of phosphates.

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