Teka Kom. Ochr. Kszt. Środ. Przyr. – OL PAN, 2009, 6, 328–334

MOBILISATION OF HUMIC ACIDS ORIGINATED FROM MUCKS AS A RESULT OF SODIUM, CALCIUM AND PHOSPHATE IONS INTERACTION

Zofia Sokołowska, Patrycja Boguta

Department of Physical Chemistry of Porous Materials, Institute of Agrophysics, Polish Academy of Sciences,
Doświadczalna 4 str., 20–290 Lublin, zosia@maja.ipan.lublin.pl, p.warchulska@ipan.lublin.pl,

Summary. The main aim of these studies was to investigate the relationship between the state of humic acids contained in sorption complex of mucks and such significant ions as sodium, calcium and phosphates. The study was conducted on five samples of mucks from the Polesie Lubelskie Region (Wieprz-Krzna Canal) and Biebrza River Valley. Samples were collected from depths of 5–20 cm. Humic acids were obtained through alkaline extraction using the method given by Schnitzer. Sodium and calcium salts of humic acids were treated with Ca_3PO_4 and NaH_2PO_4, respectively. Salts of Ca_3PO_4 and NaH_2PO_4 were added in different concentrations and in varied pH circumstances. The investigation of sodium phosphate influence on calcium humates at different pH values has shown that the process of organic matter releasing increases with increase of pH and with increasing amount of sodium monohydrogen (ortho) phosphate added to humates. In turn, the addition of calcium phosphate with increasing concentration and in different pH conditions to sodium forms of humic acids caused that the concentration of total organic carbon increased in the solution, as a result of which humic substances were released. However, it was proven that increasing amount of humic acids in solution was caused only by increasing of pH, not by calcium cations addition.

Key words: humic acids, muck, peptisation, coagulation

INTRODUCTION

Ionic composition, similarly as pH, temperature and microbiological activity, belongs among the most important factors which determine equilibrium of soil organic matter [Sokołowska and Matyka-Sarzyńska 2002a, b, 2006, Sokołowska *et al.* 2006]. Elements such as sodium or calcium play a significant role as plant nutrients [Buchanan *et al.* 2000]. Calcium determines correct functioning of plant tissue, and forms cell walls. It is included in the composition of enzymes and determines the assimilation of other elements by plant. On the other hand, sodium, in spite of being an element not necessary for plants, supports growth and improves yielding. Thanks to osmotic properties of sodium, it can replace potassium which is important for proper development of cells. However, researches proved that these elements also can interact with soil humic substances [Yingge Wang *et al*. 2001]. Sodium with humic acids creates soluble salts what make it more mobile. Whereas, calcium has coagulation properties – it immobilises humic acids in the form of insoluble calcium humates. Calcium and sodium concentrations in soils are quite high, but additionally these cations are introduced to soil as fertilisers, usually as phosphates [Zawadzki 1999]. Different pH circumstances, addition of fertilisers and competitive impact of soil cations cause that equilibrium between peptisation and coagulation of humic acids in soil may be shaken. Excessive release of organic matter from soil complex to soil solution can cause pollution of ground waters, quick loss of organic carbon which should be assimilated by plants, forming of toxic combinations with pesticides or others organic compounds, including the formation of carcinogenic compounds [Galland and Gunten 2002]. On the other hand, excessive amounts of coagulate cations immobilise organic matter, making it unavailable for plants. For the reasons mentioned above, the main aim of this study was to investigate the influence of sodium and calcium addition in phosphate forms to humic acids derived from mucks, and to determine of effect of pH on competitive action of these ions on peptisation and coagulation processes.

MATERIALS AND METHODS

The study was conducted on five samples of mucks from the Polesie Lubelskie Region (Wieprz-Krzna Canal) and Biebrza River Valley. Samples of mucks were collected from depth of 5–20 cm. Basic properties of studied mucks are presented in Table 1 [Sokołowska and Matyka-Sarzyńska 2006].

Table 1. Selected physicochemical properties of studied mucks [Sokołowska and Matyka-Sarzyńska 2006]

No	W_1	pH H_2O	pH KCl	Ash. % d.m	Bulk density g cm^{-3}	Total porosity % vol.
1	0.44	5.1	4.5	22.7	0.21	88.5
2	0.55	5.5	5.2	17.6	0.25	84.6
3	0.65	5.5	5	18.9	0.31	80.9
4	0.72	5.0	4.5	18.0	0.36	77.8
5	0.74	5.8	5.3	22.3	0.39	78.7

Explanation: W_1 – water holding capacity index according to Gawlik [2000]

Humic acids were obtained through alkaline extraction using the method given by Schnitzer [Gonet 1990]. Sodium and calcium salts of humic acids were obtained from hydrogen forms for the purpose of investigation of the competitive influence of the two cations. In this case, NaHA (sodium humate) and CaHA (calcium humate) were treated with Ca_3PO_4 and NaH_2PO_4, respectively. Salts of Ca_3PO_4 and NaH_2PO_4 were added in increasing concentrations and at varied pH circumstances.

A. The influence of phosphate (V) anions, calcium cations and pH on humic acids was investigated by acting with fresh calcium phosphate (V) precipitate on humic acid extracts in the sodium forms. Phosphates were added in different amounts, taking into consideration cation exchange capacity (CEC). Additions of phosphate (V) anions were adjusted to 0, 1 and 3 meq (assigned adequately as: Na-0, Na-P and Na-3P) and added to humate sodium suspension (1000 ppm) with different pH values (4, 5, 6, 7, 8 and 9). pH of each solution was measured again after the additions of calcium phosphates. In suspensions prepared in this manner the content of total organic carbon (TOC) was determined.

B. The influence of phosphate (V) anions, sodium cations and pH on humic acids was investigated by acting with sodium phosphate (V) at different concentrations (0, 0.33, 0.66, 1, 2 and 6 meq of Ca in relation to input suspension) on HA extracts in the calcium forms. The amounts of added sodium phosphates were consequently designated as Ca-0P, Ca-1/3P, Ca-2/3P, Ca-3/3P, Ca-6/3P and Ca-PMax. Precipitates of each humate were prepared with the following pH values: 4, 5, 6, 7, 8 and 9. In order not to cause a change of calcium humate pH by sodium phosphate, presence of buffers with respective pH was necessary. In the solutions obtained as above the total organic carbon (TOC) was measured.

Total organic carbon was measured in each case from solution using TOC analyser (Analytik Jena Multi NC 2000).

RESULTS

Addition of sodium phosphate in different concentrations and at varied pH circumstances to calcium humates revealed that the process of organic matter release increases with increase of pH (Fig. 1B) and of the amount of sodium monohydrogen (ortho) phosphate added to the humates (Fig. 1A).

At pH values of 4, 5 and 6, the amount of released organic matter increased very slowly with increase of sodium phosphate addition. At high pH values, the amount of released organic matter increased urgently and the higher it was, the higher the pH of the experiment. However, significant growth of humic acid in solution was visible only when higher concentrations of sodium phosphate addition were applied (> 1 meq Ca).

Increase of calcium phosphate concentration which was added to sodium humate caused an increase in the initially adjusted pH (Fig. 2).

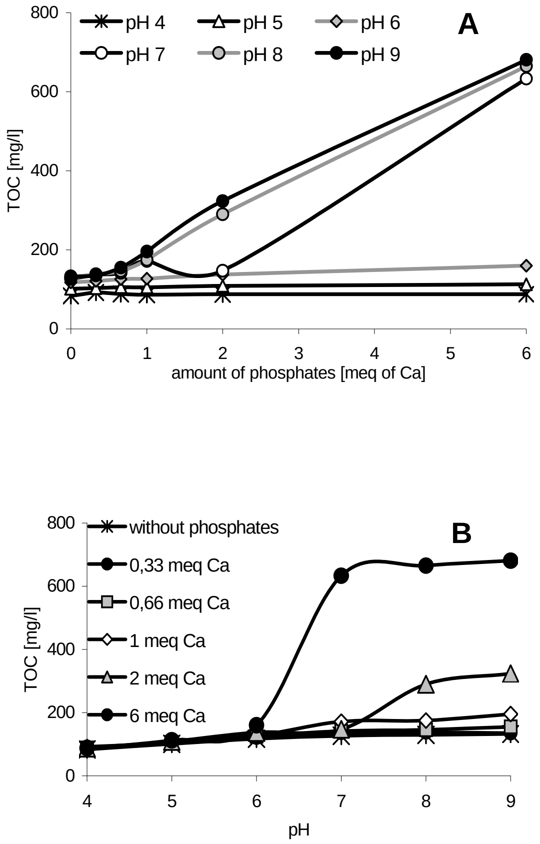

Fig. 1. Release of humic acid from calcium humate at different pH (A) and under influence of different concentrations of sodium phosphates (B) for muck extract No. 1 and humic acid concentration of 1000 mg dm^3

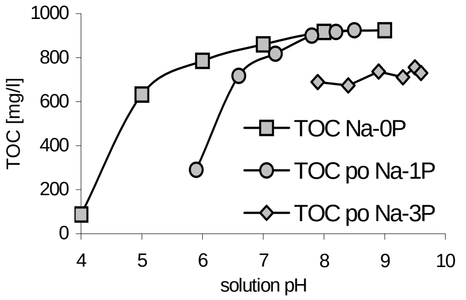

Fig. 2. Relationship between total organic carbon in solution and amount of added calcium phosphates to sodium humate under different pH conditions for muck extract No. 1 and humic acid concentration of 1000 mg dm^3

Simultaneously, the higher the pH value of the studied system, the higher the humic acid concentration in solution. Significant effect of pH on release process of humic acids was observed in the range of 4–7. Over pH 7, increase in the amount of released organic matter was slower. On the other hand, concentration of peptised organic matter (in the same pH conditions) decreased with increase of added calcium phosphate.

DISCUSSION

Increase of concentration of organic carbon in solution during the addition of sodium phosphate to calcium humate results above all from the properties of substituted sodium cation. First of all, addition of sodium phosphate caused exchange of sodium cations with calcium cations. Thus, sodium humate was created and it was much more soluble than calcium humate. Therefore, concentration of releasing organic matter increased with increase in the amount of sodium phosphate which was added to the solution. However, growth of concentration of released organic matter depended in a different way on pH and amount of added sodium phosphate. It was relatively slow at low pH value (4, 5 and 6) and intense above pH 7. The reason for such a mechanism could be found in the structure and nature of humic acid particles. The complex structure of humic acids contains a number of functional groups. These groups reveal different acid-base properties. The presence of weakly, medium or strongly acid functional groups causes that dissociation of compounds like humic acids strongly depends on pH. Groups with strong acid nature start to dissociate above pH 4, medium acid in neutral range of pH, whereas weakly acid, like -OH, do not dissociate until in alkaline conditions [Kononowa 1966].

Sodium phosphate addition caused increased peptisation of organic matter over the whole range of sodium phosphate concentrations, but significant influence had additions of more than 1 meq of Ca. It might be a result of non-stoichiometric ratio of reagents. Calcium humate released small, yet increasing, amounts of organic matter at low pH of sodium phosphate, whereas growth of pH and sodium concentration caused that calcium cations were displaced from the precipitate. It is an evidence of strong competitiveness of sodium cations in relation to calcium ones at high pH conditions. Sodium ions displace coagulating calcium, causing humic acid to be more dissolved, and it gradually becomes a part of the solution.

In turn, addition of calcium phosphate with increasing concentration and pH to sodium HA forms caused an increase in TOC concentration, but this growth should rather be treated only as a result of increase of pH values and not calcium phosphate influence (Fig. 2). The achieved results show that at constant pH the amount of organic matter in the solution is the highest for samples without calcium phosphate and much lower for samples with the highest calcium phosphate concentration. The reasons for decrease of organic matter concentration in the solution are calcium cations that at big surplus begin to displace sodium ions. This is equal to coagulation of humic acid. Overrun of coagulation value causes precipitation of calcium humate.

The effect of phosphates appears in those studies in the form of influence of the whole system on pH, as well as on the creation of buffer conditions. It is difficult to come to a conclusion about the change of structure of humic acids as a consequence of phosphate interaction or phosphate connection with organic matter. That complication is that humic acids in the above investigation were purified during the extraction from cations and a consequence of this was the removal of aluminium and iron cations which can, in natural conditions, bond phosphate anion to humic acid particle and thus change humic acids properties [Schnitzer and Khan 1978, Wagar *et al*. 1986, Sposito 1989]. It is known that the process of dissolving of humic acids in the presence of phosphates takes place in environment circumstances [Reemtsma *et al*. 1999, Turner *et al*. 2002].

CONCLUSIONS

– Addition of sodium ions in the sodium phosphate form to calcium humate precipitate causes peptisation of humic acid.

– Competitiveness of sodium cations in relation to calcium ones is shown especially at higher pH (7–9). The amount of HA released to the solution is the highest at pH 9 and at the highest addition of sodium phosphate.

– Peptisation effect is also additionally supported by phosphate anions.

– Addition of calcium ions in the calcium phosphate form to sodium humate suspension causes increase of HA concentrations in the solution. However, such behaviour is caused only by increasing pH and phosphate influence.

– Calcium ions have coagulation action. Overrun of coagulation value causes precipitation of calcium humate.

– Different effects of sodium and calcium cations are connected with their different chemical properties, especially with ion radius.

REFERENCES

Buchanan B.B., Gruissem W., Jones R.L., 2000. Biochemistry & Molecular Biology of Plants. Am. Soc. Plant Physiol., (Rockwille, Maryland).

Gawlik J., 2000. Division of differently silted peat formation into classes according to their state of secondary transformations. Acta Agrophys. 26, 17–24.

Galland H.U., von Gunten U., 2002. Chlorination of natural organic matter: kinetics of chlorination and of THM formation. Water Res. 36, 65–74.

Gonet S.S., 1990. The methodological guide to investigations of organic matter of soils (in Polish). PTG, Warsaw, 33–34.

Kononowa M.M., 1966. Soil Organic Matter. Pergamon, Elmsford, N.Y.

Reemtsma T., Bredow A., Gehring M., 1999. The nature and kinetic of organic matter release from soil by salt solutions. Europ J. Soil Sci. 50, 5–53.

Schnitzer M., Khan S.U., 1978. Soil organic matter. Elsevier. Sci. Pub. Comp., N.Y.

Sokołowska Z., Matyka-Sarzyńska D., 2002a. Investigation of iron status in Terric Histosols. Inter. Agrophys. 16, 133–137.

Sokołowska Z., Matyka-Sarzyńska D., 2002b. Iron content in selected mucks (in Polish). Acta Agrophys. 68, 123–139.

Sokołowska Z., Szajdak L., Matyka-Sarzyńska D., 2006. Effect of temperature on dissolved organic master release from moorsh (in Polish) [in:] Brandy T., Szajdak L., Szatyłowicz J. (eds), Phisical and Chemical Propertys of Organic Soils. SGGW, Warszawa, 33–40.

Sokołowska Z., Matyka-Sarzyńska D., 2006. Peptization of humic acids originated from mucks at different concentrations of phosphate ions. Acta Agrophys., 8(1), 181–189

Sposito G., 1989. The Chemistry of Soils, N.Y., Oxford, Oxford University Press.

Turner B.L., McKelvie I.D., Hayagarth P.M., 2002. Characterisation of water-extractable soil organic phosphorus by phosphatase hydrolysis. Soil. Biol. Bioch. 34, 27–35.

Wagar B.I., Stewart J.W.B., Moir J.O., 1986. Changes with time in the form and availability of residual fertilizer phosphorous on Chernozemic soils. Can. J. Soil. Sci. 66, 105–119.

Wang Y., Combe C., Clark M.M., 2001. The effects of pH and calcium on the diffusion coefficient of humic acid. J. Membrane Sci. 183 (2001) 49–60.

Zawadzki S., 1999. Soil Science (in Polish). PWRiL, Warsaw, Poland.

URUCHAMIANIE KWASÓW HUMUSOWYCH POCHODZĄCYCH Z MURSZY JAKO REZULTAT WZAJEMNEGO ODDZIAŁYWANIA JONÓW SODU, WAPNIA I FOSFORANÓW

Streszczenie. Celem pracy było zbadanie zależności pomiędzy stanem kwasów huminowych zawartych w kompleksie sorpcyjnym gleby a tak ważnymi jonami, jak sód, wapń i fosforany. Doświadczenie przeprowadzono na wybranych próbkach murszy pochodzących z terenów Polesia Lubelskiego (Kanał Wieprz-Krzna) i doliny rzeki Biebrzy. Próbki zostały pobrane z głębokości 5–20 cm. Kwasy huminowe otrzymano na drodze alkalicznej ekstrakcji, przy zastosowaniu metody proponowanej przez Schnitzera. Sól sodową i wapniową kwasu huminowego potraktowano odpowiednio fosforanem wapnia Ca_3PO_4 i diwodorofosforanem sodu NaH_2PO_4. Sole Ca_3PO_4 i NaH_2PO_4 dodawano w różnych stężeniach i w zróżnicowanych warunkach pH. Badania wpływu fosforanu sodu na humian wapnia przy różnych wartościach pH wykazały, że proces uruchamiania materii organicznej jest tym intensywniejszy, im pH środowiska jest wyższe, a także im większe jest stężenie monowodorofosforanu sodu dodawanego do humianu wapnia. Z kolei dodatek fosforanu wapnia o wzrastającym stężeniu i w różnych warunkach pH do humianu sodu powodował ogólnie wzrost stężenia węgla całkowitego w roztworze, co dowodzi występowania procesu peptyzacji i uwalniania substancji huminowych. Jednak w badaniach dowiedziono, że wzrost stężenia kwasu huminowego w roztworze był spowodowany jedynie wzrostem pH, nie dodatkiem kationów wapnia.

Słowa kluczowe: kwasy humusowe, mursz, peptyzacja, koagulacja