

THE RELATION OF pH TO DEGREE OF BASE SATURATION OF SOILS

G. Józefaciuk, J. Stawiński, E. Kozak, J. Gliński

Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-236 Lublin, Poland

A b s t r a c t. The relationships between base saturation (BS) and pH were evaluated basing on three different definitions of degree of base saturation: expressing BS in terms of the total (pH 8.2), 'effective' and 'actual' cation exchange capacities. The first two approaches lead to differentiation of BS/pH curves for different cationic as well as solid phase compositions (presence of organic matter) of exchange complex. The third approach differentiated soils only in respect to cationic composition.

K e y w o r d s: base saturation, acidification, pH

INTRODUCTION

In his early work from 1925, Hissink [9] introduced to soil science literature the term 'degree of saturation with bases' which expressed the relative content of basic cations in soil exchange capacity. The degree of base saturation (BS) is concerned up to date as one of most important parameters for soil taxonomy purposes as well as for evaluation of liming and nutrition criteria.

According to Bradfield and Allison [3] the criterion of 100 % base saturation is pH 8.2, because at this pH the soil is in equilibrium with an excess of calcium carbonate at a partial pressure of carbon dioxide equal to atmospheric. So the degree of base saturation has been expressed as the relative content of basic cations in total exchange capacity of soils [17,18]. Further the other (lower) pH's were proposed as criteria for 100 % BS taking into account that at higher salt concentrations (as have been used for laboratory measurements)

the soil pH is about one unit lower than in a field, as well as that for natural, biologically active soils the higher partial pressures of CO₂ occur, however they found no common acceptance in the literature. In 1959 Coleman and Thomas [4] proposed that BS should be expressed not by the total but by 'effective' CEC - measured by the neutral salt extraction.

By the intuition there is expected the evident relationship between pH and base saturation because the neutralization of protons by bases always leads to the increase of BS, however, just in 1926 Joffe and Mc Lean [10] stated as a result of their experiments that BS and pH have not much to do with each other. In 1941 Peech found for sandy soils of Florida the BS/pH relationship similar to the titration curve of weak monobasic acid, what was further certified for New York soils [15]. Blosser and Jenny [2], however, found the straightline dependence. Mehlich [17,18] stated that at pH 7 montmorillonitic soils are 80 % and kaolinitic soils are 30-50 % base saturated. For soils containing intergrade minerals or iron oxides coatings the BS is about 35 % at pH 6 and 50 % at pH 7 [4]. The similar values were observed for organic soils [8,16]. Turner and Nichol [20], stated that BS better correlates with lime potential than with pH of soils.

Using different criteria, definitions and measuring methods and collecting the huge

amount of empirical data, the general BS-pH dependence has, however, been not found and the present understanding of the problem is not far from the first authors proposals [1,7,16]. In general it is accepted that the differences in BS for different soils at that same pH are due to: nature and content of soluble acids, nature and content of soil humus, mineralogical composition, silica and sesquioxides content, total CEC, degree of Fe and Al oxides coatings of minerals [19].

In the authors opinion, however, at least some of the above mentioned discrepancies may be related to the fact that in the experimental methods applied for BS evaluation not only exchangeable ions are measured. As 'pure' exchangeable ions one has to consider only these being electrostatically bound in a diffuse double layer surrounding negatively charged solid particles. From this point of view the protons present in unassociated surface groups of variable charge soil constituents (organic matter, sesquioxides, etc.) are not exchangeable but they become dissociated due to pH rise and/or neutral salt addition as well, and so they are taken as exchange acidity in present experimental procedures what leads to the decrease of BS measured. It is also seen that any arbitrary taken pH value for 100 % BS has no direct physicochemical sense. It seems then that a more correct definition of BS should be based upon actual values of soil exchange acidity and exchange capacity. Among the most correct measuring methods for evaluating the above values, e.g., Gillman [6] method can be considered.

The purpose of the present work was to compare the relationships between base saturation and pH for some clay fractions of acidic Polish soils applying different BS measuring methods being in consistency with different definitions of BS.

MATERIALS AND METHODS

For calculations of BS at different pH's the experimental data of the CEC at pH 8.2, the actual CEC values, the values of the sum of exchangeable bases, and the values of acidities

of 1 N KCl salt extracts were taken from earlier papers [11-14]. The data were obtained for sodium and aluminum forms of clay fractions separated from six soils: degraded black earth formed from loess (Jabłoń locality), brown soil formed from loess (Tarnawatka), acidic brown soil formed from flysh (Bukowina), degraded chemozem formed from loess, (Machnów), leached brown loamy soil (Baligród) and light loamy podzol (Dubica). The clay fractions were investigated in their natural forms and after a successive depletion of organic matter, iron oxides, and aluminum oxides and amorphous silica. The detailed characteristic of the investigated samples and measuring methods can be found elsewhere [11].

The values of base saturation at different pH's were calculated as following:

- 1) for classical definition of BS, the sum of exchangeable bases at a given pH was divided by CEC at pH 8.2;
- 2) for Coleman's definition of BS, the sum of exchangeable bases at a given pH was divided by the sum of exchangeable bases plus the acidity of the salt extract at that same pH;
- 3) for expressing BS in terms of actual CEC, the sum of exchangeable bases was divided by the value of the negative surface charge at a given pH.

RESULTS AND DISCUSSION

Evaluated in the above manners BS vs. pH curves are presented in Figs 1, 2, and 3, respectively.

From Fig. 1 it is seen, that the degree of base saturation calculated in classical way increases almost linearly with pH for sodium forms of clays. The above dependence is apparently due to the increase of negative charge (CEC) with pH, as far as for sodium samples the input of exchange acidity (in this case it is only exchangeable hydrogen) is small and it is limited to low pH range [14]. At pH 3 the sorption complex is base saturated in about 30 % for natural clays and about 80 % for organic matter depleted clays. For aluminium forms one can observe a rapid increase of BS

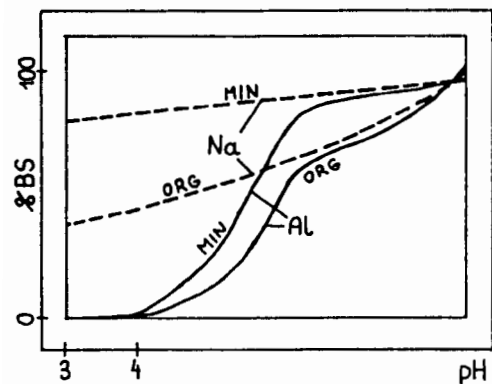


Fig. 1. Dependence between base saturation percentage (%BS) and pH as calculated on the base of the total CEC. Abbreviations in the figure: ORG - natural clays, MIN - clays with depleted organic material, Na - sodium forms of clays, AL - aluminium forms of clays.

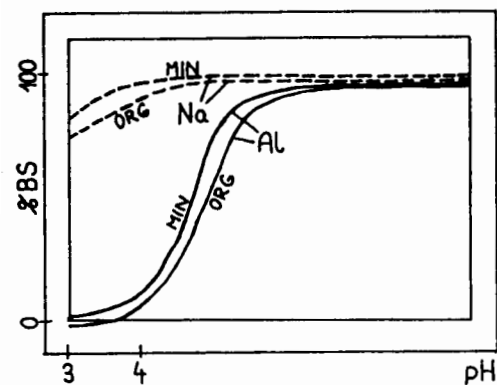


Fig. 2. Dependence between base saturation percentage (%BS) and pH as calculated on the base of the neutral salt CEC. Abbreviations as in Fig. 1.

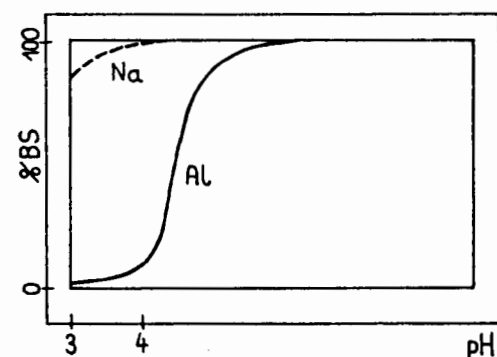


Fig. 3. Dependence between base saturation percentage (%BS) and pH as calculated on the base of the actual CEC. Abbreviations as in the Fig. 1.

up to pH 6 and a further slower increase above pH 6. The low BS values at low pH are connected with a high amounts of exchangeable aluminium, which is responsible for almost total amount of exchangeable acidity.

It is important to note that the evident differences in BS vs. pH curves race occur for natural samples (having organic matter) and samples containing mineral components only what is pronounced for both sodium and aluminium forms. This is due to the markedly higher increase of CEC with pH for organic that for mineral constituents. It is also seen that above pH 8.2 the BS exceeds 100 %, what is caused by the increase of CEC in the whole pH range.

From Fig. 2, illustrating the dependence of BS and pH as calculated basing on the Coleman's definition, it is seen that the exchange complex is fully base saturated at any pH value. It can be due to the fact, that within the whole pH range the concentrated salt addition always leads to the dissociation of variable charge surface protons and they give the input to the acidity of the salt extract and are herein regarded as exchangeable acidity. The BS values calculated according to Coleman are, however, significantly higher than these basing on the total CEC. The differences between the curves for natural and organic matter depleted samples occur here also, however they are less pronounced as in the previous case.

The dependence of BS vs. pH calculated basing on actual CEC, presented in Fig. 3, gives only two curves: one curve for sodium forms and the second for aluminium forms of clays. There is the surprising lack of the differences between mineral samples and samples containing organic matter. Exchangeable adsorption of ions at the charged surface should depend primarily on the ionic composition of the equilibrium solution as well as on the values of surface potentials of solid particles. The soil solution composition has the evident influence on exchange equilibria of basic and acidic ions what is clearly seen for AL and Na forms of clays. The lack of the differentiation between organic and inorganic solids and so on

the nature and quality of the charged surfaces provokes the statement that the surface potentials of the organic and mineral soil constituents are more or less similar, at least at low pH's where their effect on acidic ions adsorption influences the value of BS.

In the whole pH range the BS of sodium forms is very high, what is connected to very low quantities of exchange hydrogen ions. At pH above 4.5 the exchange complex is fully saturated with bases. As it was proved [5] the protons are exchangeably adsorbed that same like any other monovalent cation so at pH 4.5, where their concentration in the solution is less than 0.0001 N, protons cannot occur as exchangeable ions in soils in measurable amounts. Frequently observed high affinity of hydrogen ions to soils is not a question of exchange adsorption.

For aluminium forms the BS is very low at pH's lower than 4 and above this pH it rapidly increases up to pH 6, where it reaches 100%. Above pH 6 the exchangeable aluminium does not occur.

CONCLUSIONS

On the basis of the results obtained it can be stated that the degree of base saturation is due mainly to the composition of soil equilibrium solution. It seems possible to reach about 0% of base saturation at high pH (extremely low salt concentrations) as well as almost 100% BS at low pH (at extremely high salt concentrations). It may be a reason that BS of different soils differs at that same pH value and that the general dependence of BS and pH is difficult to be found. However, it seems that the expression of BS by the value of the actual exchange capacity in dependence not directly to pH but to any value related to the total ionic composition of soil solution (similar to the lime potential) may give the comprehensive picture for different soils.

REFERENCES

1. **Bache B.W.:** Measurements and mechanisms in acid soils. Materials Int. Conf. 'Plant-Soil Interactions at Low pH', Alberta, 1987.
2. **Blosser D.L., Jenny H.:** Correlations of soil pH and percent base saturation as influenced by soil forming factors. Soil Sci. Soc. Am. Proc., 35, 1017-1018, 1971.
3. **Bradfield R., Allison W.:** Criteria of base saturation in soils. Int. Soc. Soil Sci., Comm. II, Trans. A., 63-69, 1933.
4. **Coleman N.T., Thomas G.W.:** The basis chemistry of soil acidity. In: Soil Acidity and Liming (Eds R.W. Pearson, F. Adams). Agron., 12, ASA, Madison Wisc., 1-41, 1967.
5. **Gilbert M., Laudelout H.:** Exchange properties of hydrogen ions in clays. Soil Sci., 100, 157-162, 1965.
6. **Gillman G.P.:** A proposed method for the measurements of exchange properties of highly weathered soils. Aust. J. Soil. Res., 17, 129-139, 1979.
7. **Hargrove W.L., Thomas G.W.:** The chemistry of soil acidity. In: Soil Acidity and Liming (Eds R.W. Pearson, F. Adams). Agron., 12, Madison, Wisc., USA, 1984.
8. **Helling C.S., Chesters G., Corey R.B.:** Contributions of organic matter and clay to soil cation exchange capacity as affected by the pH of the saturating solution. Soil Sci. Soc. Am. Proc., 28, 517-520, 1964.
9. **Hissink D.J.:** Base exchange in soils. General views. Trans. Faraday Soc., 20, 551-556, 1925.
10. **Joffe J.S., Mc Lean H.C.:** Colloidal behaviour of soils and soil fertility. II. The soil complex capable of base exchange and soil acidity. Soil Sci., 21, 181-125, 1926.
11. **Józefaciuk G.:** Negative surface charge distribution among constituents of the soil clay fraction as influenced by pH changes. Zesz. Probl. Post. Nauk Roln., 398, 73-77, 1992.
12. **Józefaciuk G.:** Soil acidity relations with surface charges of soil constituents and their dependence on pH. Zesz. Probl. Post. Nauk Roln., 398, 83-89, 1992.
13. **Józefaciuk G., Stawiński J., Arsova A., Urumova-Peshewa A.:** The influence of aluminum on negative soil charge. Zesz. Probl. Post. Nauk Roln., 398, 79-81, 1992.
14. **Józefaciuk G., Stawiński J., Brzeziniński K., Raychev T., Popandova S.:** Exchangeable aluminum and hydrogen ions in acidic soils - dependence on pH. Zesz. Probl. Post. Nauk Roln., 398, 91-96, 1992.
15. **Lathwell D.J., Peech M.:** Interpretation of chemical soil tests. Cornell Univ. Agr. Exp. Sta. Bull., 995, Ithaca, N.Y., 1964.
16. **Mc Lean E.O., Owen E.J.:** Effects of pH on the contributions of organic matter and clay to soil cation exchange capacities. Soil Sci. Soc. Am. Proc., 33, 855-857, 1969.
17. **Mehlich A.:** Base unsaturation and pH in relation to soil type. Soil Sci. Soc. Am. Proc., 6, 150-156, 1942.
18. **Mehlich A.:** The significance of percentage base saturation and pH in relation to soil differences. Soil Sci. Soc. Am. Proc., 7, 167-174, 1943.
19. **Schachtschabel P., Renger M.:** Beziehung zwischen V- und pH-wert von boden. Z. Pfl. Dung. Bodenkn., 112, 238-248, 1966.
20. **Turner R.C., Nichol W.E.:** Relation between the

lime potential and percent base saturation of negatively charged clays in aqueous salt suspensions. Soil Sci., 94, 58-63, 1962.

RELACJA pH DO STOPNIA NASYCENIA GLEB ZASADAMI

Dane doświadczalne składu jonowego kompleksu sorpcyjnego dla frakcji ilastych gleb kwaśnych przy różnych wartościach pH wykorzystano do obliczeń zależności stopnia wysycenia glebowego kompleksu sorpcyjnego jonami zasadowymi (BS) od pH przy zastosowaniu trzech różnych sposobów definiowania BS:

a) wyrażając BS jako stosunek ilości zasad wymien-

nych (EB) do pojemności wymiennej całkowitej przy pH 8.2;

b) jako stosunek EB do efektywnej pojemności wymiennej,

c) jako stosunek EB do aktualnej pojemności wymiennej.

Pierwsze dwa podejścia dawały w efekcie zróżnicowanie wielkości BS przy tym samym pH dla próbek o różnym składzie glebowej fazy stałej oraz dla różnych składów glebowego roztworu równowagowego. Ostatnie podejście dawało obraz bardziej jednorodny: wartość BS dla różnych próbek przy danym pH zależała jedynie od składu jonowego roztworu jednowagowego.

S ł o w a k l u c z o w e: wysycenie gleb zasadami, zakwaszenie, pH.