SOIL ACIDITY INVESTIGATION BY POTENTIOMETRIC TITRATIONS

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Introduction

Buffering capacity is the ability of the soil to resist changes in pH. These results from the ions associated with the solid phase buffering the changes in ion concentration in the solution phase (Foth, 1990). The clay minerals, organic colloids (humus), and the amount of $CaCO_3$ are mainly responsible for acid/alkaline buffer properties of the soil /Filep and Rédlyné (1988), and Filep (1988)/. Acid-base buffer efficiency of soils can most readily be characterized by potentiometric titration curves of the soil suspension (Filep, 1998). Buffer capacity is defined as the area between the titration curve of the soil suspension and that of the soil-free solution, or, alternatively, as the quantity of acid or base that causes the pH to change by one unit (Filep, 1998).

The objective of this study was to apply potentiometric titrations to investigate the sensitivity of some acid mineral soils.

Methods

The buffering capacity was determined by computer-aided potentiometric titrations (Figure 1) (Czinkota et al., 2002) for the A, E, and B horizons of some mineral soils (Table 1.). Soil suspension was prepared with distilled water and 1 M KCl solution. The pH of the soil suspension was continuously measured with a pH-selective electrode. Base (0.1 M KOH) was gradually added to the soil suspension by the automatic burette in order to increase the pH. This allowed the determination and comparison of the sensitivity of the sample of the different horizons and different soils by the obtained titration curves. After each lapse of the time interval the software saves the time, pH and added quantity data on the disk. The measurement system was built using Radelkis OP-0808P pH electrode, Schott Titronic 96 automatic burette, ALTAIR BT AAD2816S amplifier and analog digital converter and an I486 personal computer (Czinkota et al., 2002).

The following analytical methods were used for determining the general laboratory data: pH(H_2O) and pH(KCl) were determined electrometrically with a soil to liquid ratio of 1:2.5 (Buzás, 1988). The cation exchange capacity (CEC) was measured by the unbuffered salt extraction method by Grove et al. (1982). Soil organic matter (OM) was determined by the Walkley–Black method (Walkley, 1947). Particle size fractionation was performed using the modified procedures described by Jackson (1969).

DOI: 10.1556/CRC.34.2006.1.71

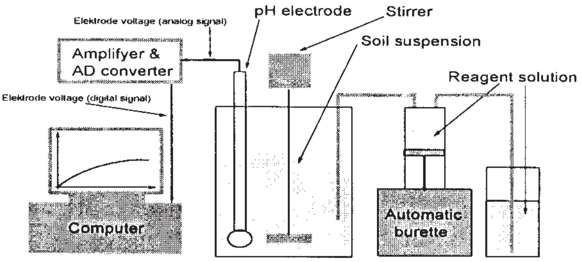

Figure 1. Theoretical outline of the titration equipment Czinkota et al. (2002)

Results and discussion

Buffering capacity can be defined as: $\beta=\Delta m_b/\Delta pH=-\Delta m_s/\Delta pH$, where: β: is the buffering capacity of the soil; m_b: is the given base ($cmol*kg^{-1}$); m_s: is the given acid ($cmol*kg^{-1}$) /Van Slyke (1922)/. Thus, the degree of buffering capacity is the quantity of acid or base that causes the pH to change by one unit.

During the experiment for each horizon the 0.1 M KOH base solution was added to the soil suspension at a 0.025 mL rate, every 0.3 seconds. This way, we had several hundred measuring points for each sample. Based on this large number of observations, the sensitivity of the soil can be accurately determined by finite difference, by the following equation: $1/\beta=\Delta pH/\Delta m_b$.

To illustrate the results of titrations, the $1/\beta$ curves (the reciprocal buffer capacity, or "sensitivity curves") will be discussed. As for the $1/\beta$ or sensitivity curve for all horizons of the Karád sample (Figure 2), we can see that the $1/\beta$ curve increases drastically and steeply at the very beginning of the measurement, until it reaches its maximum point, and then decreases steeply. This maximum point or maximum sensitivity occurs around the inflexion point of the titration curve. The maximum point is the amount of base for which the soil reacts in a most sensitive way to the incoming basic effects (Table 1).

In case of the Karád site, the sensitivity (0.65 $pH*kg*cmol^{-1}$) (Table 2) is the highest in the leached E horizon (Figure 2), thus the E horizon shows the highest sensitivity to the given base and has the lowest buffering capacity. However, in the Bt2 horizon, the sensitivity was lower (0.38 $pH*kg*cmol^{-1}$) compared to the E horizon, showing the least sensitivity; and the A horizon showed medium sensitivity (0.49 $pH*kg*cmol^{-1}$) among these three examined horizons, thus have medium sensitivity and medium base buffering capacity. This soil is a lessivated brown forest soil with clay accumulation Bt2 horizon, which is rich in swelling clay mineral fraction (smectite). In the A horizon, the medium high buffering capacity can be explained by the high fresh organic matter (5.8 %) content along with the still relatively high clay content (18.96 %), that gave a 11.7 $cmol_c\ kg^{-1}$ of charge and fairly high buffering capacity. The E horizon showed the highest sensitivity to basic input. This result was expected, since the E horizon is leached, thus the $CaCO_3$, the organic matter, the Fe and Al oxides, and some of the clay fraction have probably been washed out, therefore there is not much soil colloidal component remaining (mainly quartz) to buffer the incoming effects. The E horizon has a CEC of 6.70 $cmol_c\ kg^{-1}$.

Table 1. Maximum values of sensitivity, organic matter (OM), pH, cation exchange capacity (CEC), and the clay content of the examined horizons.

Sample (U.S. Soil Taxomony)	**Hor.**	**Depth (cm)**	**Max. sensitivity (pH* kg *cmol^{-1})**	**OM (%)**	**pH (H_2O)**	**pH (KCl)**	**CEC (cmol* kg^{-1})**	**Clay (%)**
Karád (Typic Haplustalfs)	A E Bt2	0-5 5-20 45-70	0.49 0.65 0.38	5.80 0.91 0.22	5.18 4.96 5.69	4.19 3.29 3.80	11.7 6.70 16.2	18.96 19.01 30.98
Oltárc (Typic Haplustalfs)	A E Bt2	0-5 5-20 40-70	0.42 0.66 0.54	3.10 0.72 0.34	5.50 5.16 5.07	4.63 3.56 3.42	11.0 7.00 13.4	19.94 23.52 40.92
Velem (Dystric Ustochrepts)	A E BC	0-5 5-20 40-70	0.50 0.59 0.49	4.75 1.28 0.55	4.97 4.61 5.08	3.81 3.47 3.51	8.44 5.46 5.30	25.49 19.55 23.33
Gödöllő (Typic Ustochrepts)	AB BC	0-20 40-60	0.16 0.28	1.29 0.28	7.54 7.66	6.69 6.34	13.08 5.63	11.56 8.47

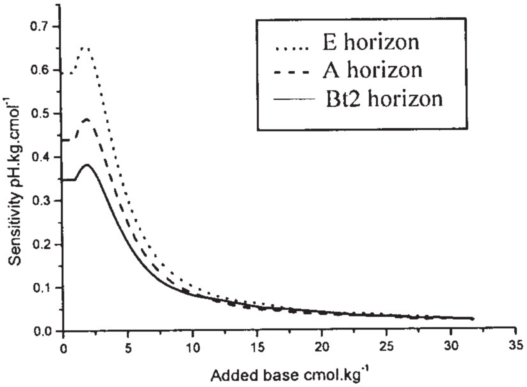

Figure 2. The sensitivity curves of the soil at Karád site

Conclusions

It was found that the leached E horizons showed the highest sensitivity to the incoming basic inputs. It is probably because the organic and inorganic colloid fractions, that would have been able to buffer the incoming base, have been washed out from this E horizon. The B horizon showed the lowest sensitivity, in general, probably due to the large amount of clay that accumulated there. In most cases, the organic matter rich A horizon gave medium sensitivity due to the buffering effect of the accumulated organic matter. Potentiometric titration, thus, is a good method to investigate soil acidity and soil sensitivity. Sensitivity is a horizon specific property, thus, it should be examined and evaluated by horizons and not the whole soil profile.

Acknowledgements

Hungarian Scientific Research Fund (OTKA – Nr. T 046358)
Hungarian Scientific Research Fund (OTKA – Nr. D 048592)
GVOP - 3.1.1. 0286/3.0

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