The Buffer Capacity of Calcareous Soils in Gansu Province of China

Chu Taiwei[a]; Du Jinzhou[a]; Song Yongjie[a]; Tao Zuyi[a]

[a] Department of Modern Physics, Lanzhou University, Lanzhou, P.R. of China

PLEASE SCROLL DOWN FOR ARTICLE

THE BUFFER CAPACITY OF CALCAREOUS SOILS IN GANSU PROVINCE OF CHINA

CHU TAIWEI, DU JINZHOU, SONG YONGJIE
and TAO ZUYI*

Department of Modern Physics, Lanzhou University,
Lanzhou 730 000, P.R. of China

In this study, we added increments of acid and base to three calcareous soils from the eastern, middle and western parts of Gansu Province (China) and to three treated soils to remove calcium carbonate, organic matter and both carbonate and organic matter, respectively. The titration curves were measured and the magnitudes of buffer capacities as a function of pH were computed. It was found that the buffer capacity of calcareous soil is mainly attributed to calcium carbonate, as expected from the chemical composition of calcareous soil, while cation exchange system, silicate buffer system and organic matter play a minor role. The results clearly show that these soils of Gansu Province will not become a problem in the near future from the entrance of H^+ into these soils.

Keywords: Calcareous soils; buffer capacity; potentiometric titration

INTRODUCTION

Gansu Province is located in the northwestern part of China and is an arid area. The main soil type of this province is calcareous soil containing little organic matter and much calcium carbonate.

The entrance of H^+ into the soil causes the soil to react by means of buffer systems which are able to produce or consume H^+ in such a way that the pH of the solution hardly varies. These systems are,
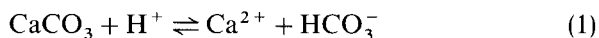
---

according to Ulrich (1983):

- $CaCO_3$ system (pH range 6.2–8.0)
- Silicate system (pH range 5.0–6.2)
- Cation exchange system (pH range 4.2–5.0)
- Aluminium system (pH range 3.8–4.2)
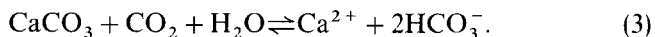- Ferric oxide system (pH range 2.4–3.8).

In calcareous soil, the H^+ can be neutralized by dissolution of calcium carbonate according to

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \tag{1}$$

and the bicarbonate can also be formed from dissolved carbon dioxide and water according to

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+; \tag{2}$$
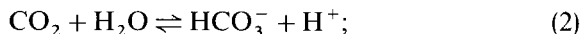
the combination of Equations (1) and (2) gives (De Vries *et al.*, 1989)

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-. \tag{3}$$

The buffer capacity of a soil (β) is used as an index of the potential effect of acid precipitation. Buffer capacity is defined as the number of moles of H^+ or OH^- that must be added to lower or raise the pH of 1 kg of soil by 1 pH unit. Buffer capacity is, therefore, the reciprocal of the slope of the titration curve of the soil. Such titrations have been made by many authors (Federer *et al.*, 1985; James *et al.*, 1986; Qiu *et al.*, 1986; Mowbray *et al.*, 1988; Louzao *et al.*, 1990). However, to our knowledge, the titration curves have not been measured for calcareous soils. Hence, the objectives of this study were:

1 to measure the titration curves of three calcareous soils from the eastern, middle and western parts of Gansu Province
2 to determine the buffer capacities of these soils
3 to evaluate the potential for acid rain to affect these soils
4 to measure the titration curves of three treated soils to remove calcium carbonate, organic matter and both calcium carbonate and organic matter, respectively
5 to estimate the contribution of calcium carbonate to the buffer capacity of calcareous soil.

MATERIALS AND METHODS

Three soil samples representing the main soil type of Gansu Province were collected from the surface horizon (0–20 cm) of agricultural lands. They were air-dried and ground to pass a 1 mm sieve. Selective properties of these untreated soils used are given in Table I. The pH in water was measured with a glass electrode using a 1:1 sample/water ratio. Organic content was determined by the dichromate oxidation method (Nelson *et al.*, 1982). Calcium carbonate was evaluated by the modified manometric method (Nelson, 1982) and cation exchange capacity (CEC) was determined in barium chloride by the Gillman method (Gillman, 1979). Clay ($< 1 \mu m$) content was measured by the hydrometer method. The samples were dried at 105°C and the difference between the weights before and after heating provided the moistures. Two portions of the soil sample No. 111 were treated with acetic acid-ammonium acetate ($0.5 \text{mol} \, l^{-1}$) at pH 5 for removal of calcium carbonate. One portion of the soil sample No. 111 was treated with 30% hydrogen peroxide for removal of organic matter (Kunze *et al.*, 1986). One portion of the soil treated to remove calcium carbonate was again treated with 30% hydrogen peroxide for removal of organic matter. Three treated samples were washed with double distilled-deionized water, finally air-dried and ground to pass a 1 mm sieve.

To measure the titration curves of these soils, a batch method was used to ensure that the full equilibration was reached. Known masses (0.10–0.11 g) of the soil were weighed into 25 ml glass-stoppered tubes, increasing amounts of sodium hydroxide or nitric acid were added to the sample, the $0.001 \text{ mol} \, l^{-1}$ calcium chloride and the 25 ml final volume were adjusted by adding a calculated quantity of water and a concentrated solution of calcium chloride. The systems were shaken for 8 hours in a reciprocating shaker (100 cycles min^{-1}) and left to rest for 16 hours at 25°C. This contact time was suggested from the preliminary experiment. After equilibration, the suspensions were centrifuged (4000 rpm, 15 min) and the pH values of the supernatants were measured by using a model pHS-3 pH meter and model 231 glass electrode. No precautions were taken to prevent air from entering the solution.

In most instances, the titration curves for the duplicate soil samples were parallel so we combined them by averaging values of a given

T. CHU *et al.*

TABLE I Selected properties of three soils

Soil No.	Location	Classification	$CaCO_3$ %	Organic matter %	Moisture %	CEC $meq(100g)^{-1}$	pH	Clay %
111	Yu-Zhong county, He-Ping country, middle part	sierozen	13.7	0.98	1.38	5.92	8.09	12.45
21	Jiu-Quan county, Guo-Yuan country, western part	irrigating warped soil	13.5	1.72	1.61	5.94	8.30	10.45
31	Qing-Yang county, Bai-Ma country, eastern part	loess	16.4	0.96	2.04	5.30	8.39	6.60

addition. The titration curves then were fitted to a polynomial equation and the magnitudes of buffer capacities as a function of pH were obtained from the reciprocal of the slope of the polynomial equation.

As for the preliminary experiment, 0.10–0.11 g No. 111 sample and 0.26 mmol nitric acid (HNO_3) were added instead of different amounts of HNO_3; the systems were shaken for certain different contact times fixed in advance.

RESULTS AND DISCUSSION

Effect of Contact Time

The dependence of pH values on the contact times for No. 111 sample is shown in Figure 1. The neutralization of the added H^+ was carried out fundamentally by the calcium carbonate and the pH values increased with increasing contact time. As can be seen from Figure 1, pH changes very little when shaking continues more than 6 hours after the 0.26 mmol HNO_3 is added. Therefore, 8 hours shaking and 16 hours resting time was applied for measuring titration curves. According to Equation (1), because of adding the amount of HNO_3 (0.26
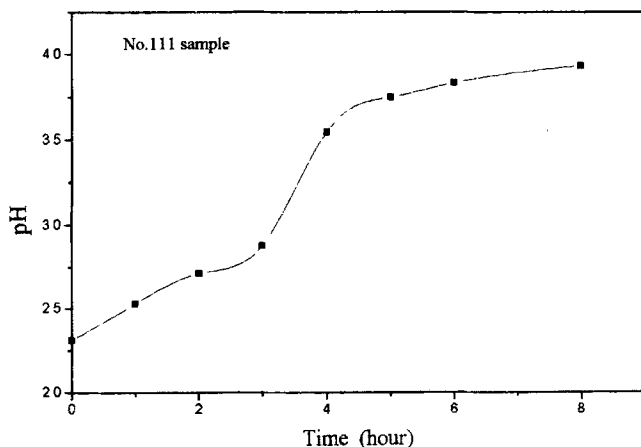

FIGURE 1   Effects of shaking time on pH.

mmol), the calcium carbonate (0.13 mmol) in the soil was exhausted and the pH increased only up to 4.

Three Untreated Soils

The titration curves for three untreated soils are shown in Figure 2. It can be seen that the three titration curves are almost identical over the pH range we covered and have two inflection points, and the hydroxyl added did not react with the soil components. The corresponding buffer capacities (β) are shown in Figure 3. One can clearly see that the titration curves are steeper at pH ranges 7.6–10.6 and 3.0–5.4, this means that the buffer capacities for three untreated soils are smaller at the two pH ranges, and are larger at pH range 5.4–7.6. However, as compared with Figures 3A and 3B, the magnitude of buffer capacity at peak of Figure 3C is slightly larger, and this result is in agreement with the higher content of calcium carbonate of No. 31 sample. According to Ulrich (1983), for three untreated soils, both the carbonate system and the silicate system controlled the buffering.
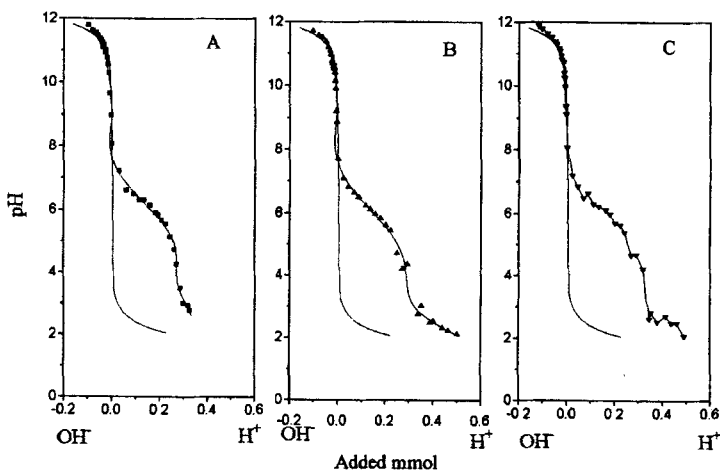

FIGURE 2   Titration curves for three calcareous soils, solid line represents no soil in titration, A–No. 111; B–No. 21; C–No. 31.
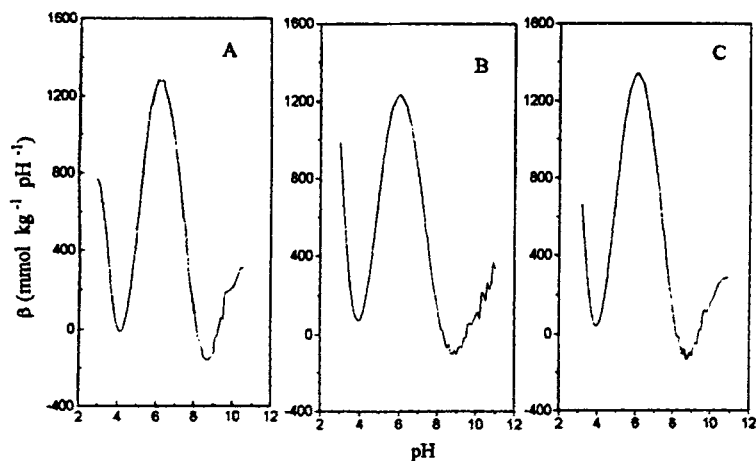
FIGURE 3   Buffer capacity for three calcareous soils, A–No. 111; B–No. 21; C–No. 31.

Three Treated Soils

The titration curves for three treated soils to remove calcium carbonate, organic matter, and both calcium carbonate and organic matter are shown in Figure 4. Figures 4A and 4C only have one inflection point and the corresponding buffer capacities are shown in Figure 5. After comparing Figure 4A and Figure 2A, Figures 3A and Figure 5A, it can be concluded that the carbonate system acts as the principal buffer. After comparing Figure 4B and Figure 4C, and Figure 5B, Figure 5C, one can see clearly that the organic matter is not the principal buffer. As shown in Figures 5A and 5C, though β was strongly dependent of pH, the relatively low β values at pH range 4.0–7.6 indicate that cation exchange system and silicate system play a minor role in this pH range. A comparison between Figure 3A and Figure 5B indicates that organic matters also play a minor role, since the removal of organic matter slightly decreases the buffer capacity.

Calcium Carbonate System

The 0.013 g pure calcium carbonate, which is the weight of calcium carbonate of 0.10 g No. 111 soil was used for titration, and the titration curve is shown in Figure 6. In Figure 6, the titration curve of
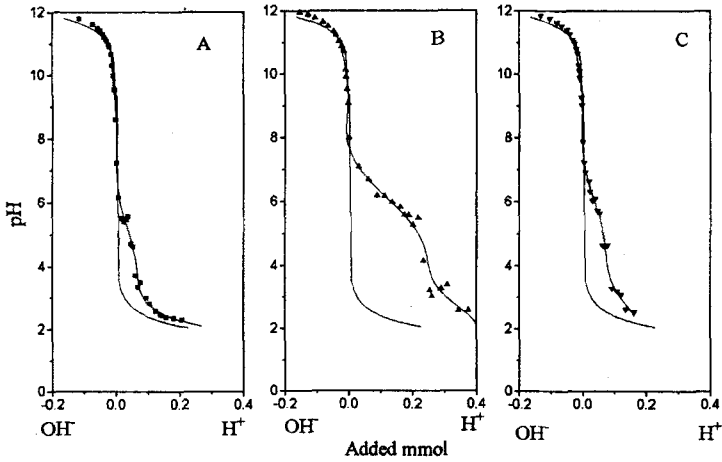
T. CHU *et al.*

FIGURE 4   Titration curves for three treated soils, solid line represents no soil in titration, A–treated soil to remove $CaCO_3$; B–treated soil to remove organic matter; C–treated soil to remove both $CaCO_3$ and organic matter.
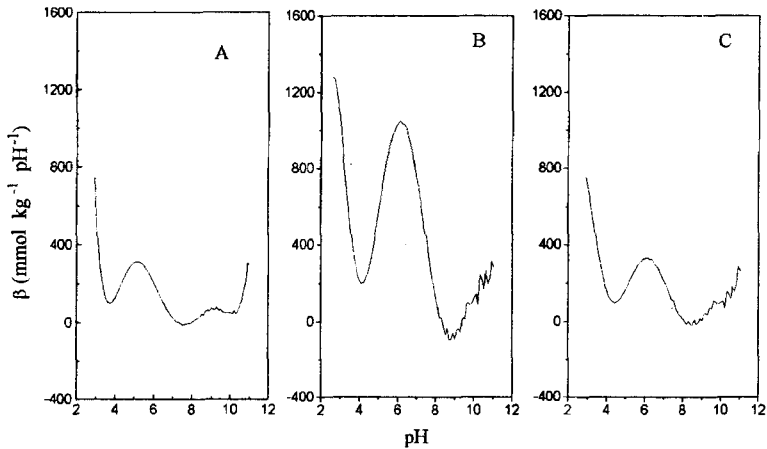

FIGURE 5   Buffer capacity for three treated soils, A–treated soil to remove $CaCO_3$; B–treated soil to remove organic matter; C–treated soil to remove both $CaCO_3$ and organic matter.

No. 111 soil is also shown for comparison. It can be seen that when the amount of calcium carbonate used was equal to the content of calcium carbonate of 0.10 g No. 111 soil, the two titration curves are almost coincident. Therefore, this result further substantiates the
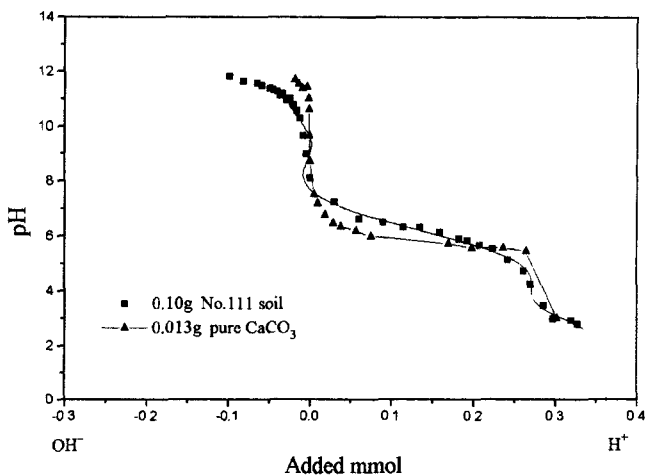
FIGURE 6   Comparison of titration curves between No. 111 sample and pure $CaCO_3$.

conclusion that the carbonate system is the principal buffer of cal-
careous soil.

CONCLUSIONS

The results described above are reasonably consistent with Ulrich's
concept (1983) of buffer ranges of soil.

  Buffer capacity of calcareous soil directly arise from calcium car-
bonate, though cation exchange buffer system, silicate buffer system
and organic matter play a minor role.

  Buffer capacity of calcareous soil can be remained until calcium
carbonate is exhausted.

  The high buffer capacity of these calcareous soils shows these soils
will not become a problem in the near future from the entrance of H^+
into these soils.

References

De Vries, W., Posch, M. and Kamari, J. (1989) Simulation of the longterm soil
    response to acid deposition in various buffer ranges, *Water, Air and Soil Pollution*,
    48, 349–390.

Federer, C. A. and Hornbeck, J. W. (1985) The buffer capacity of forest soils in New England, *Water, Air and Soil Pollution*, **26**, 163–173.

Gillman, G. P. (1979) A proposed method for the measurement of exchange properties of highly-weathered soils, *Australian Journal of Soil Reseach*, **17**, 129–139.

James, B. R. and Riha, S. J. (1986) pH buffering in forest soil organic horizons: Relevance to acid precipitation, *Journal of Environmental Quality*, **15**, 229–234.

Kunze, G. W. and Dixon, J. B. (1986) Pretreatment for Mineralogical Analysis, in A. Klute (ed), *Methods of Soil Analysis*, Part 1: Physical and Mineralogical Methods, 2nd. edition, American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, USA., *Agronomy*, **9**, 91–100.

Louzao, M. J., Leirós, M. C. and Guitián, F. (1990) Study of buffering systems in soils from Galicia, N. W. Spain, *Water, Air and Soil Pollution*, **49**, 17–33.

Mowbray, T. and Schlesinger, W. H. (1988) The buffer capacity of organic soils of the Bluff Mountain Fen, North Carolina, *Soil Science*, **146**, 73–79.

Nelson, D. W. and Sommers, L. E. (1982) Total Carbon, Organic Carbon and Organic Matter, in A. L. Page *et al.* (eds.), *Methods of Soil Analysis* (Part 2), 2nd edition, American Society of Agronomy, Inc., Madison, Wisconsin, *Agronomy*, **9**, 539.

Nelson, R. E. (1982) Carbonate and Gypsum, in A. L. Page *et al.*, (eds.), *Methods of Soil Analysis* (Part 2), 2nd edition, American Society of Agronomy, Inc., Madison, Wisconsin, *Agronomy*, **9**, 183.

Qiu, X. and Zhu, Y. (1986) Spectrophotometric determinations of pH value, buffer capacity, and rate of lime need in acidic soil using chrysoidine as a chromogenic agent, *Soil Science*, **142**, 275–288.

Ulrich, B. (1983) Soil acidity and its relations to acid deposition, in B. Ulrich *et al.* (eds.), *Effects of Accumulation of Air Pollutants in Forest Ecosystems*, D. Reidel Publishing Company, Dordrecht, Holland, pp. 127–146.