

Reactivity of Southern Murray Mallee Soil Carbonates

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ABSTRACT

Acid inputs to soils are increasing due to more intensive cropping and the increased use of nitrogen fertilisers. Carbonates buffer the soil but highly reactive surface carbonates decompose rapidly leaving less reactive carbonates to maintain soil buffering. Although soils with calcareous layers are common throughout the Southern Cropping Zone of Australia, their reactivity has been largely ignored. Several methods for determining soil carbonate reactivity exist. These methods generally require the rapid stirring of a soil sample and titration under steady-state conditions with strong acids. These conditions are generally unrealistic and do not reflect actual field conditions. This study has undertaken steady-state titrations of intact soil samples under conditions that better reflect those experienced by soil carbonates in the field to determine their natural behaviour on exposure to agricultural acids.

KEY WORDS

Soil carbonates, reactivity, pH buffering, pH-stat.

INTRODUCTION

Soils with calcareous (calcium and magnesium carbonate) layers are common throughout the Southern Cropping Zone of Australia. These carbonates provide buffering that helps maintain soil pH values around 8. Acids from agriculture, especially those that result from increased nitrogen fertiliser use, decompose these carbonates and alter soil pH buffering and fertility. Although they have been classified and described, the reactivity of carbonates in Australian soil has not been investigated and their behaviour on exposure to acid is not known.

This project investigates the reactivity of soil carbonates from the Murray Mallee in South Australia using weak acids in the laboratory and slow pH-stat titration reactions to better simulate field conditions. Existing methodology for assessing carbonate reactivity such as those outlined in Von Tress *et al.* (4), Moore *et al.* (3), del Campillo *et al.* (1) and Hartwig *et al.* (2) use unrealistic conditions and acid strengths. Modifications were made to observe effects over much longer periods (up to 100 hours) using weaker acids and at more realistic equilibrium soil pH values (4 to 5.5).

RESULTS AND DISCUSSION

Titration curves, cumulative plots of acid addition (expressed as Calcium Carbonate Equivalent, CCE {mg}) vs time, at pH 4.0, for two soil profiles from the Murray Mallee, South Australia are shown in Figures 1 and 2. The slope of these plots at any point in time during the reaction represents the reaction rate or rate of carbonate decomposition (CCE{mg}/hr) at that instant. Titration curves were determined by titrating under steady-state conditions 0.01 M HNO₃ against a mass of soil containing 50 mg CCE. While the liquid was thoroughly stirred, the soil was allowed to remain static, better preserving the physical properties of the soil carbonates.

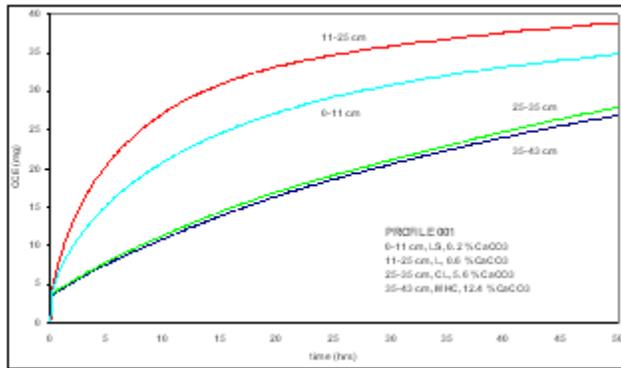


Figure 1.

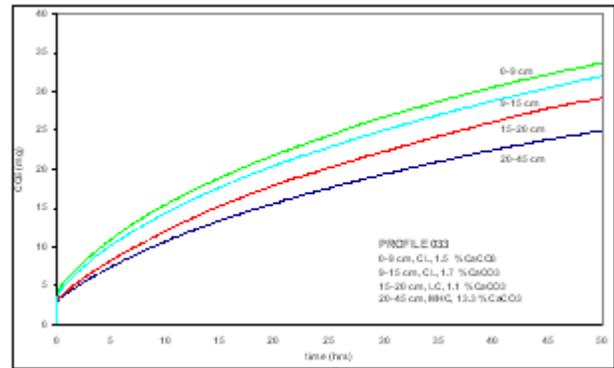


Figure 2.

Results indicate that the carbonates with the highest reactivity are generally associated with soils of coarser texture. Those soils higher in clay generally contain soil carbonates that exhibit a sustained, lower reactivity. This result may be attributable to the diffusion characteristics of the soils. A clay rich soil with an abundance of natural aggregates and fine, close packed grains will impose diffusion limits on the reaction rate. This allows regions of the soil, either within stable aggregates or grains sufficiently removed from preferred water movement paths, to be effectively protected from acid attack within a soil micro-environment.

Micro-environments do not reflect the chemical or physical characteristics of the whole soil and as such can act to shield the soil carbonates from challenging chemical or physical conditions. As the reaction proceeds and carbonates are decomposed, aggregate stability may decrease allowing slaking and further diffusion and continuously exposing shielded carbonates to bulk soil conditions. This process increases soil carbonate longevity compared to sandier soils and subsequently decreases overall reactivity. Evidence for this micro-environmental shielding of soil carbonate grains is observed when the soil sample itself is stirred in mid reaction. Stirring destroys carbonate-shielding micro-environments by removing diffusion limitations and exposing shielded carbonates to the bulk soil conditions. This results in an instant and dramatic increase in the reactivity of the soil as highly reactive grains are exposed to acidic conditions. This is followed by a steady decrease to minimal reactivity as the majority of the carbonate is decomposed.

Increasing the longevity of carbonates within the soil profile will also promote the formation of larger, less reactive carbonate grains from fine reactive grains again decreasing the soil carbonate's overall reactivity.

Soils of coarser texture, with fewer natural aggregates do not develop such diffusion limiting conditions and therefore carbonate preserving micro-environments. Carbonates present within these soils experience the bulk soil chemical and physical conditions and as a result, decompose rapidly.

CONCLUSIONS

Acidification of calcareous soil due to carbonate decomposition has important implications for soil buffering capacity, nutrient availability and profile pH gradients. The reactivity of a soil carbonate is not only a measure of rate of decomposition but also an indication of its longevity within the soil profile, an important factor when considering soil acidification.

Results indicate that carbonates in soils from the Murray Mallee of South Australia exhibit a wide range of reactivities. Results also indicate that soils with finer textures limit diffusion allowing for the formation of soil micro-environments that can act to shield soil carbonates from bulk soil conditions, aiding in their longevity and decreasing their overall reactivity. Results also suggest that soils of coarser texture promote the rapid decomposition of soil carbonates.

It is probable that physical protection from acids produced by agriculture is important and that exposure of new surfaces to acids following tillage will accelerate the loss of soil carbonate. Reduced tillage is likely to be more protective and lengthen the time period in which carbonates will buffer soil pH. Increased nitrogen use is less protective of soil carbonates. The results of this work also have application to the reactivity of agricultural liming materials.

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