The Role of Organic Matter in Soil Acidification

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Abstract

The pH and buffer capacity of two soils increased or remained constant after incubation with different amounts of plant material (lucerne chaff) at field capacity and when air dry. For both soils, the pH changes were greater at field capacity, whereas the buffer capacities were independent of the water treatments.

The pH changes observed could be explained in terms of the organic anion concentration of the plant material. The results indicate that the initial soil pH and the anion concentration (i.e. the per cent dissociation of soluble organic acids when released into the soil) determine the acidifying effect of organic matter.

Introduction

Continuing soil acidification under clover pastures has been observed in several parts of Australia (Williams and Donald 1957; Russell 1960; Williams 1980) and has been attributed to the accumulation of organic matter in the soils. However, the accumulation of organic matter is not the only mechanism that can lead to soil acidification in cultivated soils. The process of nitrogen cycling in an open system (Helyar 1976), and the removal of greater amounts of inorganic cations than anions in plant products (Riley and Barber 1969), have also been identified as potentially important factors in the development of acid soils.

Williams (1980) pointed out that the decrease in soil pH with years of pasture production occurred at depths >30 cm, whereas organic matter accumulation only occurred in the top 10 cm of the soil. Jarvis and Robson (1983) have observed a pH increase in a soil that had been used for pasture production for over 20 years, even though the organic matter content of the cultivated soil was more than double that of the virgin soil.

There are two possible explanations for these conflicting observations. Either organic matter accumulation does not necessarily result in pH decreases or other mechanisms causing pH change are more dominant. It would appear that the role of organic matter in soil acidification is not fully understood and merits further investigation.

There have been no systematic studies of the effect of the addition of plant material on soil pH under natural conditions. Indeed, most work with organic matter has used purified material previously extracted by strong acids or alkali. Also, no clear distinction has been made between the roles played by soluble and insoluble components of the breakdown products in their natural state.

Consequently, the work reported here was initiated to investigate some properties of lucerne chaff and the effect of its addition on soil pH.

Materials and Methods

Soils

The soils used in the study were selected on the basis of their low organic matter content and different pH values. Soil samples were collected from the 0–10 cm layer of a lateritic podzolic (Yalanbee) and from a yellow earth (Merredin) at 30–60 cm depth. Some properties of the two soils are given in Table 1. All samples were air-dried and sieved through a 2 mm mesh sieve before use.

Table 1. Soil properties

Property	Soil	
	Yalanbee	Merredin
Great soil group	lateritic-podzolic	yellow earth
Organic matter (%)	1·06	0·09
pH[A]	5·66	4·31
Ionic strength	1×10^{-3}	$2{\cdot}4 \times 10^{-3}$
Cation exchange capacity (C g^{-1})	5·8	2·9
Buffer capacity[B]	1·30	1·21
Gravimetric water content at field capacity (g g^{-1})	0·104	0·101
Gravimetric water content when air dry (g g^{-1})	0·01	0·01

[A] 1:5 soil : 0·002 M $CaCl_2$ ratio.

[B] Rate of change in pH per mmole of acid or base added to 100 g soil.

Soil Incubation

The two soils were incubated for 32 days at 30°C with four levels of added plant material at two soil water contents (air-dry and field capacity). The higher soil temperatures were used to speed up incubation times. At 30°C, microbial activity is increased with a minimum of disturbance to the population composition and little change in the by-products produced by metabolic processes (Griffin 1972). The chemical reaction rates and microbial activity of the elevated temperature may be described by the Arrhenius equation (Castellan 1970), and so the conditions of incubation are equivalent to 90 days at 15°C, i.e. the average soil temperature during winter in the regions where the soils were collected (Cotterill, personal communication).

Air-dried lucerne chaff (*Medicago sativa*), ground to pass through a 0·5 mm mesh sieve, was thoroughly mixed with 300 g subsamples of each soil at the rates of 0, 2·3, 4·4 and 6·5 g $100g^{-1}$ for the Yalanbee soil and 0, 2·5, 5·0 and 7·2 g $100g^{-1}$ for the Merredin soil. Distilled water was added to bring the water content to the desired value. The mixture was placed in a 500 ml plastic container, and plastic beads were placed on the top of the soil to reduce evaporation. Water was added to the field capacity treatments each day to keep them at field capacity. After incubation, the field capacity treatments were dried at 30°C and then all soil samples were stored at 4°C before analysis.

Plant Analysis

A nitric–perchloric acid digest was used to determine Ca, Mg, Na and K by AAS and P by the molybdovanadate method (Black 1965). N (Kjeldahl method), C (Walkley–Black method; Black 1965), ash content and ash alkalinity (Pierre and Banwart 1973) were also determined. A water soluble extract was prepared by shaking with deionized water at a ratio of 1:10 for 16 h. The pH of the extract was noted and the solution potentiometrically titrated using the same method as Young *et al.* (1981). The end-point of the titration was taken as the region of the curve with the greatest slope (rather than an arbitrary pH), and was considered to be the pH at which all the carboxyl groups were fully dissociated.

Soil Analysis

The soils were analysed for organic matter (the Walkley–Black method; Black 1965), ionic strength at field capacity (Gillman and Bell 1978) and CEC (1 M NH_4Cl; Black 1965).

pH was determined in 0·002 M $CaCl_2$ (i.e. approximate ionic strength of West Australian soils; Dolling and Ritchie 1985) after shaking for 16 h at a soil-liquid ratio of 1:5. A Beckman ϕ 71 pH meter with a combination electrode was used to measure the pH of the clear supernatant liquid after any pH drift was <0·005 pH units over a 30 s period.

The buffer capacity of each soil was determined before and after incubation for each treatment. The buffer capacity may be estimated from the slope of a curve of pH *versus* mmole of acid or alkali added per 100 g of soil. Eight points on the curve (in the pH range 3–7) were determined by adding known aliquots of 0·02 M calcium hydroxide and 0·1 M HCl in 20 ml of 0·002 M calcium chloride to triplicate 4 g samples of each treatment. The samples were shaken for 16 h and the pH of the supernatant measured as described previously.

Results

Properties of the Plant Material

The plant material contained (% oven dry): 48·7 C, 2·94 N, 9·6 ash, 1·48 Ca, 0·28 Mg, 0·34 Na, 2·3 K and 0·29 P, and had an ash alkalinity of 88 mmole $100g^{-1}$. The pH of the deionized water (5·7) was unchanged by the extraction of the water-soluble component of the plant material. Potentiometric titration indicated that the acids present in the water soluble component were 50% dissociated at pH 4·2 (i.e. pK_m = 4·2) and 83% dissociated at pH 5·7.

Soil Incubation with Plant Material

At field capacity, the pH of both soils increased with small organic matter additions and then appeared to reach a maximum value with larger additions (Fig. 1). The decrease in the change in pH with increasing organic matter is due to the concurrent increase in the soil buffer capacity.

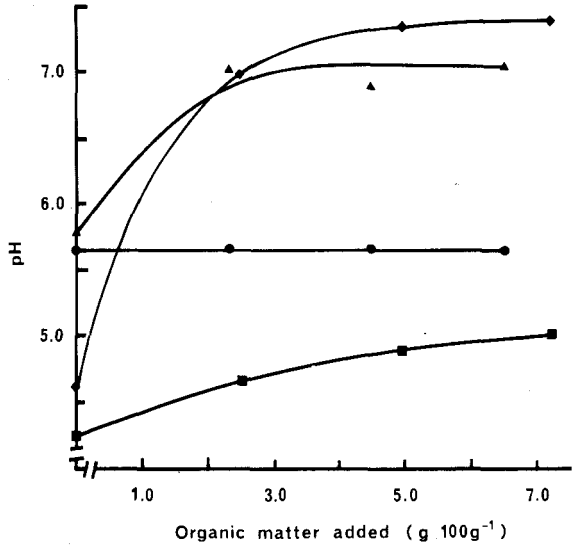

Fig. 1. Variation in soil pH with organic matter added to Yalanbee soil at field capacity (▲) and air dry (●) and to Merredin subsoil at field capacity (♦) and air dry (■).

In the nil water treatment, there was no change in pH of the Yalanbee soil, whereas the Merredin soil showed only a small increase in pH with increasing additions of plant material. The variation in soil pH with mmole of acid or alkali

added was essentially linear for all treatments (Fig. 2). Regression analysis indicated that there was no statistical improvement in the description of the curves by fitting more complex functions.

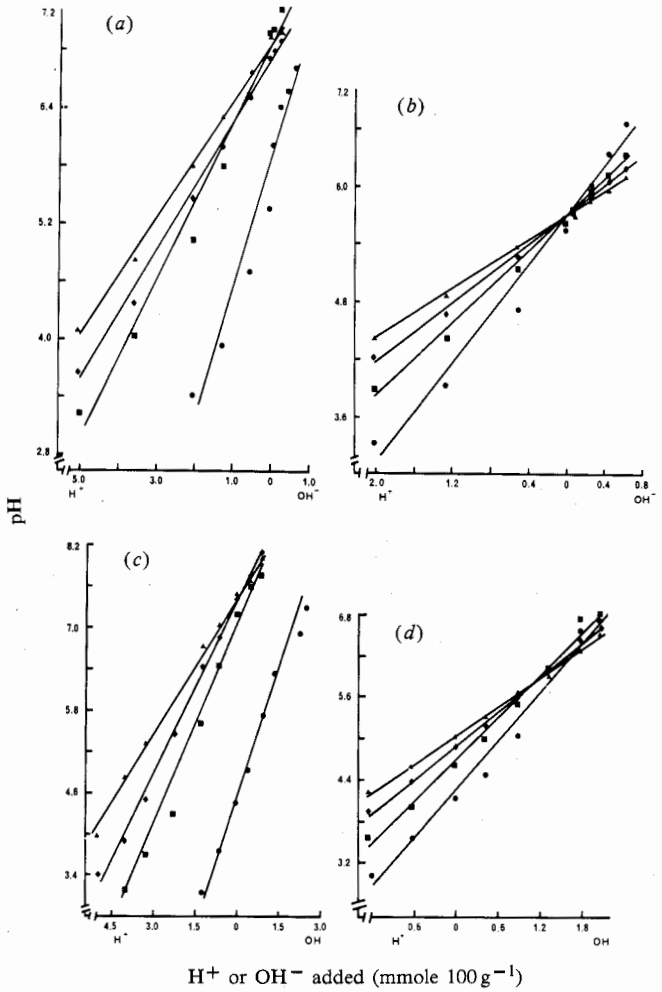

Fig. 2. Variation in soil pH with added acid or alkali (mmole 100 g^{-1}) for Yalanbee at field capacity (*a*) and air dry (*b*) with 0 (●), 2·3 (■), 4·4 (♦) and 6·5 (▲) g 100g^{-1} organic matter added; Merredin at field capacity (*c*) and air dry (*d*) with 0 (●), 2·5 (■), 5·0 (♦) and 7·2 (▲) g 100g^{-1} organic matter added.

As one might expect, the addition of plant material increased the buffer capacities of both soils, i.e. decreased the rate of change of pH per mmole of acid or base added to 100 g of soil (Fig. 2). Even though the soils did not differ markedly in their original buffer capacities, there was a slightly bigger increase in buffer capacity of the Yalanbee soil than for the Merredin soil at similar levels of organic matter addition. The water treatments did not have a significant effect on the buffer capacities of either soil.

Discussion

The results reported here illustrate that the accumulation of organic matter does not necessarily cause soil acidification.

Possible Mechanisms

Organic matter is usually considered to lower soil pH by releasing hydrogen ions that were associated with organic anions or by nitrification in an open system (Porter *et al.* 1980). On the other hand, it may cause pH increases either by mineralization of organic anions to CO_2 and water (thereby removing H^+) or because of the 'alkaline' nature of the organic material (Helyar 1976). The 'alkaline' nature of plant material arises from the dissociation of organic acids (metabolized within the plant) in response to a cation/anion imbalance caused by NH_4^+ uptake or N_2 fixation. The plant reduces this imbalance by excreting H^+ ions and so the per cent dissociation of the organic acids (i.e. the anion concentration) within the plant increases (Israel and Jackson 1978).

No net change in soil pH will be observed if the anions released by the decaying plant material are in the vicinity of the H^+ ions. In some cases, however, the anions can become separated from the H^+ by being removed in a harvest or returned to the soil surface layers rather than to the subsoil where the majority of roots originally released the H^+. pH changes would also be affected by subsequent plant growth and the type of N source available to the new crop.

The association of organic anions from the plant material with H^+ in the soil appears to be the more important process for pH changes in the systems studied here, i.e. the incorporation of imported plant material into a well-aerated soil in the absence of plant growth. The effects of mineralization (and other H^+ consuming or OH^- producing processes such as ammonia hydrolysis and nitrate reduction by microorganisms) would probably be counterbalanced by a concomitant increase in nitrification. Barrow (1960) also observed an increase in pH when soil was incubated with plant material, but attributed it to the inhibition of nitrification. In contrast to this study, however, it is not apparent that his soils were aerated during incubation.

H^+ Release by Organic Matter

The release of H^+ ions by organic mater is dependent on the initial pH of the soil and the dissociation constants (pK) of the weak organic acids (Helyar 1976). For example, if the pH of the soil is less than the pK of the weak acid groups on added organic matter, there will be an increase in pH due to association of H^+ from the soil with some of the organic anions. The acidic nature of the acid groups is usually characterized by determining a median pK at 50% dissociation, the pK_m or pK_a (Young *et al.* 1981; Stevenson 1982). However, if the organic acids are more than 50% dissociated and they are added to a soil with initial $pH < pK_m$, the magnitude of the expected pH change would be greater. If the soil $pH \approx pK_m$, the pH would rise rather than remain constant, and for soil $pH > pK_m$, the pH drop observed would be smaller than expected. Therefore, the actual per cent dissociation of organic acids (i.e. anion concentration) as they are released into the soil would be a better indicator of their ability to acidify a soil than their pK_m.

pH Changes in Air-dry Soils

The initial pH of the Merredin subsoil was approximately equal to the pK_m of the water soluble component of the added lucerne hay. However, the potentiometric properties of the plant material indicated that the organic acids were ~80% dissociated when released into the soil. Consequently, the soil pH rose as H^+ ions were removed from solution by those weak acid sites which would normally be associated at the initial soil pH. The magnitude of the change would be modified by the buffering power of the soil and the organic material itself.

The initial pH of the Yalanbee soil was greater than the pK_m of the soluble organic acids, and so one might have expected the pH to fall if the acids were 50% dissociated. In fact, there was no change in the pH of the soils upon incubation with plant material because the pH of the water extract of the plant material was approximately the same as the initial soil pH, and there was very little disturbance of the dissociation of the organic acids.

The Effect of Water Treatments on pH Changes

For both soils, the pH changes were greater at field capacity than in the air-dry water treatments. In contrast, the buffer capacity was essentially independent of the water treatments imposed. This could be because the method of measurement does not distinguish between buffering properties of the soil surfaces and the soil solution, whereas pH is a soil solution property only. Therefore, it would appear that the water soluble component of the organic material plays a major role in the pH changes.

There would be little microbial activity during the incubation of the nil water treatments due to the lack of water (Gray 1976). Therefore, the results obtained for the air-dry treatments would be approximately similar to those obtained at field capacity but with no incubation period. This is because equilibration of the weak acid groups on the plant material would occur during the pH measurement step of shaking the soil with $CaCl_2$ for 17 h. Consequently, the difference in pH between the two water treatments must be due to changes in the organic material that have occurred during incubation.

The changes in organic material with time could be explained either by microbial activity removing H^+ ions by breaking down the organic anions to CO_2 and water, further dissolution of organic anions or by reactions with soil surfaces. Parfitt *et al.* (1977) have shown that dissociated carboxyl anions of humic and fulvic acids can displace hydroxyl groups from goethite surfaces. As already discussed, the net effect on pH of microbial activity in our systems is probably negligible. Also, if mineralization was a major cause of the difference in pH increases between water treatments, then one would expect to observe a decrease in buffer capacity with time because of the removal of organic buffering materials by microbial breakdown.

The greater pH changes in the field capacity water treatments could be explained by release of more organic anions as time progresses or by their adsorption on soil surfaces.

Further release of organic anions could be a possible explanation for the difference in pH changes between water treatments for the Merredin soil but not for the Yalanbee soil. In the latter case, adsorption onto soil surfaces could have contributed to the pH increase observed. However, the rise is equivalent to a very small consumption of H^+ ions, which is 17 times less than the pH change for the Merredin soil under the same conditions.

Hoyt and Turner (1975) also observed a variation in pH with time when different organic materials were mixed with soil. Initially, the soil pH rose, but after 24 weeks' incubation the pH had nearly returned to its original value before adding organic matter. Direct comparisons with this work are not possible because they were studying an open system from which a crop of barley was harvested. However, the same trend may have been observed if longer time periods had been used.

The temporary nature of the pH changes discussed above illustrates the difficulties of monitoring pH changes in the field. It also indicates that as well as long-term changes in pH there are also short-term variations that do not necessarily reflect the overall long-term changes but may have a marked effect on plant growth.

Conclusions

Decaying plant material is less likely to contribute to soil acidification when it has a high anion concentration, and its effect on pH may vary quite widely from one soil to another and between different agricultural practices (e.g. grazing pastures versus hay production). The importance of H^+ release by organic matter may have been overestimated as a mechanism of soil acidification because the pK_m rather than the anion concentration of the organic material has been used as an indicator of the ability of organic materials to acidify soils.

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