

COMPARATIVE ASPECTS OF CYCLING OF ORGANIC C, N, S AND P THROUGH SOIL ORGANIC MATTER

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(Received January 15, 1981; accepted June 17, 1981)

ABSTRACT

McGill, W.B. and Cole, C.V., 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. *Geoderma*, 26: 267–286.

A conceptual model proposes that C and N are stabilized together and mineralized through *biological mineralization*, whereas organic P (P_o) and sulfate esters are stabilized independently of the main organic moiety and are mineralized through *biochemical mineralization*. Carbon-bonded S appears to be controlled by mechanisms similar to those for N. Biological mineralization, defined as release of inorganic forms of N and S from organic materials during oxidation of C by soil organisms to provide energy, is driven by the search for energy. Biochemical mineralization, defined as release of inorganic ions of P and S from organic form through enzymatic catalysis external to the cell membrane, is strongly controlled by the supply of and need for the element released rather than the need for energy.

Such a dichotomous system controlling both stabilization and mobilization of C and N on one hand, and of P and S on the other, should lead to converging or diverging C: P_o and N: P_o ratios during soil development, depending upon whether C or P are limiting the system. Field observations relating to the change in C:N:S:P stoichiometry in soil horizons and profiles through chrono-, climo- and toposequences have been used to examine the proposed concept.

The proposed conceptual model appears to provide a rational framework within which to interpret the interrelations of C, N, S and P over both geological and biological time scales. Data available in the literature for a wide range of soils appear to be consistent with the hypotheses flowing from the model.

INTRODUCTION

The importance of P to pedogenesis and the close relationship of organic P (P_o) content to C, N and S contents of soil was recognized early (Walker, 1964). Because C and N are added biologically and S can be absorbed from the atmosphere or enter in precipitation, Walker and Adams (1958, 1959) suggested that the P content of the parent material ultimately controlled the organic matter, N and S contents of soil. By controlling N_2 fixation, P availability to organisms could ultimately control the organic matter content of soil (Walker and Syers, 1976), as is demonstrated in data reported by

Adams and Walker (1975) and Adams et al. (1975) for a very old chronosequence in New Zealand. Organic matter and P_o accumulated and then declined as P was lost from the system by leaching. Examinations of the contents of inorganic P fractions in several chrono-, topo-, and climo-sequences of soils have helped improve understanding of soil genesis with respect to changes in soil P distribution with time, weathering intensity or stage of soil development (Smeck, 1973; Walker and Syers, 1976).

P cycles *through* soil systems on a geological time scale and as indicated above has a strong control on organic matter accretion and net loss in this time scale. In terms of cycling of elements *within* the soil-plant system, however, it is generally assumed that the immediate energy supply is the main control. Reduced C provides the main energy source within the soil system (chemolithotrophic organisms notwithstanding) for internal nutrient cycling. Unlike P, the ultimate source of C (CO_2) is not normally a limitation to soil development or elemental cycling within soil but availability of reduced C is. P strongly controls the gross dynamics of the system and C both provides an energy source to control internal cycling and is associated with N, S and P_o . Therefore, some framework within which to build an understanding of the controls on the integration of the internal cycling of these four elements is needed.

The simplest approach is to use a strict stoichiometric relationship between C, N, S and P_o . From such an approach it would follow that release of N, S, and P to the inorganic pool would occur following oxidation of C to CO_2 in ratios similar to those present in the organic component from which the C was derived. Implicit in this model is the assumption that C, N, S and P_o are stabilized together in soil by common mechanisms within a uniform stable organic component. It further implies that decomposition of stabilized material by soil organisms does not distinguish between N, S and P_o and that these elements are released from soil organisms as waste products during the search for energy which is obtained through oxidation of C to CO_2 .

An alternative model is that the mechanisms stabilizing organic C, N, S and P are not necessarily common to all four elements. From such a model it follows that any element stabilized by mechanisms different from those of other elements may accumulate at a rate independent of other elements. Further, such a model would suggest that mechanisms and pathways of mobilization are specific to the organic materials containing the various elements. An elastic system would develop with respect to cycling of C, N, S and P_o through soil organic matter. Supplies of N, S and P to plant roots from soil organic matter would not necessarily be proportional to their abundance in soil organic matter.

The purpose of this paper is first to examine the data available with regard to the nature of organic N, S and P and their modes of stabilization within soil and of mobilization or mineralization from organic form to see which of the above models may be more appropriate. A second objective is to test that model against published data on changes in contents and nature of organic C, N, S and P in soils.

BACKGROUND

Forms and stabilization

Carbon and nitrogen. Soil organic C and N are present in several distinct forms such as proteins, peptides, carbohydrates, lignin, organic acids, aromatics, lipids, some hydrocarbons, nucleic acids and amino sugars (Kononova, 1966; Bremner, 1967; Paul, 1970; Flaig, 1971; Flaig et al., 1975). The character and stability of soil organic matter cannot, however, be represented as a simple sum of the properties of these components (Minderman, 1968; Sorenson and Paul, 1971; McGill et al., 1974; McGill and Paul, 1976; Paul and McGill, 1977). Adsorption and humification help control organic C and N in soil (McGill and Paul, 1976; Jenkinson and Rayner, 1977; Paul and McGill, 1977; Anderson, 1979). Humic materials may be characterized as polydisperse, acidic, amorphous substances ranging in molecular weight from several hundred to tens of thousands with C:N ratios from 10–14 for humic acids to as high as 70 for fulvic acids (Schnitzer and Khan, 1972; Schnitzer, 1978). Humic materials are generally considered to form from condensation and polymerization reactions, primarily between phenolics or quinones and amino acids or peptides (Ladd and Butler, 1975; Haider et al., 1975; Duchaufour, 1976). Stability in soil is due to chemical recalcitrance, heterogeneity of components available for attack, physical protection, interaction with polyvalent cations and adsorption to soil inorganic colloids (Ladd and Butler, 1975; Jenkinson and Rayner, 1977; Anderson, 1979; McGill et al., 1981). A close correspondence has been shown between cycling of C and N both through soil organic matter (McGill et al., 1975).

Sulfur. The literature on organic S has been reviewed by Freney (1967), Biederbeck (1978) and Fitzgerald (1978). In most non-saline soils organic S accounts for 90% or more of the total S. Although a great diversity of compounds containing S is present in soil, two broad groups of compounds can be distinguished in HI-reducible S and C-bonded S. HI-reducible S is generally considered to be mainly sulfate esters (C—O—S) and sulfamates (C—N—S) with ester sulfates predominating (Fitzgerald, 1978). These two groupings are of significance because S bonded directly to C is likely to be incorporated into humic materials as components of amino acids etc., whereas sulfate esters may not.

Sulfhydryl groups are considered important in imparting three-dimensional structure to proteins, and S-containing amino acids are likely to have a similar effect when incorporated into humic acids. Humic acids contain 0.1–1.5% S by weight (Schnitzer and Khan, 1972; Schnitzer, 1978), and it is likely that much of it derives from C-bonded forms.

Sulfate esters may be less likely to become covalently incorporated into humic materials. Although HI-reducible S can be found in humic acids (Freney et al., 1969; Bettany et al., 1980) there is no conclusive evidence that these materials are intimately associated with the humic component. Indeed, Bettany et al. (1980) suggest they are restricted to the periphery of the

materials extracted, and Freney et al. (1971) found that most of the organic S extracted by potassium phosphate at pH 7 was in HI-reducible form. Houghton and Rose (1976) reported that sulfate esters (^{35}S labelled) and SO_4^{2-} were adsorbed to the same extent in two Welsh soils and in a third sulfate ester adsorption was about 75% that of SO_4^{2-} . Data of Scott and Anderson (1976) further suggest a dichotomy between C-bonded and HI-reducible S. Organic sulfate was correlated with C and N content of acid soils but not of calcareous soils, whereas C-bonded S was strongly correlated with C and N content of all soils. C-bonded S was also more strongly correlated with C and N than was organic sulfate. Changes in the proportion of organic S present in HI-reducible forms may occur throughout the soil profile. HI-reducible S has often been shown to form an increasing proportion of the organic S with increasing depth down the profile (Lowe, 1965; Tabatabai and Bremner, 1972; Williams, 1975). Some data summarized by Williams (1975), however, show no change in proportions down the profile. Fitzgerald (1978) concludes that a significant portion of the HI-reducible fraction is likely not an integral part of the humic component. A distinction between HI-reducible S and C-bonded S in terms of mode of stabilization and behaviour in soil appears necessary.

Phosphorus. Barrow (1961), Anderson (1967), Hayman (1975), Halstead and McKercher (1975), Dalal (1977) and Kowalenko (1978) have reviewed the literature on soil organic P. Barrow (1961) presents an excellent review of C:N:P ratios up to that time and Kowalenko (1978) has provided a summary of C:N:S:P ratios for soils since 1961. Barrow (1961) points out the rather poor relationship between C and N mineralization on one hand and P mineralization on the other. Williams et al. (1960) observed: "The correlations of organic phosphorus with carbon and nitrogen are much lower than for sulphur, and it appears to be a less integral part of the organic matter." Sekhon and Black (1969) suggest that P differs from N in that soluble P_o declines in cropped soil and cropping causes a greater decline in extractable P_o than does incubation in the absence of a plant. The C: P_o ratio has also been related to the availability of inorganic phosphorus (P_i) or the quantity of "extractable" P (Nye and Bertheux, 1957; Hawkins and Kunze, 1965). Normally, high C: P_o ratios (200 or more) are associated with soils "deficient" in P, whereas soils well supplied with available P or on which there is no yield response to added P have C: P_o ratios which are generally <100 . In summarizing data on the effect of P supply on C: P_o ratio Barrow (1961) concludes: "They suggest that neither the rate of addition of organic materials nor the P content of those organic materials has much effect on the P content of the soil organic matter. They therefore imply the existence of some other powerful determinants." Data reported by Nye and Bertheux (1957) further indicate that N and P_o are rather independent in the savannah soils they examined. They observed that although the C:N ratio dropped on cultivation of soils following tall grass "rest" of 10 years or more from 15.0 to 11.5, the C: P_o ratio was rather constant or increased slightly from 215 in the tall grass to 242 after cultivation.

To date only about 50–70% of the P_o in soil has been identified, all of

which has been present as phosphate esters (C—O—P). Although the possibility of a significant polyphosphate component and of compounds having P—C, P—N and P—S linkages cannot be eliminated, ester phosphates can continue to be considered the dominant form of P_o in soils.

Stabilization of P_o in soils has traditionally been assumed to be through incorporation into humic materials. Experimental data to support this assumption or that test it are rare. As with sulfate esters, P_o is extracted by reagents that remove humic acids from soil (Swift and Posner, 1972). The ready dispersion of P_o suggests, however, that it is not necessarily intimately associated with and stabilized as a constituent of humic materials (Dalal, 1977). In a detailed study of several soils Scott and Anderson (1976) concluded that P_o was not an integral part of the soil organic matter as was S. In their study, organic sulfate was significantly correlated with P_o but C-bonded S was not. In fact, organic sulfate was about as well correlated with P_o in acid soils as with carbon. Stability of P_o in soil may therefore be due more to the phosphate group than to the C moiety. The phosphate group in organic P molecules can be very accessible for adsorption to, or reaction with, soil inorganic components. Anderson et al. (1974) showed that inositol hexaphosphate (IHP) competed with inorganic P (P_i) for adsorption sites on all six soil samples examined. IHP was completely removed from solution at low concentrations (although still higher than occur naturally). Soil inositol phosphate contents were significantly correlated ($r = 0.91$) with acid oxalate-soluble Fe but not with organic C. They concluded that sorption would completely remove all IHP from the soil solution thus preventing its decomposition. Phospholipids may also react this way in soil. In marine sediments, phospholipids are adsorbed through the phosphate group to minerals leaving the lipid component projecting into the surrounding water (E.T. Degens, pers. comm., 1980). The observations that P_o contents of soils are closely related to phosphate sorbing power of soils (Williams, 1959) further support the hypothesis that the phosphate group rather than the C moiety is responsible for much of the stability of P_o . Consistent with this are observations that P association with organics increases rather than decreases mobility of P in soils (Rolston et al., 1975) and that half or more of the P in soil solution is organic (Dalal, 1977). The observation that P_o is more variable in soil organic matter than are N and S (Dalal, 1977) further suggests that P_o may be stabilized by mechanisms other than those stabilizing organic matter in general.

Mobilization in soil

Carbon and nitrogen. Cycling of C and N within soil organic matter have been shown to be closely linked (McGill et al., 1975; McGill et al., 1980). Mineralization or mobilization of N and of C—S occurs as the C to which they are attached is oxidized to CO_2 . This process occurs internally and is strictly catabolic. Substrates most readily used for catabolism tend to be those capable of producing the highest yield of adenosine triphosphate (ATP) and catabolic

intermediates with the lowest expenditure of energy and resources for synthesis of new catabolic enzymes. Synthesis of new catabolic enzymes is controlled by the supply of intermediates available. This control mechanism was first termed "catabolite repression" by Magasanik (1961) to explain the old phenomenon called the glucose effect. Therefore, N mineralization and mineralization of C-bonded S will occur only when soil organisms are required to use N- or S-rich materials as an energy substrate. Inhibition of amino acid deaminases by glucose has been long documented (Epps and Gale, 1942). Extracellular protease production is subject to amino acid and catabolite repression in some bacteria (Glenn, 1976). Consequently, it is primarily the need for C rather than the need for N that causes N mineralization. Similar controls should apply to S mineralization from C-bonded S.

Sulfur. Mobilization of S from ester sulfate occurs either intracellularly or in the periplasmic space, depending on the organism and substrate, but the periplasmic space appears to be the main location of the sulfohydrolases involved (Dodgson and Rose, 1975; Fitzgerald, 1978). Sulfohydrolases are present in soil (Tabatabai and Bremner, 1970; Houghton and Rose, 1975). Their formation is repressed in pure systems by sulfate, sulfite, methionine, cystine and cysteine (Dodgson and Rose, 1975). Consequently, available supplies of C-bonded S could repress their formation in soil (Fitzgerald, 1978). They are also subject to end product inhibition by SO_4^{2-} which may further control their activity in soil. Cooper (1972) reported inhibition of sulfatase by added SO_4^{2-} and a reduction by added SO_4^{2-} of S mineralization during drying in Nigerian soils. It seems likely that sulfohydrolase release of SO_4^{2-} from ester sulfate is also controlled by the need for S and not strictly by the need for C as occurs with N. Dodgson and Rose (1975) conclude that: "Studies on the production of arylsulfohydrolase activity in microorganisms provide strong evidence that the appearance of the enzymes in fungi and bacteria is a reflection of the need to acquire sulfate for growth purposes. Expressed in the most simple terms, in times of sulfur sufficiency it seems probable that the presence of sulfate or sulfur-containing intermediates on the pathway to cysteine are sufficient to repress bacterial arylsulfohydrolases."

A similar conclusion was reached regarding glycerosulfohydrolases in microorganisms (Fitzgerald, 1978). Sulfate ester production may also be a mechanism used by soil microbes to store S without altering the pH of their surroundings (Fitzgerald, 1978). This is consistent with results reported by Freney et al. (1975) using $^{35}\text{SO}_4$ added to soil in which 73% and 57% were incorporated into HI-reducible forms in two soils and the plants derived all their labelled S from this fraction.

Kowalenko and Lowe (1975) found that the relative amounts of N and S mineralized from four Canadian soils could not be predicted using ratios of C:N, C:S, N:S, H:HI-S or N:C-bonded S. They concluded: "Although microbial mineralization of soil sulfur was closely related to mineralization of soil C and nitrogen, it did not parallel these elements."

A dual mechanism system for S but not N mineralization helps explaining why results summarized by Biederbeck (1978) show no consistent relation between N and S mineralization.

Phosphorus. Mobilization of P from phosphate esters by phosphohydrolases is subject to both end product inhibition and repression (Feder, 1973). The addition of glucose and $(\text{NH}_4)_2\text{SO}_4$ increased soil acid phosphatase activity up to six-fold in the absence of added P (Spiers and McGill, 1979), but in the presence of added P, phosphatase production was completely repressed. Those authors concluded that the effects of phosphate on phosphatase operated more through its effect on enzyme synthesis than on activity of pre-existing stabilized enzyme.

The origin of phosphatases may be soil microbes, mycorrhizae or the roots themselves but the major source has not yet been identified (Hayman and Mosse, 1972; Bowen, 1973; MacDonald and Lewis, 1978; Gould et al., 1979). Phosphohydrolases are released by plant roots (Rogers et al., 1942) with the amount of activity apparently related to the need for P (Kuprevich and Shcherbakova, 1971). Phosphorus-deficiency of roots of *Spirodela oligorrhiza* increased their phosphohydrolase activity by 4–5 fold (Bielecki and Johnson, 1972). Similarly mycorrhizal phosphohydrolase activity is sensitive to phosphate with enzyme production derepressed in the absence of phosphorus (Dalal, 1977). Phosphohydrolase activity cannot influence uptake by plants if P_o in the vicinity of the root is too low (Bielecki, 1973; Martin, 1973). Either P_o must be in abundance in the soil solution in the vicinity of the plant root or the enzyme and its product must diffuse significant distances. Such diffusion is likely to be slow.

Depletion of soluble P_o during plant growth is indicated by data of Sekhon and Black (1969), suggesting a possible contribution of P_o to the P nutrition of the crop. Saunders and Metson (1971) found considerable P uptake by grasses during the spring flush of growth in New Zealand, poor response to added P and no prior build-up of "available" P. They concluded that the level of available P was the net balance between uptake by plants and supply from the P_o component. Dormaar (1972) working with alfalfa plots in Alberta observed a consistent annual loss of organic P during the period of rapid plant growth in the spring, following a gradual over-winter accumulation of P_o . Furthermore, addition of fertilizer P either prevented loss of P_o or increased P_o . Finally, Neal (1973) demonstrated that invader species of plants from Alberta grown in pots nearly doubled soil phosphatase activity over the control. The results of pure culture studies, soil incubation studies and field investigations suggest that phosphohydrolases are produced in response to need for P and are repressed by an adequate supply of P.

Lack of consistent relationships between accumulations of available P or S and phosphatase or sulfatase activities cannot be interpreted as lack of a role for these enzymes, because they are controlled by end product inhibition and repression by phosphate (Spiers and McGill, 1979) and sulfate (Fitzgerald, 1978), respectively. As with sulfate esters (Fitzgerald, 1978) cleavage

of the phosphate ester may require initial depolymerization if the P_o is present in large polymers.

An integrating concept

It would appear that patterns of cycling of C, N, S and P within soil humus can best be interpreted within the framework of a dichotomous system in which elements considered to be stabilized as a result of direct association with C (N and C-bonded S) are mineralized as a result of C oxidation to provide energy, whereas those elements existing as esters may be viewed as being stabilized through reactions of esters with soil components and may be considered to be mobilized by extracellular or periplasmic hydrolases, controlled by end product supply. The former is the classical biological mineralization process. The latter we have termed biochemical mineralization because it operates largely outside the cell membrane and is controlled by supply of the end product.

Such a model implies that separate controls may regulate individual elements or types of organics although they are all eventually interrelated and integrated within organisms. It follows that soil organisms including plant roots may preferentially hydrolyse HI-reducible S and P_o compounds if they have a need for those specific elements. C-bonded S would accumulate and diminish according to microbial need for C. Supply of S to plants from this source would then be strictly dependent upon a microbial vector. Supply of S to plants from sulfate esters would not necessarily require a microbial intermediate. This leads then to the possibility of an elastic system, with variability in C:N:S: P_o ratios and the variability greater for P_o than for S. Three concen-

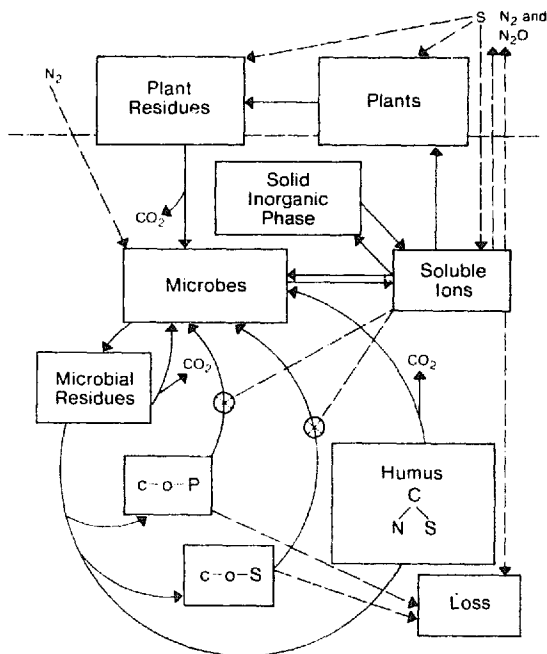


Fig. 1. Schematic illustration of interrelations of C, N, S and P cycling within soil-plant systems.

tric cycles could be envisaged if this model generalizes the system fairly (Fig. 1). It should be possible for P to "short-circuit" the cycle and for sulfate esters to do likewise if there is a need for P or S, respectively. In the absence of P or S stress, these materials should continue to accumulate organic matter beyond the point where P_o ceases to accumulate. In times of soil degradation caused by C loss, P_o and to some degree C—O—S should be lost less rapidly than C and N. In times of soil deterioration due to S loss or P loss, the losses of C and N should be less rapid than loss of P_o or C—O—S. Additionally, ratios of HI-reducible S:C-bonded S should diminish in severely S-restricted systems. The ratio of N:S should change inversely to the change in ratio of HI-reducible S:C-bonded S in soil sequences.

The above outcomes from the proposed conceptual model can be used in comparison with field observations on soil chrono-, climo- and topo-sequences to evaluate the underlying concepts and their expression in soil characteristics.

Field observations

In an aggrading system, (applied here to a soil system characterized by organic matter accumulation over time) a point is eventually reached where the amount of organic matter reaches a steady state due to equal input and output. An aggrading sequence of soils as used here refers to a sequence created by climatic or topographical gradients in which, at steady state, each successive member of the sequence has more organic matter, organic-P, -S, or -N than the preceding member, usually due to greater additions than removals. If the above concepts concerning mobilization and stabilization mechanisms and controls are correct, P_o may continue to accumulate while P_i is still readily available. In such a situation, C: P_o and N: P_o ratios should decline with time or throughout an aggrading sequence as C and N accumulation rates slow more than the P_o accumulation rate. C:N ratio should change less than N:P or C:P. Such a situation is found in a climosequence of soils in Alberta (Dormaer and Webster, 1963) and in New Zealand (Martin, 1970) (Table I). The sequence of Canadian soils from Brown through Black can be considered an aggrading sequence. Each individual soil is expected to be close to steady state with respect to organic matter content.

In some systems of the Great Plains, weathering intensity may increase with increasing moisture and temperature (Westin and Buntley, 1967; Smeck and Runge, 1971). Although C inputs increase, total C content may remain relatively constant or even decline slightly due to more rapid decomposition. In such situations P_o could continue to accumulate with increased development even if C content did not. This would require that: (1) P_i remain available or that P be added to the system; and (2) that P_o be stabilized somewhat independently of C. Such conditions appear to be reflected by the trends in the data in Table II for soil sequences in South Dakota and Illinois.

With increasing time and weathering intensity, P loss from a system may become significant. Increasing demand on P_o will prevent or slow its further accumulation due to a decreasing contribution from P_i . In such a situation

TABLE I

Surface horizons in the aggrading phase as indicated by increasing $P_o:P_i$ ratios (Walker and Adams, 1958, 1959); decreasing $N:P_o$ and $C:P_o$ ratios as P_o continues to accumulate more rapidly than C and N with increased leaching and weathering along the two climosequences

	% C	$P_o:P_i$	$N:P_o$	$C:P_o$	Soil	Reference
Alberia ↓ Increased leaching	3.3	0.47	14	203	Chin L(Ah)* ¹ (Brown)* ²	Dormaer and Webster, 1963
	4.3	0.59	11	170	Lethbridge SL(Ah) (DK Brown)	Dormaer and Webster, 1963
	5.9	0.75	10	135	Airdrie L(Ah) (Thin Black)	Dormaer and Webster, 1963
	7.9	1.0	10	129	Antler L(Ah) (Black)	Dormaer and Webster, 1963
New Zealand ↓ Increased weathering	2.4	0.81	7.0	77.5	Conroy (A)	Martin, 1970
	2.7	1.1	5.5	66.3	Carrick (A)	Martin, 1970
	2.3	2.5	5.5	66.7	Obelisk (A)	Martin, 1970

*¹ Horizon as designated in original paper.

*² Soil zone.

TABLE II

Two examples of increasing intensity of profile development associated with either constant or decreasing C content and either constant or increasing P_o content

	Total P (ppm)	Organic C (%)	$P_o:P_i$	P_o (ppm)	$N:P_o$	$C:P_o$
Increasing rainfall and temperature in transect through Borolls to Ustolls in South Dakota Ap horizons (Westin and Buntley, 1967).						
Borolls (8)* ¹	566 ± 74* ²	3.22 ± 0.29	1.15	300 ± 55	10.4 ± 1.9	110 ± 20
Ustolls (8)	594 ± 60	2.65 ± 0.36	1.16	322 ± 56	7.9 ± 1.1	83 ± 12
	Total P (g m ⁻²) to 50 cm	Organic C (g m ⁻²) to 50 cm	$P_o:P_i$	P_o (g m ⁻²) to 50 cm	$N:P_o$	$C:P_o$
Along a 43 m transect in Illinois crossing from the least developed (6) to the most developed (1) profiles; profiles 1 and 2 have gained P while profiles 5 and 6 have lost P (Smeck and Runge, 1971)						
<i>Typic Haplaquolls</i>						
6	231	11,510	0.62	88.2	—	131
5	227	10,542	0.42	67.5	—	156
<i>Mollic Albaqualfs</i>						
2	320	7,624	0.40	92.2	—	83
1	317	7,947	0.45	97.7	—	81

*¹ Number of profiles.

*² Standard deviation.

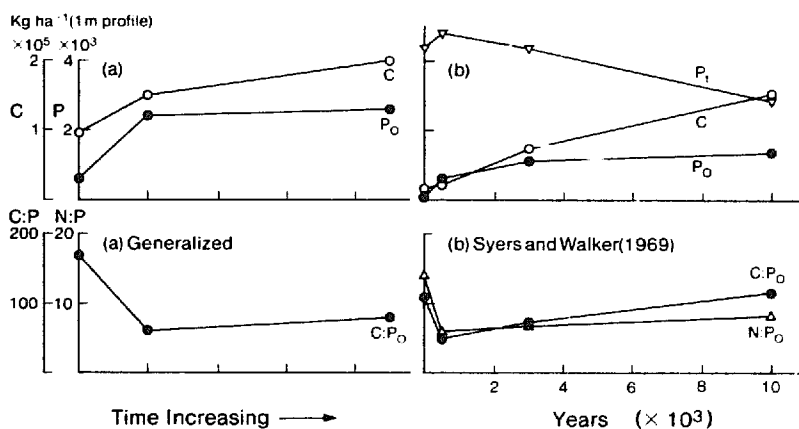


Fig. 2. Generalized (a) and observed (b) C, P_t and P_0 contents of soil indicating increasing C:P₀ and N:P₀ ratios when P stress increases due to P_t loss from the system. Data of Syers and Walker (1969) are for 1 modal profile at each stage.

C and N may continue to accumulate if P_0 can be recycled fast enough to meet the needs for N_2 fixation. Consequently, P controls this system rather than the production rate of organic matter as in the previous examples. Therefore, C:P₀ and N:P₀ ratios should decline during the aggrading phase and then increase during the degrading or climax phase of the sequence. Data of Syers and Walker (1969) from a chronosequence of soils on wind-blown sand in New Zealand demonstrate this trend (Fig. 2). Although P_0 has not started to decline, it has leveled off and the decline in total P is substantial. Under such conditions demand for internal cycling of P_0 to meet the needs for P increases. Hydrolysis of P_0 would then be expected to occur more frequently thus slowing P_0 accumulation more than that of C and N.

When continued long enough, definite degradation of the system through substantial P loss occurs (Walker and Syers, 1976). In such a situation, C and N should be retained longer than P_0 , according to the current hypothesis, because they can be stabilized independently of P_0 , and the stress on the system is for P_0 rather than for C. In such a sequence, there should be a progressive increase in C:P₀ and N:P₀ ratios. Data of Adams and Walker (1975) and of Adams et al. (1975) (Table III) exhibit this trend and provide a test of the validity of the model on an extreme weathering sequence. Data from the tropics where P leaching is severe (Dahnke et al., 1964; Westin and DeBrito, 1969) are also consistent with the proposed model (Table IV).

A bell-shaped curve should be evident with respect to C:P₀ and N:P₀ ratios as one proceeds through climosequences from immature aggrading systems (such as Brown Chernozemic — in the Canadian Soil Classification System) through the climax with respect to C content (Black Chernozemic) to degrading systems such as Dark Grey soils. Such a trend is apparent in data of Dormaar and Webster (1963) (Fig. 3). This trend can be extended to also include N:S:P relations. In situations where S is added abundantly it should be possible to store it as C—O—S, allowing S to accumulate faster than N. Consequently,

TABLE III

Loss of C and N from systems experiencing severe P stress due to P loss from the system; C:P_o and N:P_o ratios increase with a reduction in P_o:P_i ratio with increasing time in the chronosequence

Profile	Pt* ¹	C × 10 ³ * ²	P _o :P _i * ³	C:P _o	N:P _o	C:N	
	(kg ha ⁻¹ ; 56 cm)						
← Increasing age	G1	2640	100	0.17	260	11	25
	G2	1725	157	0.35	350	14	26
	G3	1025	86	0.31	360	16	23
	G4* ⁴	1150	56	1.13	92	4	23
	G5	495	63	0.06	2300	108	22

*¹ Estimated from fig. 1 of Adams and Walker (1975).

*² C and N estimated from fig. 4 of Adams et al. (1975).

*³ P_o estimated from fig. 1 of Adams and Walker (1975).

*⁴ Profile G4 appears to have an anomalous buildup of Pt (125 kg ha⁻¹) as P_o which is 250% that in G3 and higher than in any member of the sequence. G4 can not be considered to fit in position 4 of a sequence representing continuous P loss throughout the sequence. The origin of the extra P is uncertain. The only other horizons having a P_o:P_i ratio similar to that in surface of G4 (1.39) are the 150 cm depth of G4 and the 180 cm depth of G5.

TABLE IV

Decreasing total P during soil development in Latin America; due to P limitation, ratios of C:P_o tend to increase during soil development

Reference and degree of weathering	Total P (ppm)	Total C (%)	P _o as % of total	P _o (ppm)	C:P _o
<i>Westin and DeBrito (1969) Venezuela</i>					
Weak (6)* ¹	335 ± 203	1.09 ± 0.5	36	118 ± 81	92
Moderate (8)	151 ± 69	0.99 ± 0.3	44	71 ± 50	145
Strong (4)	129 ± 114	1.19 ± 1.2	30	48 ± 51	248
<i>Dahnke et al. (1964) El Salvador</i>					
Moderate (4) (308-1177)* ²	936 ± 174	4.32 ± 2.8	13	117 ± 28	369
Strong (7) (79-196)	597 ± 254	3.41 ± 1.9	14	82 ± 38	416
Very strong (5) (48-71)	352 ± 162	2.79 ± 1.3	9	31 ± 17	900

*¹ Number of profiles.

*² CEC × 100/% clay in A1 horizon calculated from Dahnke et al. (1964) and used as an approximate index of degree of weathering. Normally B2 horizons are used to avoid organic matter interference in CEC but A1 horizons were all that were consistently available here. See Van Wambeke (1967).

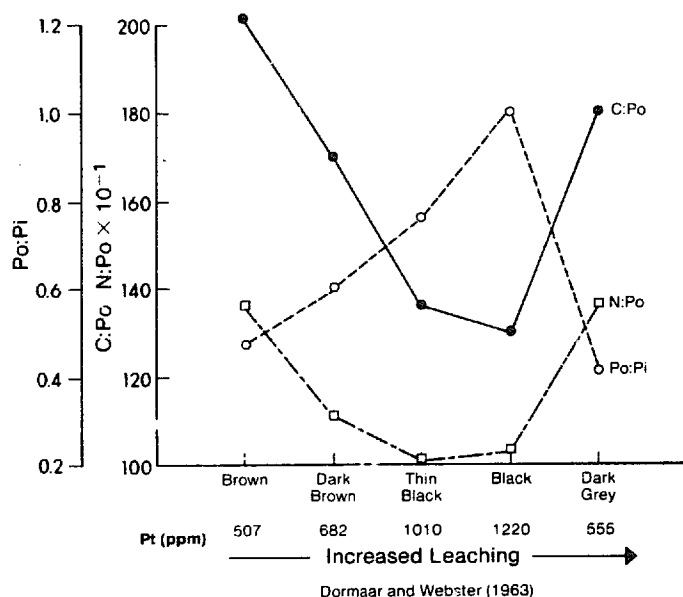


Fig. 3. Changes in C:P_o and N:P_o ratios of Ah horizons of a climosequence of soils through the aggrading phase with decreasing ratios, to the degrading phase with increasing ratios.

N and S would not be stoichiometric. The P limitation of such a system would also cause S and P not to be stoichiometric because phosphate esters would be hydrolyzed, whereas sulfate esters would not be. Such a system is summarized for comparison in Fig. 4 together with data of Walker and Adams (1959).

Consistent with the concept of different mechanisms controlling C and N stabilization and mobilization on one hand, and P_o cycling on the other, are data from drainage sequence studies (Fig. 5; Table V). P availability tends to decrease under poor drainage. This reduction may be attributed in part to reduction of ferric oxides which fix P. Should this occur, a greater need to rely on recycling of P_o would result, thus preventing accumulation of P_o. No analogous mechanism prevents N accumulation. Consequently the ratios of N:P_o or C:P_o increase markedly in moving toward the wet end of soil hydrosequences as P_o:P_i ratios decrease and total phosphorus (Pt) may either remain constant or decrease. N:P_o ratios are used in Fig. 5 to eliminate bias caused by changes in degree of decomposition and consequent C:N ratios of organic matter associated with drainage.

Ratios of N:S should be inversely proportional to ratios of HI-reducible S:C-bonded S because of the closer link between N and C-bonded S than C—O—S. This is shown in Fig. 6 with data from a climo-sequence of cultivated soils in Saskatchewan (Bettany et al., 1973, 1979) and virgin soils in Alberta (Dormaer and Webster, 1963). Further, in S-deficient soils (example, Grey Luvisolic soils) the ratio of HI-reducible S:C-bonded S should drop dramatically due to rapid re-utilization of sulfate esters under S stress conditions and the weak association of sulfate esters with the remainder of the humic component. This is evident in Fig. 6.

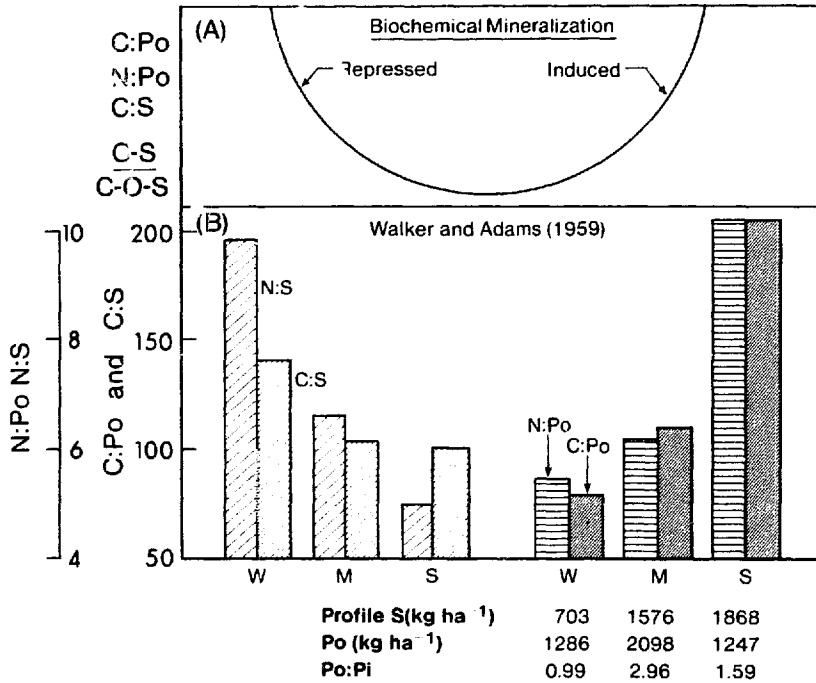


Fig. 4. Generalized (A) and observed (B) independent changes in organic N, S and P contents of soil organic matter in response to availability of the various elements. The observed data demonstrate independent changes of S and of P with respect to C and N in a weathering sequence from weak (W) through moderate (M) to strongly (S) weathered soils developed from graywacke in New Zealand.

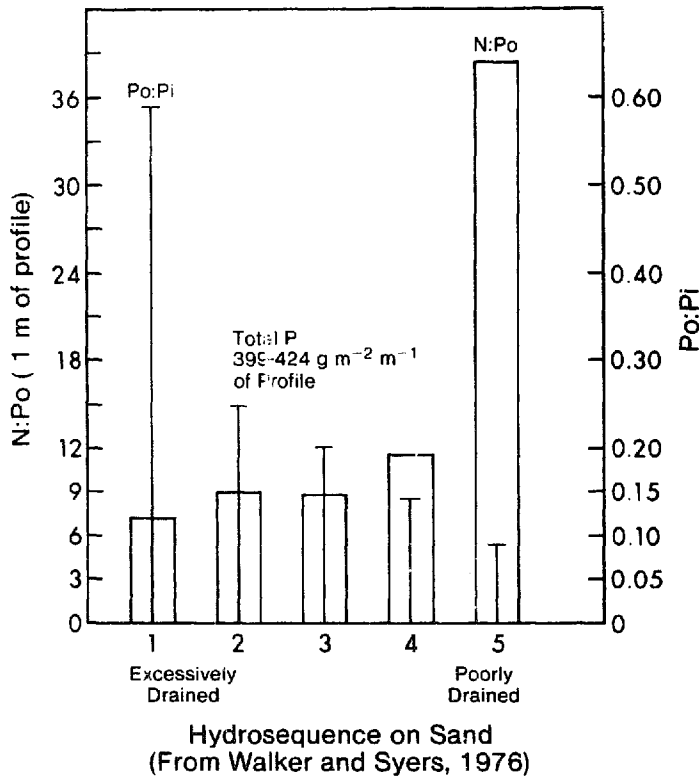


TABLE V

Changes in characteristics of organic P associated with changes in drainage in soil hydrosequences in Iowa (from Runge and Riecken, 1966)

	A1p horizons		
	moderate-well drained	imperfectly drained	poorly drained
Pt (ppm)	642	662	581
$P_o:P_i$	1.00	1.22	0.68
C:P _o	66	73	119

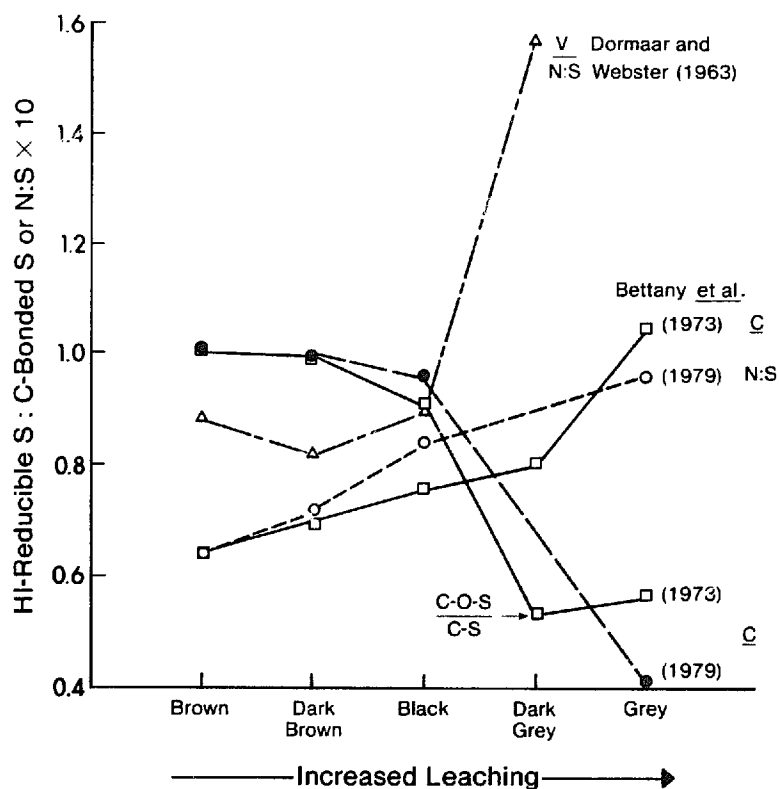


Fig. 6. Inverse relationship between change in N:S ratio and that of C—O—S:C—S through a climosequence of cultivated soils (C) in Saskatchewan. From Bettany et al. (1973, 1979). Data for virgin (V) soil over the same climosequence in Alberta, calculated from Dormaar and Webster (1963). The N:S ratios for the virgin soils is higher than for the cultivated soils. This is consistent with data presented by Bettany et al. (1980) (see text).

Fig. 5. Inverse relationship between change in $P_o:P_i$ ratio and change in N:P_o ratio in a soil hydrosequence in New Zealand.

Lee and Speir (1979) concluded that in their pot trials with ryegrass, C-bonded S was not closely correlated with plant uptake of organic S. Their data suggest that C-bonded S is less important than ester-S in supplying immediate plant needs. The proposed model is not totally consistent with these data, however, because those authors reported that ester-S was more closely correlated with soil N than was C-bonded S.

Relations between N and S can be further tested using soil fractions. According to the suggested hypothesis, soil fractions having low N:S ratios should tend to have higher HI-reducible S:C-bonded S ratios than fractions with higher N:S ratios. Such is the case in the data of Bettany et al. (1979) for two of the main S containing fractions of several soils from a climosequence in Saskatchewan (Table VI). This relation, however, did not hold for some of their humin fractions.

Data of Bettany et al. (1980) further support the notion of a dichotomy between cycling of C and N on one hand, and of S on the other. They reported that N:S ratios changed from 7.9 in a virgin Udic Haploboroll soil to 6.6 in the cultivated counterpart indicating more rapid loss of N than of S. Such being the case, the proposed hypothesis would indicate that HI-reducible

TABLE VI

Inverse relationship between HI reducible S:C-bonded S ratios and N:S ratios in organic fractions of cultivated soils through a climosequence and of the same soil cropped or in pasture

Soil zone	N:S		C-O-S:C-S	
	FA-A	HA-B	FA-A	HA-B
Brown	3.5	9.0	4.6	0.85
Dark brown	3.2	9.3	7.3	0.92
Black	2.8	9.6	5.3	0.89
Grey	3.9	10.3	2.8	0.54
Pasture	4.0	8.8	1.9	1.0
Cultivated	2.6	8.2	2.7	1.3

a Calculated from Bettany et al. (1979).

b Calculated from Bettany et al. (1980).

S should not decrease as quickly as the C-bonded S which should follow N closely. This was observed. The ratio of HI-reducible S:C-bonded S calculated from the data of Bettany et al. (1980) increased from 1.05 in the virgin to 1.30 in the cultivated soil (Table VI). This trend would further suggest that S need not be a limitation to biological activity in this soil.

The above examinations of soil C, N, S and P_o changes suggest that a rational framework has been approached within which to interpret the inter-relations of these four elements over both geological and biological time

scales. The proposed conceptual model integrates C as the driving variable with P as the ultimate control on organic matter cycling and accumulation. The concept of biochemical mineralization as separate from biological mineralization and controlled by need for S or P rather than C appears to be useful and seems valid. The concept of stabilization of ester forms independently of, but not necessarily separate from, C-bonded forms also appears to help explain observed phenomena examined. Contradictory S and P mineralization and immobilisation data can now be interpreted more rationally as can effects of man on C, N, S and P cycles locally and possibly globally.

ACKNOWLEDGEMENT

Financial support of a grant from the Natural Sciences and Engineering Research Council (to W.B. McGill) is gratefully acknowledged.

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