

## CHAPTER 8

# *Interactions of Biogeochemical Cycles in Grassland Ecosystems\**

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### ABSTRACT

The key processes involved in the cycling of carbon, nitrogen, sulphur, and phosphorus are examined within the framework of the relationships among grassland ecosystem properties and driving variables. Interactions among nutrients take place in above- and below-ground primary production, in decomposition processes, and in nutrient cycling. Control of these processes through the external driving variables climate, parent materials, vegetation relief, and man's activities determine the soil properties and plant composition. Changes in ecosystem properties (C, N, S, and P quantities and flows) are discussed.

### 8.1 INTRODUCTION

In this paper we propose to examine the biology of chemical cycling of carbon, nitrogen, sulphur, and phosphorus in grassland ecosystems (rangeland and cropland). Grasslands in some form are found in every continent throughout the world (Coupland, 1979; Breymeyer and Van Dyne, 1980), usually in the areas with 25–75 cm of annual precipitation. In general, grassland soils are fertile, yielding high production of food and fibre by virtue of their accumulation of stores of nutrients in organic forms. Significant losses of C, N, S, and P have occurred under intensive cultivation of grassland soils.

Key transformation processes of these elements are examined within a framework of an ecosystem's properties and driving variables. Our conception of the relationships among (1) an ecosystem's driving variables, (2) the

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important ecosystem processes controlling organic and nutrient turnover, and (3) ecosystem structure are depicted in Figure 8.1. Driving variables are externally imposed variables little affected by the state of the ecosystem. Important ecosystem processes include above- and below-ground primary production, decomposition, and nutrient cycling. Heat and water flow play key roles through their effects on the rates of biological and chemical processes. Our general hypothesis is that the effects of driving variables (controlling factors) are realized through their influence on ecosystem processes.

Examination of changes in elemental concentrations and forms in organic matter of soils developed along environmental gradients have given insight into possible interrelationships between C, N, S, and P. Cole and Heil (1981) summarized changes in C, N, and P that documented close linkages between organic C and N in mature soils and the P content in the original parent material. They hypothesized that given sufficient time, the supply of N comes into balance with the supply of P (assuming S is not limiting) and that microbial growth processes are the principal arenas for the adjustment of N supply to P supply.

Progress in understanding the internal cycling of nutrients in the soil-plant system has been fostered by studies designed to monitor the flows of C, N, S, P, or other nutrients (Clark *et al.*, 1980). Knowledge of C flows has only limited value in postulating nutrient flow inasmuch as each nutrient has specific flows and storage compartments that must be considered individually; flows determined for C are not directly transferable to N, nor are those for N the same as those for S or P. McGill and Cole (1981) proposed that the mechanisms stabilizing organic C, N, S, and P are not necessarily common to all four elements and that the mechanisms and pathways of mobilization are specific to the organic material containing the various elements. They proposed a dichotomous system (Figure 8.2) in which N and part of the soil-S may be stabilized as a result of direct association with C (N- and C-bonded S) and may be mineralized as a result of C oxidation (classical biological mineralization) to provide energy. However, S and P, which exist as esters (C-O-S and C-O-P), may be stabilized by the action of the ester with soil components, and may be mineralized by enzymes in response to the need for a specific element. The latter process was termed biochemical mineralization, because it operates largely outside the cell and is controlled by the need for the element released. This concept accounts for the variability found in soil organic matter composition and sets the stage for predicting the relationship between N, S, and P cycling rates in soils. Because the behaviour of S is intermediate between that of N and P, a study of S transformations has proven helpful in elucidating differences found in soil organic matter quality (Saggar *et al.*, 1981a). This review will summarize information on C, N, and P, discuss S in more detail, and examine modes of interaction. In this review no consideration has been given to the redistribution of C, N, S, and P that occurs through the grazing of plant

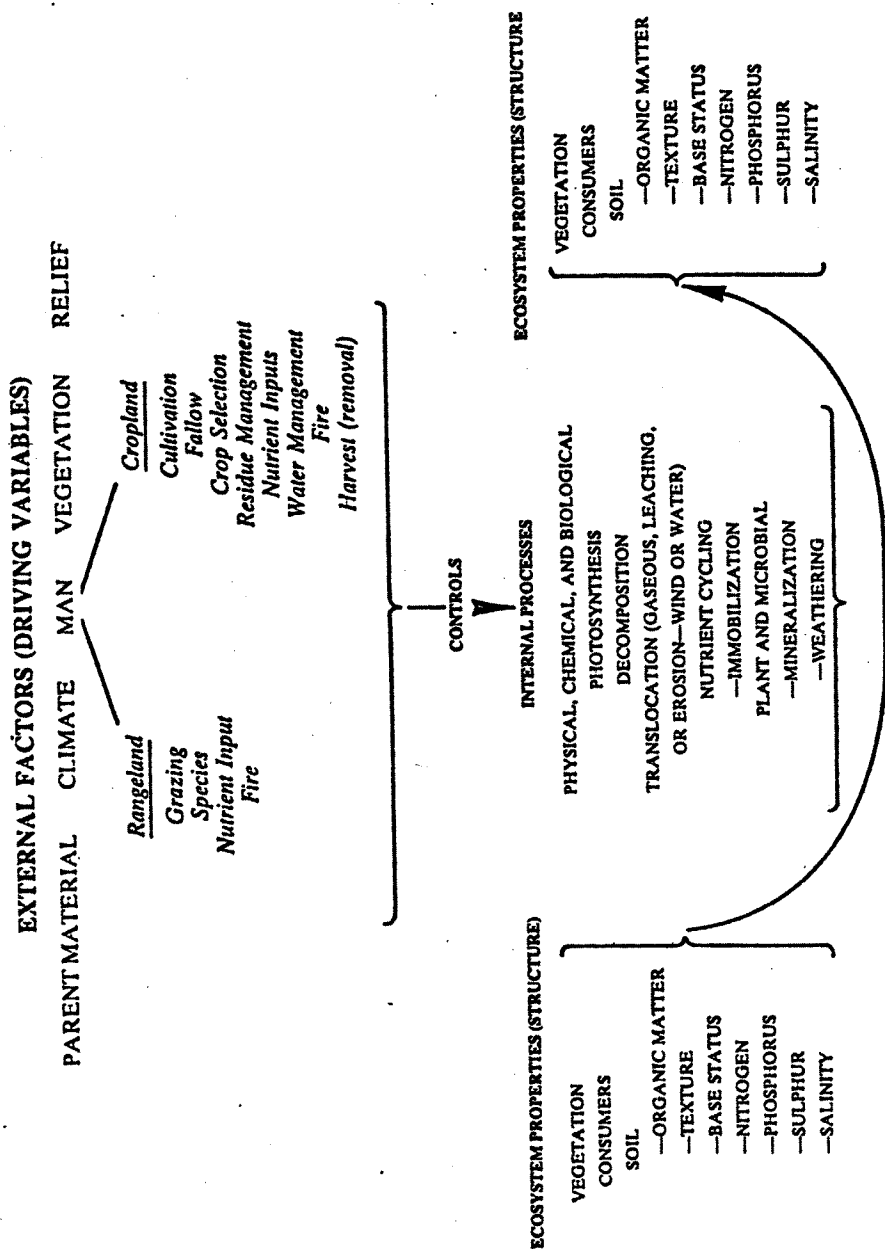


Figure 8.1 Relationships among driving variables, processes and ecosystem structure

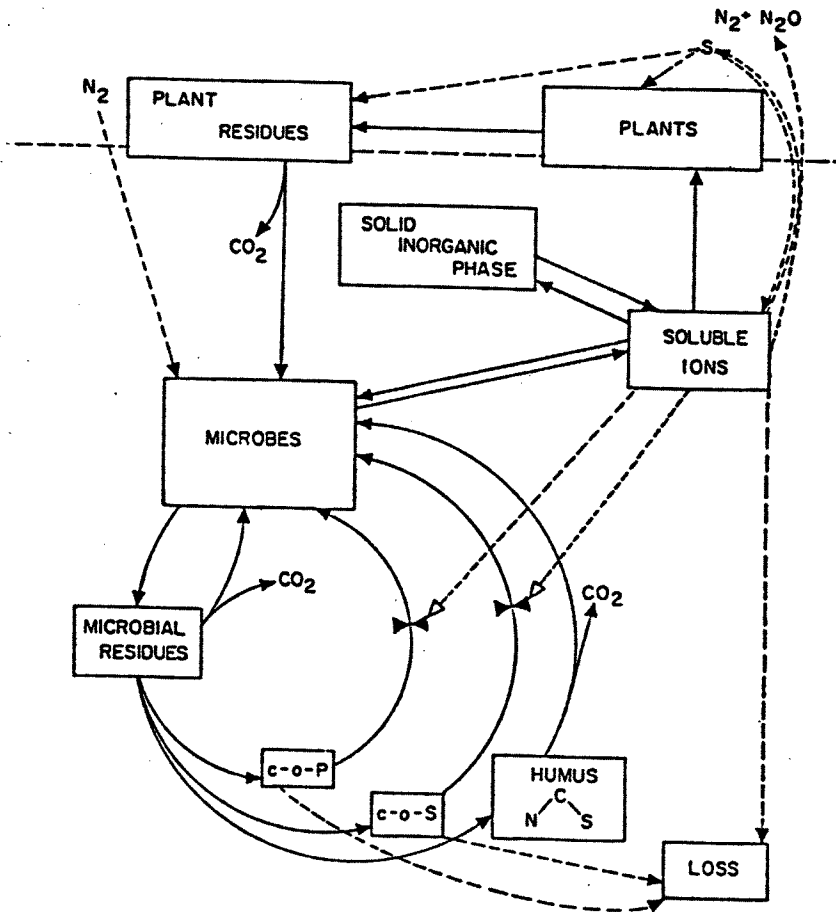


Figure 8.2 Schematic illustration of interrelationship of C, N, S, and P cycling within soil-plant systems (from McGill and Cole 1981). Reproduced by permission of Elsevier Scientific Publishing Co.

materials by large herbivores and subsequent distribution in soil. This is a deliberate omission because: a) the subject is well researched and has been the subject of other reviews (Batzli, 1978; Till, 1980; Floate, 1981); and b) in terms of net flow of nutrients within grassland ecosystems, the below-ground processes dominate.

## 8.2 DYNAMICS OF CARBON AND NITROGEN IN GRASSLAND ECOSYSTEMS

The relationship among plant processes and microbial processes and the effects of these processes on plant production, microbial secondary production, N production, and N cycling have recently been explored through simulation

modelling (McGill *et al.*, 1981). The model (Figure 8.3a, 8.3b) emphasizes the biological and biochemical soil-plant subsystem, including plants, microbes, organic residues, and mineral N. Temperature and moisture are driving variables. The mechanistic process treatments include nitrification, root uptake of inorganic N, mineralization, immobilization, and humification. Treatments of plant growth, phenology, plant response to N supply and N redistribution during growth and senescence are sufficiently mechanistic so that the primary producer submodel can provide substrates to the decomposition portion of the model. The treatments of denitrification and leaching are simplistic, and biological nitrogen fixation is included with a general atmospheric input function. Ammonia volatilization is not included, nor is non-exchangeable ammonia fixation by clays.

This model contains several concepts that were novel. A floating C:N ratio of microbes was used to link C and N cycling and control the decomposition of residues with a high C:N ratio. The model treated bacteria and fungi separately and was the first to attempt to represent two competing groups of decomposers responding somewhat differently to environment and substrate. Plant litter was separated into structural and metabolic components, thereby inferring unequal accessibility of C and N and decomposability of C and N containing molecules. This model assumed that the death of microbes was due to abiotic factors but did imply the presence of micro- and mesofauna. Mineralization and immobilization of N were concurrent and independent processes controlled by the C:N ratio of microbes. Organic matter stabilization was achieved by both humification and adsorption. Microbial decomposition of this stabilized organic matter left a residue that was more resistant to decomposition.

The concepts embodied in McGill *et al.* (1981) and in other recent reviews (Jones and Woodmansee, 1979; Clark *et al.*, 1980) have been instrumental in directing research approaches to the study of P and S.

### 8.3 DYNAMICS OF CARBON AND PHOSPHORUS IN GRASSLAND ECOSYSTEMS

The immobilization, mineralization, and redistribution of P is best discussed with reference to P cycling in soils (Cole *et al.*, 1977; Chauhan *et al.*, 1979, 1981) as represented by Figure 8.4. The main source of P in soils is from primary P minerals (mainly hydroxyapatite in North American grassland soils). This material is sparingly soluble and releases small amounts of phosphate to solution, where it enters in equilibrium with labile inorganic P ( $P_i$ ) (i.e. surface-adsorbed or precipitated as soluble calcium phosphates, such as octocalcium phosphate, that are exchangeable to  $^{32}P$  and extractable by anion-exchange resins). Secondary  $P_i$  compounds of reduced solubility and occluded forms of  $P_i$  may also be present, especially in more weathered soils.

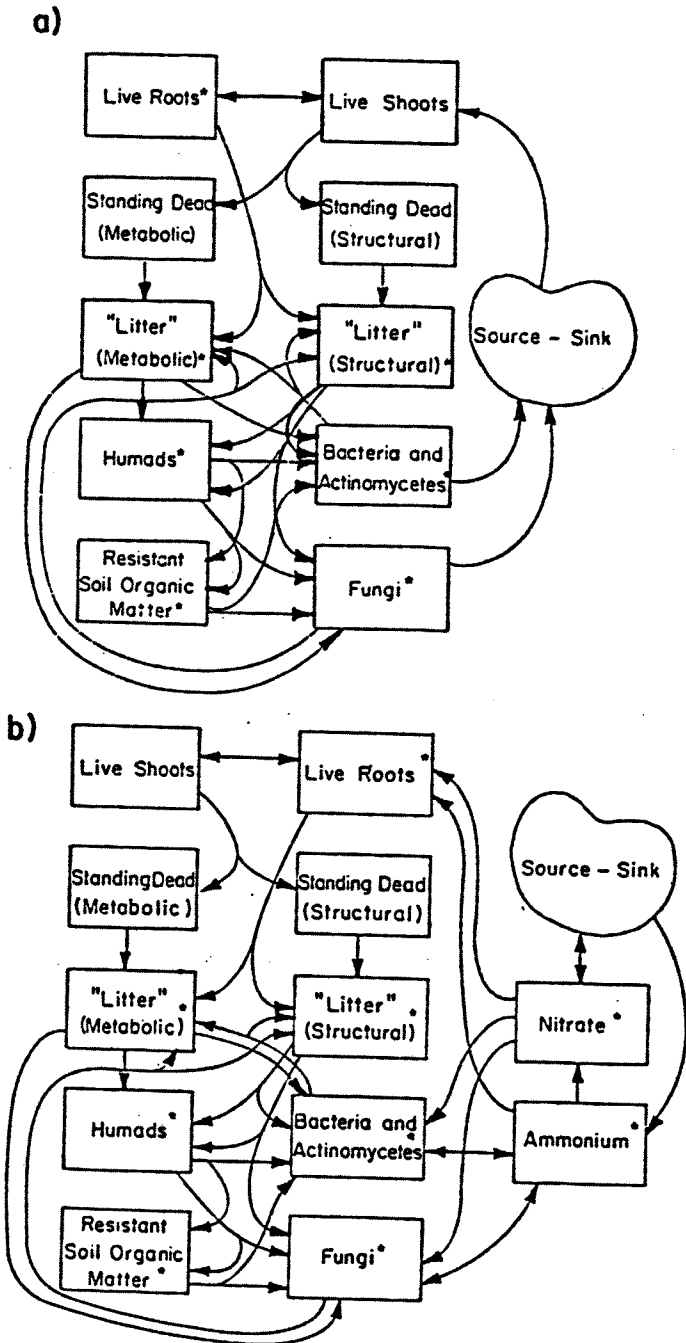


Figure 8.3 Compartment design for (a) C and (b) N flows. The asterisk indicates state variables replicated by depth (0-2, 2-6, 6-14, 14-30 cm) (from McGill *et al.*, 1981). Reproduced by permission of Swedish Natural Science Research Council

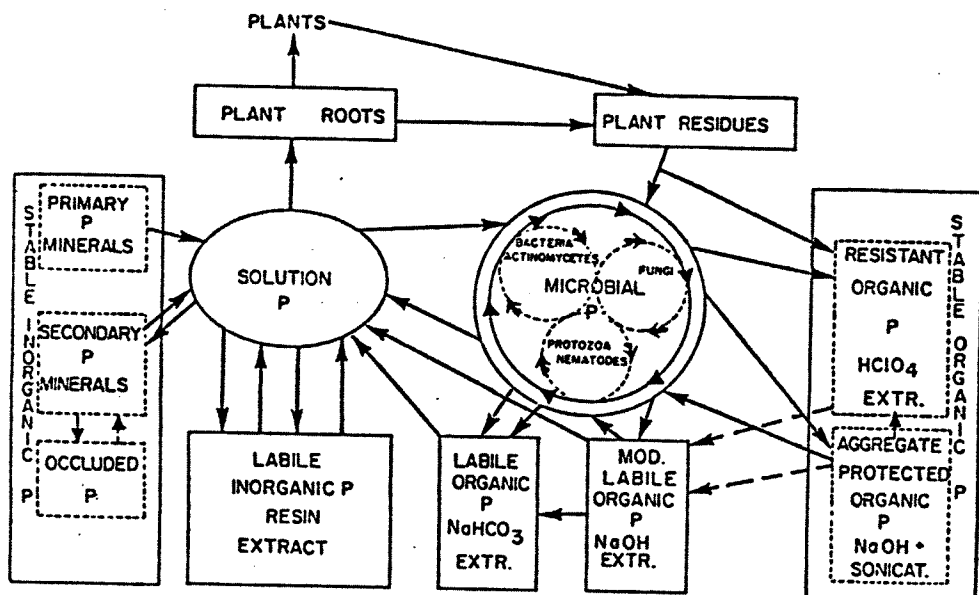


Figure 8.4 Compartments and flows of P in the P cycle (Chauhan *et al.*, 1981). Reproduced by permission of Agricultural Institute of Canada

P in solution may be taken up by plant roots or by bacteria and fungi. Bacteria and fungi differ in the way they immobilize P, which alters subsequent redistribution of organic P ( $P_o$ ) in soil (Hedley and Stewart, 1982). Mineralization rates of  $P_o$  depend on the availability of solution P to the microbial population because the C:P ratio of the bacteria and fungal biomass influences mineralization rates (Chauhan *et al.*, 1981). Both the availability of P from solution and the amount of energy available for microbial growth influence the composition of the bacterial and fungal cells and also their subsequent redistribution in soil. Chauhan *et al.* (1981) found that in soils that had an adequate supply of resin-extractable  $P_i$ , incubation with cellulose resulted in a build-up of labile and moderately labile organic-P forms (extractable by  $\text{NaHCO}_3$  and  $\text{NaOH}$ , respectively). When resin-extractable  $P_i$  content was low, although the addition of cellulose resulted in approximately the same microbial biomass, the net result was markedly different in that there was no change in the amount of labile  $P_o$ , moderately labile  $P_o$ , or aggregate-protected  $P_o$  forms. The C:P ratio in the soil biomass was large (45:1 to 60:1), and with repeated addition of cellulose the supply of P limited the microbial decomposition of the cellulose.

These studies give us some insight into the possible redistribution of P in soils. Studies carried out in microcosms in which combinations of single bacterial, amoebal, and nematode species were added to sterilized soils in the presence of an energy source (Cole *et al.*, 1978) also have provided insight into

the biological transformations of  $P_o$  in soils and into the abiotic effects, such as freezing and thawing (Cole *et al.*, 1977).

#### 8.4 DYNAMICS OF CARBON AND SULPHUR IN GRASSLAND ECOSYSTEMS

Detailed descriptions of the S cycle have been reported elsewhere (Postgate, 1968; Peck, 1974). Sulphur, a constituent of amino acids and co-factors, is essential to the structure and function of all living cells. Unlike C and N, S can be utilized to some extent in its most highly oxidized, naturally occurring form,  $SO_4^{2-}$ . In general however, plants and micro-organisms reduce sulphate to S(-II) and use this to form S-containing amino acids and other reduced-S compounds required for their existence. Higher animals utilize these reduced organic compounds, after which they are reformed to the original inorganic compounds, a process that occurs to varying extent in all organisms (Roy and Trudinger, 1970).

The sulphur compounds found in nature may be classified as

##### 1. *Sulphur Amino Acids and Related Compounds.*

These include methionine, cysteine (cystine), cellular metabolites such as glutathione, and S amino acid intermediates such as homocysteine and cysteic acid. Other reduced species of biological importance include co-factors such as co-enzyme A, antibiotics, vitamins, and iron sulphur proteins.

##### 2. *Sulphonic Acids and Related Compounds.*

The sulphonic acids contain direct C-S linkages and are important as intermediates in the oxidation and reduction of cysteine. The common property of these compounds is that they cannot yield  $SO_4^{2-}$  under conditions where  $SO_4^{2-}$  esters are rapidly hydrolysed.

##### 3. *Oxyacids.*

Sulphate, thiosulphate, sulphite, dithionate, and polythionate have been shown to be involved as intermediates in various phases of the reductive and oxydative metabolism of S (Roy and Trudinger, 1970).

##### 4. *Ester Sulphates.*

Ester sulphates or sulphonic acid esters and other related sulphotoconjugates constitute a very diverse group of compounds widely distributed throughout



micro-organisms, plants, and animals. The true S ester has the general formula  $\text{ROSO}_3$  and contains a C-O-S bond. Related to the true ester  $\text{SO}_4^{2-}$  are compounds in which sulphate is present in other linkage forms (Fitzgerald, 1976, 1978). These compounds fall into two categories: N-O-S linkage, typified by glucosinolates, and N-S linkage, typified by sulphamates. As commonly used, the term 'ester sulphates' includes compounds containing these linkages.

### 5. Sulphatophosphates.

Adenosine 5'-sulphatophosphate (APS) and adenosine 3'-phosphate 5'-sulphatophosphate (PAPS) have important functions in the activation of  $\text{SO}_4^{2-}$  in the formation of ester  $\text{SO}_4^{2-}$  (Postgate, 1968; Roy and Trudinger, 1970; Schiff and Hodson, 1973; Siegel, 1975).

#### 8.4.1 Sulphur in Plants

In general, plants contain approximately as much S as P, with an average content of about 0.25% (by dry weight). A wide variety of S-containing compounds have been found in plants, but only a few are known to be required for normal cell function. The essential compounds include the S amino acids, glutathione, thiamine, vitamin B, biotin, ferredoxin, lipoic acid, co-enzyme A, and the sulpholipid of the chloroplasts. Compounds of non-essential or unknown function in plants include glucosinolates, which are found in the cruciferaes, choline sulphate, and penicillin. A variable portion of the S in plants is in the form of inorganic  $\text{SO}_4^{2-}$ .

Generally, the S amino acids contain approximately 90% of the S found in plants (Blair, 1979). However, in some species, a considerable portion of the total S content of the plant may be contained in secondary plant products (Anderson, 1975). The total C:S ratios of plant material are shown in Table 8.1 (Stotzky and Norman, 1961).

The largest portion of S in plants is in protein either as cysteine, cystine, or methionine. Plant proteins generally contain 1% S and 17% N (Dijkshoorn *et al.*, 1960; Pumphrey and Moore, 1965). A review of published data up to 1967 indicates that the average N:S ratio in proteins was 13.7 for gramineous plants and 17.5 for legumes (Dijkshoorn and van Wijk, 1967). For three field crops (wheat, corn, and beans) an N:S ratio of about 12-15:1 was required for protein synthesis (Stewart and Porter, 1969).

For any plant species the composition of a given protein, which is controlled by genetics, is constant. Therefore, environmental factors such as N and S supply, age of plant, etc., should have no influence on the N:S ratio in plant proteins. However, the total N:total S ratio can be greatly affected by environmental factors. When S is adequate, non-protein S (mainly

Table 8.1 Total S content and C:S ratio of plant material<sup>a</sup>

Plant material		Average S content (%)	C:S ratio <sup>b</sup>
Alfalfa hay		0.22 <sup>c</sup>	205
Barley	Grain	0.19	237
	Straw	0.19	237
Corn	Grain	0.12	375
	Straw	0.17	265
Oats	Grain	0.23	196
	Straw	0.24	188
Rapeseed	Grain	0.30 <sup>d</sup>	150
	Straw	0.10	450
Rye	Straw	0.12	374
Wheat	Grain	0.19	237
	Straw	0.19	237

<sup>a</sup>Adapted from Stotzky and Norman (1961); Kowalenko (1978).

<sup>b</sup>C content of plant material assumed to be 45%.

<sup>c</sup>Pumphrey and Moore (1965).

<sup>d</sup>Maynard and Stewart (1980).

$\text{SO}_4^{2-}$ ) will accumulate in the plant and the total N:total S ratio will be less than the N:S ratio in protein. When S is deficient, protein formation is suppressed and non-protein N accumulates. The resulting bulk plant N:S ratio is greater than the N:S ratio of the proteins.

In most plants inorganic  $\text{SO}_4^{2-}$  is the main component of the HI-reducible S fraction. Plants absorb S as  $\text{SO}_4^{2-}$ , which is reduced and incorporated into amino acids as a precursor for protein synthesis. Any excess  $\text{SO}_4^{2-}$  that is not metabolized accumulates unchanged in the tissue. When S is in short supply, most of this  $\text{SO}_4^{2-}$  is incorporated into protein and little remains free in the tissue. Westermann (1975) found that increases in total S above 0.14% in alfalfa were the result of accumulation of  $\text{SO}_4^{2-}$ . In plants of the Cruciferae family, ester  $\text{SO}_4^{2-}$  of glucosinolates could make up a significant portion of the HI-reducible fraction. The glucosinolates are a class of organic anions (see section 8.4), with more than 60 individual compounds identified in plants (Kjaer, 1976).

A considerable range in the concentration of inorganic sulphate and HI-reducible fraction in plants has been reported. Dijkshoorn and van Wijk (1967) indicated the absence of  $\text{SO}_4^{2-}$  in rape, radish, and clover growing in S-deficient soil with an abundant supply of other nutrients; all available  $\text{SO}_4^{2-}$  was apparently used. The percentage of total S that was HI-reducible was recently reported as being as high as 60% in rapeseed of S-sufficient plants sampled at the rosette growth stage and as low as 8% of the total S concentration in S-deficient rape plants (Maynard and Stewart, 1980). In wheat, HI-reducible S concentrations decreased from 250 to 60 ppm in the

tops as the wheat matured ((Freney *et al.*, 1978). However, when expressed as a percentage of the total S, the critical value indicating S sufficiency remained constant at 10%. Critical values of 10% and 26–28% have been reported for green panic grass (Smith and Dolby, 1977), and rape plants (Maynard and Stewart, 1980), respectively.

There is little published data on other ester  $\text{SO}_4^{2-}$  in plants. Nissen and Benson (1961) first reported the identification of choline  $\text{SO}_4^{2-}$  in roots and leaves of barley, corn, and sunflowers. Sulphated polysaccharides have not been found in higher plants but are present in cell wall constituents of algae (Schiff and Hodson, 1973) and may constitute up to 70% of the dry matter of some red seaweed (McCandless and Craigie, 1979). These algal polysaccharides include carrageenan in red algae, agar and fucodin in brown algae (Bidwell, 1972). From the information available, Schiff and Hodson (1973) suggest that the occurrence of sulphated polysaccharides probably represents the adaptation of particular groups of organisms to special needs.

Studies on the decomposition of plant material indicate that net mineralization of S was mainly related to the content of S in the material added to the soil (Freney, 1967). No net mineralization of S occurred from plant material if it contained less than 0.13% S. Stewart *et al.* (1966) found that it was necessary for the S content of wheat straw to exceed 0.15% to obtain the maximum rate of decomposition. Barrow (1960, as cited in Freney, 1967) observed only a broad relationship between net S mineralization from organic materials and the C:S ratio of the material during a 12-week incubation; increased S concentration of plant material did not affect decomposition rates. Atmospheric deposition of  $\text{SO}_2$  has been shown to inhibit decomposition, probably due to the accumulation of toxic products of  $\text{SO}_2$  oxidation such as  $\text{H}^+$  (Dodd and Lauenroth, 1981).

#### 8.4.2 Sulphur in Soils

In soils most of the S occurs in organic rather than inorganic form (Biederbeck, 1978; Kowalenko, 1978). Soil organic-S is generally divided into two major fractions called hydriodic acid-reducible (HI-reducible S) and C-bonded S. The carbon-bonded S fraction, operationally defined as soil sulphur not reduced by a hydriodic acid mixture, contains cysteine and methionine and other sulphonic acids but not ester  $\text{SO}_4^{2-}$ . HI-reducible S is more precisely defined as that fraction of organic S that is reduced to  $\text{H}_2\text{S}$  by a mixture of hydriodic, formic, and hypophosphorous acids. This mixture produces  $\text{H}_2\text{S}$  only from compounds containing C-O-S, N-S, and NOS linkages, but does not rupture the C-S bond.

In many ways the cycling of S in soils (Figure 8.5) is analogous to that of P. The main difference is that the atmosphere is an important source of S, primarily in the form of sulphate. In addition to this, the weathering of minerals

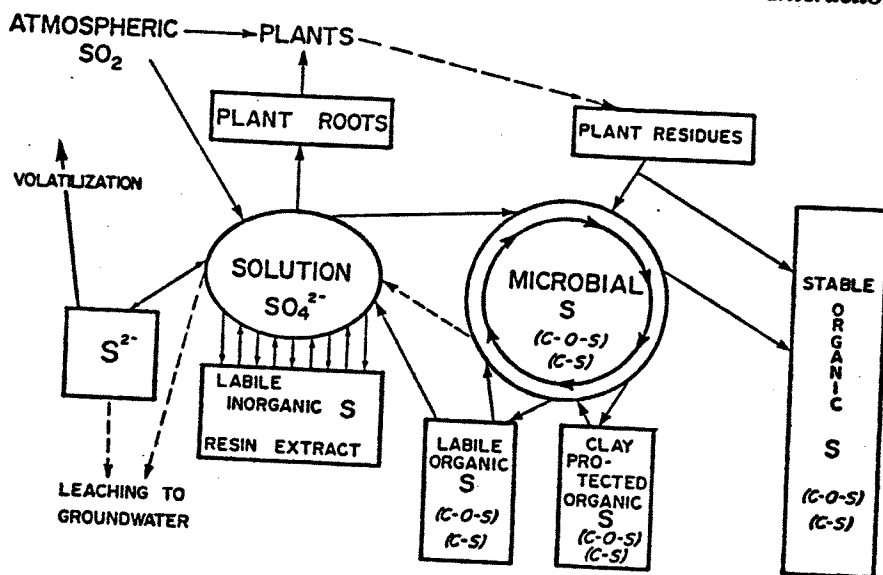


Figure 8.5 Compartments and flows of S in the S cycle

may provide solution  $\text{SO}_4^{2-}$ . Solution  $\text{SO}_4^{2-}$  can adsorb onto the surfaces of clay minerals, although the strength of such adsorption is much weaker than that of  $\text{PO}_4^{3-}$  and would be of some consequence only in weathered soils of low pH ( $<5$ ). In extremely weathered soils,  $\text{SO}_4^{2-}$  is occluded by iron and aluminium compounds. Various organic sulphur compounds are also volatilized from water-saturated agricultural and tidal marsh soils (Farwell *et al.*, 1979).

Both bacteria and fungi accumulate  $\text{SO}_4^{2-}$ , and at lower concentrations most of the  $\text{SO}_4^{2-}$  is converted to amino acid (C-S bonds). At higher soil solution concentrations, bacteria do not accumulate excess  $\text{SO}_4^{2-}$ , whereas fungi have the ability to store  $\text{SO}_4^{2-}$  as organic  $\text{SO}_4^{2-}$  compounds. Fitzgerald (1976), in a review of the literature, suggests that choline sulphate is the most probable form of organic  $\text{SO}_4^{2-}$  that accumulates. Saggar *et al.* (1981b) developed a method for the measurement of microbial-S and found differences in the accumulation of C-bonded S and HI-reducible S between bacteria and fungi (Table 8.2). On the death or decrease of microbial biomass, organic-S in two forms, bonded S (C-S) and ester sulphate (C-O-S), would be released to interact with the soil mineral colloids and form soil organic S. Because there are two types of organic S in the soil, the rates of mineralization will depend on two different processes, viz., biological and biochemical mineralization.

The hydrolysis of ester  $\text{SO}_4^{2-}$  probably occurs by the splitting of the C-O-S bond by sulphatase enzymes (sulphohydrolases). There is a large number of sulphohydrolases, each apparently characterized by a high

Table 8.2 Sulphur concentrations of bacteria and fungi grown at three sulphur concentrations (from Saggiar *et al.*, 1981b).  
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Treatment*	<i>A. globiformis</i>	<i>P. cepacia</i>	<i>F. solani</i>	<i>T. harzianum</i>
	a) Total S ( $\mu\text{g S g}^{-1}$ o.d. wt)			
Low-S	928	1108	1013	852
Medium-S	1123	1341	2318	1261
High-S	1355	1339	2772	2034
LSD <sub>0.01</sub> )	47	36	108	93
	b) HI-reducible S ( $\mu\text{g S g}^{-1}$ o.d. wt)			
Low-S	96	141	116	51
Medium-S	119	136	565	216
High-S	98	163	1159	752
LSD <sub>0.01</sub> )	NS	NS	83	27
	c) Proportion of total S as HI-reducible S (%)			
Low-S	10.3	12.7	11.5	6.0
Medium-S	10.6	10.1	24.4	17.1
High-S	7.2	12.2	41.8	37.0

\*Low-S, medium-S, and high-S represent 1, 4, and 16  $\mu\text{g S ml}^{-1}$  of culture medium, respectively.

specificity towards the organic part of the molecule and an absolute specificity for the S moiety (Houghton and Rose, 1976). Harada (1964) showed that at least three sulphohydrolases—two arylsulphatases and a choline sulphatase—were formed by *Pseudomonas aeruginosa*.

The sulphohydrolases of micro-organisms also play an important role in the mineralization of soil ester  $\text{SO}_4^{2-}$  outside the cell. Recent studies lend support to the theory that several sulphohydrolases are located on microbial cell surfaces (Fitzgerald and Scott, 1974; Fitzgerald and George, 1977; Fitzgerald, 1978; Maca and Fitzgerald, 1979).

Arylsulphatase activity has been reported in soil (Tabatabai and Bremner, 1970; Cooper, 1972; Speir, 1977; Lee and Speir, 1979). However, little correlation between sulphatase activity and S mineralization has been found. Lee and Speir (1979) did find that sulphatase activity correlated with plant uptake of S from organic sources but indicated that the evidence was inconclusive. They also indicated that, because sulphatase is only one of many enzymes involved in organic S mineralization, a direct relationship between sulphatase activity and organic-S mineralization is improbable. Speir *et al.* (1980) found differences in arylsulphatase activity between cropped and fallow soils, with the latter soils showing a decrease in activity over 21 weeks. These authors postulated that temperature-dependent denaturation of sulphatase occurred in both soils but that roots replaced lost sulphatase in cropped soils.

### 8.5 INTERRELATIONSHIPS OF CARBON, NITROGEN, SULPHUR, AND PHOSPHORUS

Major interactions of C, N, S, and P are observed in the effects of these elements on the plant and animal productivity of ecosystems. Changes in species composition and the balance between grasses and legumes and the nutrient quality of the plants have been observed (Chapin, 1980). N, P, and S all affect C accumulation by plants. Another category of interactions occurs where P uptake by plants is influenced by available N in the soil and N content of plant material (Williams, 1948; Grunes, 1959; Cole *et al.*, 1963). Similarly, S supply has a major effect on N accumulation and, conversely, N can affect the utilization of S within plants (Rendig and McComb, 1959). Although the ratio of N to S in protein remains constant under various environmental conditions, the total N to S ratio can be greatly affected by environmental factors.

The second major category of interaction for these elements relates to the decomposition of plant material and formation of soil organic matter. In general, nutrient-poor plant residues require additional supplies of N, P, and S for microbial decomposition because decomposition processes are very sensitive to imbalances in the supplies of these elements. Another major example of interactions mediated by microbes is the effect of P supply on N fixation in plants, algae, and heterotrophic organisms (Cole and Heil, 1981).

In cultivated systems, residue management affects the distribution of C residues in the upper layers of the soil. This affects N, S, and P cycling and may increase the amounts of these elements in organic forms. Management practices also alter moisture and temperature regimes in the soil, and these effects may be compounded. Management practices that accelerate losses of C from ecosystems result in increased net mineralization of organic forms of N, P, and S. Inorganic forms of N and S are subject to leaching and gaseous loss, whereas P may revert to less available mineral forms.

Various approaches have been adopted to study the C, N, S, and P relationships in soils. These include comparisons of the amounts of organic matter N, P, and S in soils from environmental gradients. Bettany *et al.* (1973) found that the amounts of total S, organic N, and organic C, and HI-reducible S obtained from the  $A_p$  layers of 54 soils collected from five major soil zones vary considerably with location within any one zone. However, in the soil organic matter the mean C:S and N:S ratios and the percentage of total S that is HI-reducible showed similar and consistent trends. The C:N:S ratios ranged from 58:6.4:1 in the arid Chernozemic Brown soils to 129:10.6:1 in the more moist Luvisolic (Gray-Wooded) soils. The HI-reducible S was approximately 50% of the total S the Chernozemic soils, in contrast to 36% in the Luvisolic soil. Separation of representative soils from each zone by use of a combined chemical and physical technique showed greater differences in the C:N:S ratios of conventional humic acid (HA-A) fractions than in those of the total soil organic matter. The HA-A fraction was thought to be representative of the end-product of the humification processes and to represent the most resistant fraction (Bettany *et al.*, 1979). However, chemical separation can be criticized due to the severity of the procedure and the possibility of mixing and re-precipitating organic matter.

Comparison of the amounts and forms of C, N, and S in soil organic matter fractions after 65 years of cultivation reveal large differences in organic matter contents and relatively lower net losses of sulphur (38%), compared with carbon (44%) and nitrogen (49%) losses (Bettany *et al.*, 1980). Smaller C:N:S ratios in the cultivated soil indicated that S is more resistant to mineralization during cultivation processes than C and N.

In a similar study the effect of long term cultivation on the concentration and total amounts of carbon, nitrogen, organic and inorganic phosphorus was a loss of 35% in the carbon concentration and losses of between 18 and 34% in nitrogen concentration, depending on the inclusion of legume crops in rotation. Phosphorus concentrations were reduced by 12%, and in clay and silt soils all P losses were from the organic matter. In a similar period of cultivation of a lighter-textured sandy loam, there were greater reductions of C, N, and P (46, 46, and 29%, respectively), and P was lost from both organic and inorganic fractions (Tiessen *et al.*, 1982).

It has not yet been demonstrated that humus can be chemically removed

from soils without alteration or that any isolated fraction is either biologically or chemically homogeneous. One method that attempts to do this is the separation of soil organic matter on the basis of particle size fractions. Various techniques involve dispersion in water, either by continued agitation or ultrasonic energy, followed by sieving, sedimentation, and centrifugation. Results from studies of this sort (Turchenek and Oades, 1979; Young and Spycher, 1979; Anderson *et al.*, 1981) indicate that most organic matter is associated with the  $<20\text{-}\mu\text{m}$  size fractions and that the C:N and C:S ratios decrease significantly with decreasing particle size. Similar studies with P show that the more labile fractions of inorganic and organic P are associated with the clay size particles.

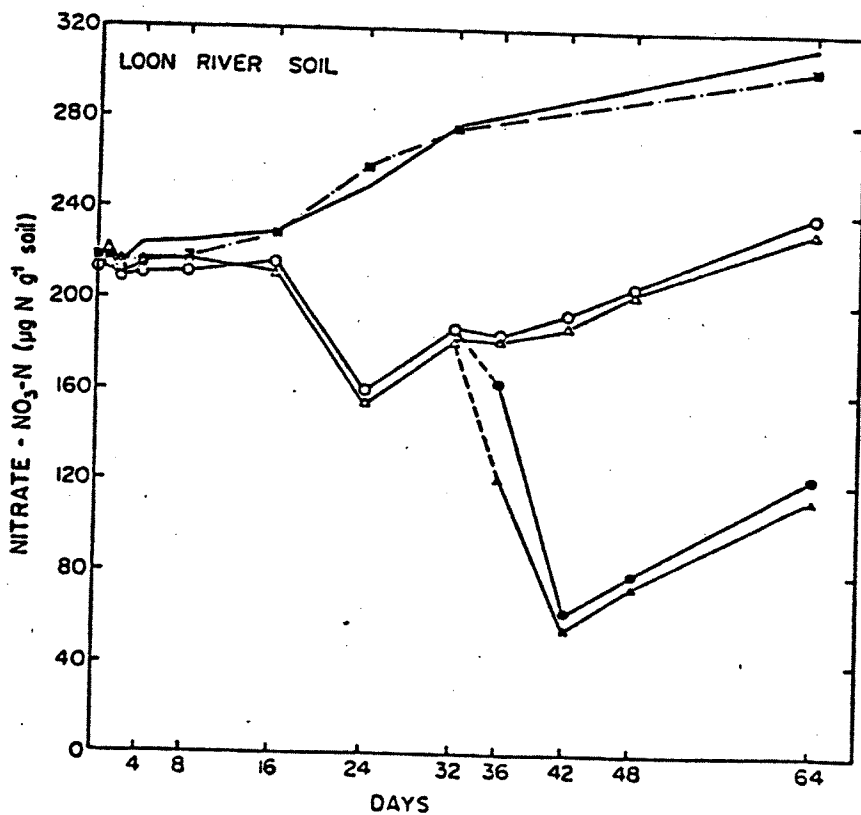
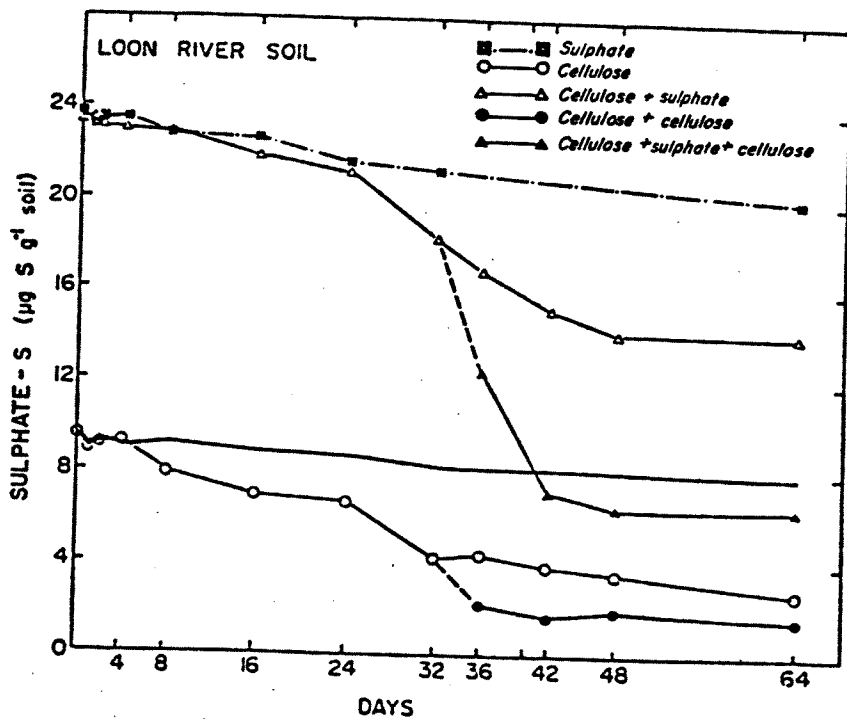
### 8.6 CYCLING STUDIES

By using radioisotope and stable isotope tracers and  $^{14}\text{C}$  dating, the fractions that are significant in cycling organic-bound nutrients may be identified (McGill *et al.*, 1975; Paul and Van Veen, 1978; Chauhan *et al.*, 1979, 1981). Additional information on the rates of P and S immobilization and redistribution has been gained from incubations of soil that have had cellulose added (Cole *et al.*, 1978; Coleman *et al.*, 1978; Chauhan *et al.*, 1979, 1981; Hedley *et al.*, 1982). In a study of S transformations during an incubation of two grassland soils (Saggar *et al.*, 1981a), changes in biomass S, C, and N were evaluated and the transformations of  $^{35}\text{S}$ -labelled sulphate among organic matter fractions were followed. During the 64 days of incubation (Figure 8.6) there was a net immobilization of S with and without the addition of cellulose or sulphate. In contrast, a net mineralization of N occurred. Cellulose decomposition rates responded to the supply of S available for synthesis of new microbial cells. Fluctuations in the amounts of biomass S during incubation followed biomass C and N changes, and C:S and C:N ratios of the biomass ranged from 47 to 121 and 4.9 to 4.7, respectively. Microbially incorporated S was concentrated within the biomass or partially transformed into soil organic matter.

Fractionation of the soil after incubation by a  $0.1\text{ M NaOH}$ – $0.1\text{ M Na}_4\text{P}_2\text{O}_7$  extraction technique revealed a significant increase in the C:N ratio in the conventional humic acid (HA-A) and fulvic acid (FA-A) and humin ( $<2\text{ }\mu\text{m}$ ) fractions. Biomass C accounted for 20–64% of the observed increases in these fractions, suggesting that differences were due partly to transformed microbial products and partly to microbial cell organic constituents released on lysis of cells or trophic effects during incubation. In contrast to C and N, the contents of total S and HI-reducible S increased in the FA-A fraction only and

Figure 8.6 The effect of sulphate-S and cellulose addition on  $10\text{ mM CaCl}_2$ -extractable-S concentrations ( $\mu\text{g S g}^{-1}$  soil) and nitrate-N concentrations ( $\mu\text{g NO}_3\text{-N g}^{-1}$  soil) during 64 days incubation (from Saggar *et al.*, 1981a). Reproduced by permission of Pergamon Press Ltd.





accounted for 45 to 76% of the immobilized labelled S. These results indicated that inorganic  $\text{SO}_4^{2-}$  was immobilized and organic S was accumulated simultaneously in the cellulose treatment of both soils. Incorporation of S mainly in the FA-A fraction obtained during this short incubation further substantiates the idea that organic S compounds synthesized during short periods are relatively labile in nature, but over a prolonged period these compounds are transformed into relatively resistant fractions, such as HA-A, HA-B, and humins. In contrast, rates of S mineralization were highly correlated with rates of N mineralization when  $\text{SO}_4^{2-}$ -S was removed periodically by leaching during the incubation period (Tabatabai and Al-Khafaji, 1980).

Microbial biomass plays a major role in the redistribution of P into different forms (Stewart *et al.*, 1980). Incubation of the soils with added cellulose in the presence of a large supply of  $\text{P}_i$  resulted in the accumulation of labile  $\text{P}_o$  forms in the soil. When soils deficient in phosphorus were incubated under the same treatments, labile  $\text{P}_o$  forms did not increase. Chauhan *et al.* (1981) and Hedley *et al.* (1982) postulated that these changes were due to increased mineralization rates of labile  $\text{P}_o$  forms when labile  $\text{P}_i$  was in short supply and to differences in the microbial P contents and forms.

Structured models of microbial populations are becoming more important in ecological research. These models take simultaneous account of several population variables, such as number, mean cell size, total biomass, and nutrient content (Hunt, 1977). Hunt *et al.* (1977) modelled the growth of bacteria limited by either C, N, or P. Their model distinguished between storage compartments for C and P and a pool of small precursor molecules, as well as the structural and synthetic components. The model was adjusted to fit published data on the chemical composition of bacteria growing in a chemostat limited by either C, N, or P. The model successfully predicted the kinds of waste products produced under various conditions, the transient response to a change in dilution rate, and the response to a change in the make-up of the medium. These predictions were made even though the observations were not used to formulate the model or establish parameter values.

Phosphorus-cycling, nitrogen-cycling, and sulphur-cycling simulation models (Cole *et al.*, 1977; Chapin *et al.*, 1978; Harrison, 1978; Mishra *et al.*, 1979; Coughenour *et al.*, 1980; McGill *et al.*, 1981) have integrated the effects of moisture, soil properties, plant phenology, and microbial decomposition of organic matter on P flows. These models revealed gaps in knowledge of key processes—such as organic P mineralization, influences of phosphatases on P mineralization, and influence of the microbial biomass on the redistribution of  $\text{P}_i$  and  $\text{P}_o$  in soils—thereby giving direction to future research.

We are currently modelling the interaction of ecological driving variables and plant processes, microbial processes, and soil chemical processes in an attempt to integrate C, N, P, and S interactions in grassland ecosystems. To

date we have represented these processes in the flow of C, N, and P in soil microcosms (Cole, Hunt, Stewart, Woods, and Coleman, in preparation). A simulation model of C, N, S, and P flows based on these concepts is described in a companion paper (Hunt *et al.*, chapter 10, this volume).

## 8.7 REFERENCES

- Anderson, D. W., Sagar, S., Bettany, J. R., and Stewart, J. W. B. (1981) Particle size fractions and their use in studies of soil organic matter. I. The nature and distribution of forms of carbon, nitrogen and sulphur, *Soil Sci. Soc. Amer. J.*, **45**, 767-772.
- Anderson, J. W. (1975) The function of sulphur in plant growth and metabolism, in McLachlan, K. D. (ed.) *Sulphur in Australasian Agriculture*, Sydney, Sydney University Press, 87-97.
- Barrow, N. J. (1960) The effect of varying the nitrogen, sulphur and phosphorus content of organic matter on its decomposition, *Aust. J. Agric. Res.*, **11**, 317-330.
- Batzli, G. O. (1978) The role of herbivores in mineral cycling, in Adriano, D. C. and Brisbin, I. L. (eds) *Environmental Chemistry and Processes, Department of Energy Series 45*, Washington, D. C. U.S. Department of Energy, 95-112.
- Bettany, J. R., Sagar, S., and Stewart, J. W. B. (1980) Comparison of the amounts and forms of sulphur in soil organic matter fractions after 65 years cultivation, *Soil Sci. Soc. Amer. J.*, **44**, 70-75.
- Bettany, J. R., Stewart, J. W. B., and Halstead, E. H. (1973) Sulphur fractions and carbon, nitrogen and sulphur relationships in grassland, forest and associated transitional soils, *Soil Sci. Soc. Amer. Proc.*, **37**, 915-918.
- Bettany, J. R., Stewart, J. W. B., and Sagar, S. (1979) The nature and forms of sulphur in organic matter fractions of soils selected along an environmental gradient, *Soil Sci. Soc. Amer. J.*, **43**, 981-985.
- Bidwell, R. G. S. (1972) *Plant Physiology*, New York, MacMillan.
- Biederbeck, V. O. (1978) Soil organic sulphur and fertility, in Schnitzer, M., and Khan, S. U. (eds) *Soil Organic Matter*, New York, Elsevier Scientific, 273-310.
- Blair, G. J. (1979) *Sulphur in the Tropics*, Muscle Shoals, Alabama, International Fertilizer Development Center.
- Breymeyer, A. I., and Van Dyne, G. M. (eds) (1980) *Grasslands, Systems Analysis and Man, IBP Synthesis Series 19*, Cambridge, Cambridge University Press.
- Chapin, F. S. (1980) The mineral nutrition of wild plants, *Ann. Rev. Ecol. Syst.*, **11**, 233-260.
- Chapin, F. S., Barsdate, R. J., and Barel, D. (1978) Phosphorus cycling in Alaska coastal tundra: A hypothesis for the regulation of nutrient cycling, *Oikos*, **31**, 188-199.
- Chauhan, B. S., Stewart, J. W. B., and Paul, E. A. (1979) Effect of carbon additions on soil labile inorganic, organic and microbially held phosphate, *Can. J. Soil Sci.*, **59**, 387-396.
- Chauhan, B. S., Stewart, J. W. B., and Paul, E. A. (1981) Effect of labile inorganic phosphate status and organic carbon additions on the microbial uptake of phosphorus in soils, *Can. J. Soil Sci.*, **61**, 373-385.
- Clark, F. E., Cole, C. V., and Bowman, R. A. (1980) Nutrient cycling, in Breymeyer, A. J., and Van Dyne, G. M. (eds) *Grasslands, Systems Analysis and Man*, Cambridge, Cambridge University Press, 659-712.
- Cole, C. V., and Heil, R. D. (1981) Phosphorus effects on terrestrial nitrogen cycling, in Clark, F. E., and Rosswall, T. (eds) *Terrestrial Nitrogen Cycles, Processes, Ecosystem and Management Impact.*, *Ecol. Bull. (Stockholm)*, **33**, 363-374.

- Cole, C. V., Elliott, E. T., Hunt, H. W., and Coleman, D. C. (1978) Trophic interactions in soils as they affect energy and nutrient dynamics. V. Phosphorus transformations, *Microb. Ecol.*, 4, 381-387.
- Cole, C. V., Grunes, D. L., Porter, L. K., and Olsen, S. R. (1963) The effect of nitrogen on short-term phosphorus absorption and translocation in corn (*Zea mays*), *Soil Sci. Soc. Amer. Proc.*, 27, 671-674.
- Cole, C. V., Hunt, H. W., Stewart, J. W. B., Woods, L. and Coleman, D. C. Simulation of carbon nitrogen and phosphorus flows in soil microcosms, in preparation.
- Cole, C. V., Innis, G. S., and Stewart, J. W. B. (1977) Simulation of phosphorus cycling in semiarid grassland, *Ecology*, 58, 1-15.
- Coleman, D. C., Anderson, R. V., Cole, C. V., Elliott, E. T., Woods, L., and Campion, M. K. (1978) Trophic interactions in soils as they affect energy and nutrient dynamics. IV. Flows of metabolic and biomass carbon, *Microb. Ecol.*, 4, 373-380.
- Cooper, P. J. M. (1972) Aryl sulphatase activity in northern Nigerian soils, *Soil Biol. Biochem.*, 4, 333-337.
- Coughenour, M. B., Parton, W. J., Lauenroth, W. K., Dodd, J. L., and Woodmansee, R. G. (1980) Simulation of a grassland sulphur cycle, *Ecol. Model.*, 9, 179-213.
- Coupland, R. T. (ed.) (1979) *Grassland Ecosystems of the World: Analysis of Grasslands and Their Uses*, IBP Synthesis Series 18, London, Cambridge University Press.
- Dijkshoorn, W., Lampe, J. E. M., and van Burg, P. F. J. (1960) A method of diagnosing the sulphur status of herbage, *Plant Soil.*, 13, 227-241.
- Dijkshoorn, W., and van Wijk, A. L. (1967) The sulphur requirements of plants as evidenced by the sulphur-nitrogen ratio in the organic matter. A review of published data, *Plant Soil.*, 26, 129-157.
- Dodd, J. L., and Lauenroth, W. K. (1981) Effects of low-level SO<sub>2</sub> fumigation on decomposition of western wheatgrass litter in a mixed-grass prairie, *Water Air Soil Pollut.* 15, 257-261.
- Farwell, S. O., Sherrard, A. E., Pack, M. R., and Adams, D. F. (1979) Sulphur compounds volatilized from soils at different moisture contents, *Soil Biol. Biochem.*, 11, 411-415.
- Fitzgerald, J. W. (1976) Sulphate ester formation and hydrolysis: A potentially important yet often ignored aspect of the sulphur cycle in aerobic soils, *Bacteriol. Rev.*, 40, 648-721.
- Fitzgerald, J. W. (1978) Naturally occurring organosulphur compounds in soils, in Nriagu, J. O. (ed.) *Sulphur in the Environment. Part II. Ecological Impacts.*, New York, Wiley, 391-443.
- Fitzgerald, J. W., and George, J. R. (1977) Localization of arylsulphatase in *Pseudomonas C<sub>12</sub>B*, *Appl. Environ. Microbiol.*, 34, 107-108.
- Fitzgerald, J. W., and Scott, C. L. (1974) Utilization of choline-O-sulphate as a sulphur source for growth by a *Pseudomonas* isolate, *Microbios*, 10, 121-131.
- Floate, M. G. S. (1981) The effects of grazing by large herbivores on nitrogen cycling in agriculture ecosystems, in Clark, F. E. and Rosswall, T. (eds) *Terrestrial Nitrogen Cycles, Processes, Ecosystem and Management Impact.*, *Ecol. Bull. (Stockholm)*. 33, 585-601.
- Freney, J. R. (1967) Sulphur-containing organics, in McLaren, A. D., and Peterson, G. H. (eds) *Soil Biochemistry*, Vol. I, New York, Dekker, 229-259.
- Freney, J. R., Spencer, K., and Jones, M. B. (1978) The diagnosis of sulphur deficiency in wheat, *Aust. J. Agric. Res.*, 29, 729-738.

- Grunes, D. L. (1959) Effect of nitrogen on the availability of soil and fertilizer P to plants, *Adv. Agron.*, 11, 369–396.
- Harada, T. (1964) The formation of sulphatases by *Pseudomonas aeruginosa*, *Biochim. Biophys. Acta*, 81, 193–196.
- Harrison, A. F. (1978) Phosphorus cycles of forest and upland grassland systems and some effects of land management practices, in *Phosphorus in the Environment: Its Chemistry and Biochemistry*, CIBA Foundation Symp. 57, Amsterdam, Elsevier/North-Holland, 175–195.
- Hedley, M. J., and Stewart, J. W. B. (1982) A method to measure microbial phosphate in soils, *Soil Biol. Biochem.* 14, 377–385.
- Hedley, M. J., Stewart, J. W. B., and Chauhan, B. S. (1982) Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices, *Soil Sci. Soc. Amer. J.* 46, 970–976.
- Houghton, C., and Rose, F. A. (1976) The liberation of sulphate from sulphate esters by soils. *Appl. Environ. Microbiol.*, 31, 969–976.
- Hunt, H. W. (1977) A simulation model for decomposition in grasslands, *Ecology*, 58, 469–484.
- Hunt, H. W., Cole, C. V., Klein, D. A., and Coleman, D. C. (1977) Simulating the effect of predators on the growth and composition of bacteria. in Lohm, U. and Persson, T. (eds) *Soil Organisms as Components of Ecosystems*, *Ecol. Bull. (Stockholm)*, 25, 409–419.
- Hunt, H. W., Stewart, J. W. B., and Cole, C. V. (1983) A conceptual model for the basis of interactions among carbon, nitrogen, sulphur, and phosphorus transformations, chapter 10, this volume.
- Jones, M. B., and Woodmansee, R. G. (1979) Biochemical cycling in annual grassland ecosystems, *Bot. Rev.*, 45, 111–144.
- Kjaer, A. (1976) Glucosinolates in the Cruciferae, in Vaughan, J. G., MacLeod, A. J., and Jones, B. M. (eds) *Biology and Chemistry of the Cruciferae*, London, Academic Press, 207–219.
- Kowalenko, C. G. (1978) Organic nitrogen, phosphorus and sulphur, in Schnitzer, M., and Khan, S. U. (eds) *Soil Organic Matter*, New York, Elsevier Scientific, 95–136.
- Lee, R., and Speir, T. W. (1979) Sulphur uptake by ryegrass and its relationship to inorganic and organic sulphur levels and sulphatase activity in soil, *Plant Soil*, 53, 407–425.
- Maca, H. W., and Fitzgerald, J. W. (1979) Evidence for a periplasmic location in *Comamonas terrigena* of the inducible tyrosine sulphate sulphohydrolase, *Can. J. Microbiol.*, 25, 275–278.
- McCandless, E. L., and Craigie, J. S. (1979) Sulphated polysaccharides in red and brown Algae, *Ann. Rev. Plant Physiol.*, 30, 41–53.
- McGill, W. B., and Cole, C. V. (1981) Comparative aspects of organic C, N, S and P cycling through soil organic matter during pedogenesis, *Geoderma* 26, 267–286.
- McGill, W. B., Hunt, H. W., Woodmansee, R. G., and Reuss, J. O. (1981) Phoenix, a model of the dynamics of carbon and nitrogen in grassland soils, in Clark, F. E., and Rosswall, T. (eds) *Terrestrial Nitrogen Cycles, Processes, Ecosystem and Management Impacts*, *Ecol. Bull. (Stockholm)*, 33, 49–116.
- McGill, W. B., Shields, J. A., and Paul, E. A. (1975) Relation between carbon and nitrogen turnover of soil organic fractions of microbial origin, *Soil Biol. Biochem.*, 7, 57–63.
- Maynard, D. G., and Stewart, J. W. B. (1980) Sulphur deficiency in rapeseed—diagnostic plant analysis. *Proc. 1980 Soils and Crops Workshop*, University of Saskatchewan, Saskatoon, 155–176.

- Mishra, B., Khanna, P. K., and Ulrich, B. (1979) A simulation model for organic phosphorus transformation in a forest soil ecosystem, *Ecol. Model.*, **6**, 31-46.
- Nissen, P., and Benson, A. A. (1961) Choline sulphate in higher plants, *Science*, **134**, 1759.
- Paul, E. A., and Van Veen, J. (1978) The use of tracers to determine the dynamic nature of organic matter, *Trans. 11th Int. Congr. Soil Sci.*, **3**, 61-102.
- Peck, H. D., Jr (1974) The evolutionary significance of inorganic sulphur metabolism, in *Evolution in the Microbial World, 24th Symposium of the Society for General Microbiology*, (Imperial College, London), London, Cambridge University Press, 241-262.
- Postgate, J. R. (1968) Inorganic sulphur chemistry, in Nickless, G. (ed.) *The Sulphur Cycle*, New York, Elsevier Publ. Co., 259-272.
- Pumphrey, F. V., and Moore, D. P. (1965) Diagnosing sulphur deficiency of alfalfa (*Medicago sativa* L.) from plant analysis, *Agron. J.*, **57**, 364-366.
- Rendig, V. V., and McComb, E. N. (1959) Effect of nutritional stress on plant composition: I. The interaction of added nitrogen with varying sulphur supply, *Soil Sci. Soc. Amer. Proc.*, **23**, 377-380.
- Roy, A. B., and Trudinger, P. A. (1970) *The Biochemistry of Inorganic Compounds of Sulphur*, Cambridge, Cambridge University Press.
- Saggar, S., Bettany, J. R., and Stewart, J. W. B. (1981a) Sulphur transfers in relation to carbon and nitrogen in incubated soils, *Soil Biol. Biochem.* **13**, 499-511.
- Saggar, S., Bettany, J. R., and Stewart, J. W. B. (1981b) Measurement of microbial sulphur in soil, *Soil Biol. Biochem.* **13**, 493-498.
- Schiff, J. A., and Hodson, R. C. (1973) The metabolism of sulphate, *Ann. Rev. Plant Physiol.*, **24**, 381-414.
- Siegel, L. H. (1975) Biochemistry of the sulphur cycle, in Greenburg, D. M. (ed.) *Metabolism of Sulphur Compounds*, Vol. VII of *Metabolic Pathways*, 3rd Edn, New York, Academic Press, 217-286.
- Smith, F. W., and Dolby, G. R. (1977) Derivation of diagnostic indices for assessing the sulphur status of *Panicum maximum* var. *trichoglume*, *Comm. Soil Sci. Plant Anal.*, **8**, 221-240.
- Speir, T. W. (1977) Studies on a climosequence of soils in tussock grasslands. II. Urease phosphatase and sulphatase activities of topsoils and their relationships with other properties including plant available sulphur, *New Zealand J. Sci.*, **20**, 159-166.
- Speir, T. W., Lee, R., Pansier, E. A., and Cairns, A. (1980) A comparison of sulphatase, urease, and protean activities on planted and fallow soils, *Soil Biol. Biochem.*, **12**, 281-291.
- Stewart, B. A., and Porter, L. K. (1969) Nitrogen-sulphur relationships in wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), and beans (*Phaseolus vulgaris*), *Agron. J.*, **61**, 267-271.
- Stewart, B. A., Porter, L. K., and Viets, F. G., Jr (1966) Effect of sulphur content of straws on rates of decomposition and plant growth, *Soil Sci. Soc. Amer. Proc.*, **30**, 355-358.
- Stewart, J. W. B., Hedley, M. J., and Chauhan, B. S. (1980) The immobilization, mineralization and redistribution of phosphorus in soils, in Harapiak, J. T. (ed.) *Proc. Western Canada Phosphate Symposium*, Edmonton, Alberta Soil Science Society, 276-306.
- Stotzky, G., and A. G. Norman (1961) Factors limiting microbial activities in soil. II. The effect of sulphur, *Archiv. Fur Mikrobiol.*, **40**, 370-382.
- Tabatabai, M. A., and Bremner, J. M. (1970) Arylsulphatase activity of soils, *Soil Sci. Soc. Amer. Proc.*, **34**, 225-229.

- Tabatabai, M. A., and Al-Khafaji, A. A. (1980) Comparison of nitrogen and sulphur mineralization in soils, *Soil Sci. Soc. Amer. J.*, 44, 1000-1006.
- Till, A. R. (1980) Sulphur cycling in soil-plant-animal systems, in Freney, J. R. and Nicholson, A. J. (eds) *Sulphur in Australia*, Canberra, Aust., Australian Academy of Sciences, 204-217.
- Turchenek, L. W., and Oades, J. M. (1979) Fractionation of organo-mineral complexes by sedimentation and density techniques, *Geoderma*, 21, 311-343.
- Tiessen, H., Stewart, J. W. B., and Bettany, J. R. (1982) Cultivation effects on the amounts and concentration of carbon, nitrogen and organic and inorganic phosphorus in grassland soils, *Agron. J.* 74, 831-835.
- Westermann, D. T. (1975) Indexes of sulphur deficiency in alfalfa. II. Plant analysis, *Agron. J.*, 67, 265-268.
- Williams, R. F. (1948) The effect of phosphorus supply on the rates of intake of phosphorus and nitrogen, and upon certain aspects of P metabolism in gramineous plants, *Aust. J. Sci. Res.*, 1, 311-361.
- Young, J. L., and Spycher, G. (1979) Water-dispersed soil organo-mineral particles. I. Carbon and nitrogen distribution, *Soil Sci. Soc. Amer. J.*, 43, 324-328.

SCOPE 21

# **The Major Biogeochemical Cycles and Their Interactions**

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