Biogeochemistry 2: 163–177 (1986)

Concepts of sulfur, carbon, and nitrogen transformations in soil: evaluation by simulation modeling

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Key words: sulfur, carbon, nitrogen, mineralization, simulation model

Abstract. The dynamics of sulfur immobilization and mineralization in soil were simulated to test hypotheses about their regulation by the availability of carbon and nitrogen. The concept of chemical bond classes was incorporated into the model to account for variation in composition of carbon, nitrogen, and sulfur compounds. Microbial biomass was differentiated into bacteria and fungi, and the element ratios of both groups were assumed to vary. Organic residues were divided between dead microbes plus microbial products, and the more labile fraction of stabilized soil organic matter. Concepts and hypotheses in the model were tested by applying it to data on microbial biomass, sulfate, nitrate, and CO_2 evolution obtained in laboratory incubations of two soils amended with sulfate and cellulose. An important mechanism of regulation tested in the model was the stimulation of sulfohydrolase enzyme production depending on sulfur stress in microbial biomass. The hypothesis that excess sulfate is stored as ester sulfate was supported by model dynamics.

Introduction

Recently there has developed an increasing interest in interactions among element cycles in ecosystems (Bolin and Cook, 1983). A concurrent trend in simulation modeling has improved the realism with which element interactions are represented (Hunt et al., 1983). The most important advance is that different elements are less often treated separately, and the biochemical mechanisms responsible for element interactions are included explicitly. These developments pertain mainly to nitrogen, carbon, and phosphorus, while sulfur has received much less attention.

The objective of the present paper is to test hypotheses about the regulation of sulfur immobilization and mineralization by the availability of carbon and nitrogen in soils. Our procedure will be to incorporate the hypotheses into a simulation model and then evaluate the ability of the model to mimic laboratory data on the effects of S and C supply on the dynamics of decomposition. If the model fails to account adequately for the patterns in the data, both the model and its underlying hypotheses may be rejected. If the model succeeds, the underlying hypotheses are thereby established as sufficient over the range of conditions tested.

An important concept in the model is the distinction among elemental

bond classes. Five classes of chemical bonds (C–C, N–C, S–C, S–O–C, and P–O–C) are distinguished. Nitrogen and sulfur atoms stabilized as a result of covalent bonding with carbon (N–C and S–C) are assumed to be mineralized by organisms oxidizing C to provide energy, whereas S and P atoms existing as esters (S–O–C and P–O–C) are stabilized through reaction of the ester with soil components and are mineralized by the action of extracellular enzymes according to the need for the element (McGill and Cole, 1981).

Another important concept in the model is that organisms regulate uptake of resources and release of wastes resulting in the maintenance of element ratios within bounds. Hunt et al. (1983) showed how this concept follows from information about the chemical composition of the structural and biosynthetic components of biomass, the identity of the growth-limiting factors, and the kinds and amounts of storage products present.

The model was tested by adapting it to laboratory data on C, N, and S transfers in sulfate- and cellulose-amended soils (Saggar et al., 1981b). These data are especially useful because biomass S, C, and N were estimated simultaneously, and the transformations of ^{35}S-labelled SO_4^{2-} among organic matter fractions were followed during incubation. The data set did not have biomass divided into fungi and bacteria, although a predominance of fungi can be inferred from similar treatments of Haploboroll soils (Chauhan et al., 1981). Samples from the Ap horizon of Indian Head (Udic Haploboroll) and Loon River (Typic Cryoboroll) soils were dried and large pieces of plant matter removed. The soil was ground (< 2mm) and preincubated aerobically to allow recovery from the effects of handling. Treatments included a control, S amendment (15 μg K_2SO_4–S/g soil), C amendment (1500 μg cellulose–C/g soil at time 0), S + C amendment, double C amendment (additional 1500 μg C/g soil at 32 days), and S + double C amendment. Micronutrients, N and P were added to relieve any other nutrient limitations. The soils were incubated in the laboratory for 64 days at 80% of field capacity and a day/night temperature of 21 °/16 °C, and were analyzed for extractable SO_4^{2-}, NH_4^+, NO_3^-, and ^{35}S activity at intervals during the incubation. Carbon dioxide evolution was measured daily. Fumigation with chloroform was used to estimate microbial C (Jenkinson, 1976), N (Voroney et al., 1981), and S (Saggar et al., 1981a). HI-reducible S was determined by reaction with hydriotic reducing mixture. Saggar et al. (1981b), give a fuller description of experimental design and analytical methods.

Model structure

State variables

Fungi and bacteria were distinguished in the model (Figure 1) because of the greater propensity of fungi to break down cellulose (Campbell, 1977; Gyllenberg and Eklung, 1974) and to store oxygen-bonded S (Saggar et al., 1981a). Microbial metabolic wastes and microbes dying from nutritional

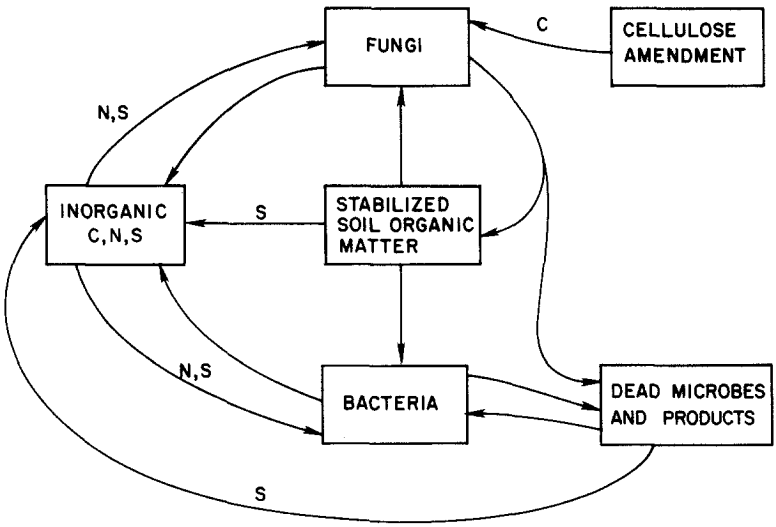

Figure 1. State variables and processes in the model. Arrows labelled with elements transfer only those elements. Unlabelled arrows transfer C, N, and S.

stresses were combined together into a single compartment, assumed to be used efficiently only by bacteria (Gyllenberg and Eklung, 1974). Stabilized soil organic matter consists of the resistant fraction of microbial products (cell walls of melanic fungi) plus the products of condensation between lignin and small molecular weight nitrogenous compounds (McGill et al., 1981).

Although about half of total S in the two soils is O-bonded S (Saggar et al., 1981b), much of this organic sulfate presumably is sequestered within particulates or protected by adsorption to clay (Anderon, 1979). Bettany et al. (1973) postulated that organic sulfate would be associated with the more active aliphatic side chain components of humus. Therefore, we assumed that stabilized organic matter is the source of O-bonded S operated on by sulfohydrolases released by microbes in response to S limitation. In order that this S–O–C pool not be unreasonably large, it was initialized to a fraction of the total organic sulfate actually present.

The model includes several distinct state variables for each of the compartments in Figure 1. For the inorganic pool, these state variables consist of CO_2, NO_3^-, NH_4^+, and SO_4^{2-}. Each organic pool includes state variables for C, carbon-bonded sulfur (S–C), oxygen-bonded sulfur (S–O–C), and N. In addition, we modeled ^{35}S isotope in SO_4^{2-} and in the S–C and S–O–C fractions of each organic pool.

Element ratios

The rates of decomposition, uptake, release of wastes and production of sulfohydrolases are functions of organism element ratios (Hunt et al., 1983).

Microbes were assumed to allocate S between S–C and S–O–C, so that their S–C to N ratio is fixed at the S-to-N ratio of proteins (0.067 for bacteria and 0.033 for fungi) and so that excess S is held in the oxygen-bonded form. The values used for ratios of S–C to N are in the range observed for bacterial proteins (Laskin and Lechevalier, 1973). These assumptions allow the model to correctly predict that bacteria and fungi have about 7–15% and 7–50%, respectively, of their total S in the form of S–O–C. depending on the degree of S limitation. No constraints were placed on the element ratios of state variables other than microbes. However, it was assumed that during decomposition the uptake of all elements by microbes is in the ratio they exist in the substrate (with the exception of the action of sulfohydrolases on ester S), which can be justified on the basis that walls and cytoplasm, the cell fractions that might be expected to differ most in decomposition rate, are not as different in elemental composition either in bacteria (Hunt et al., 1977) or fungi (Villanueva, 1966) as in plants. Furthermore, it is not clear that microbial cytoplasm decomposes any faster than cell walls in soil (Nakas and Klein, 1979). Thus during all stages of decomposition of microbial cells, monomers released will include C, N, and S, and the element ratios of decomposing microbes and products will tend to be similar to those of living microbes.

Decomposition and uptake

The uptake of inorganic nutrients and the use of cellulose were assumed to be affected by the demand for that nutrient. Figure 2 defines the effects of organism C:N and C:S ratios on demand for C, N, and S. Both S and N content affect demand for C, and the most limiting nutrient is assumed to control DC_b and DC_f, the demand factors for C by bacteria and fungi, respectively. These demand factors were formulated to keep predicted element ratios within observed bounds.

Use of all substrates is governed by Michaelis-Menten equations. A general expression for the rate of uptake, U [μg element (g dry soil)$^{-1}$d^{-1}] is

$$U = D * \frac{V_m * X * B_c}{K_s + X}, \tag{1}$$

where the demand factor, D (a nondimensional variable ranging from zero to one), reflects the demand for a substrate by either bacteria or fungi, V_m [μg element (μg biomass C)$^{-1}$d^{-1}] is the maximal uptake rate, X [μg element (g soil)$^{-1}$] is substrate concentration, K_s [μg element (g soil)$^{-1}$] is the half-saturation constant for uptake, and B_c [μg C (g soil)$^{-1}$] is bacterial or fungal biomass. Table 1 gives the values used for uptake constants and specifies the demand factors used for combinations of substrate and microbe.

Metabolic wastes

Respiration rate was predicted using yield and maintenance factors (Hunt, 1977):

$$R = U_t * (1 - Y_{max}) + M * B_c, \tag{2}$$

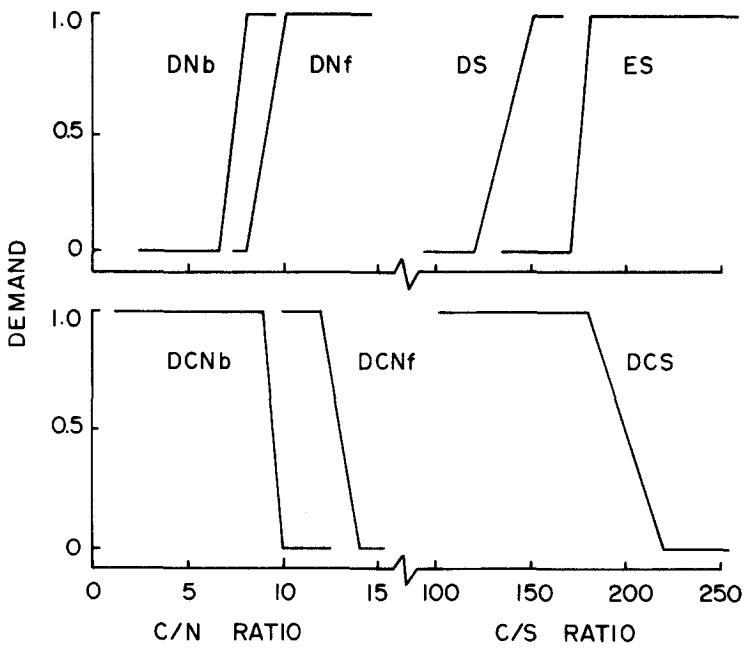

Figure 2. Effects of microbial C:N ratio on demand for nitrogen by bacteria (DNb) and by fungi (DNf) and demand for carbon by bacteria (DCNb) and fungi (DCNf). Effects of microbial C:S ratio on demand for sulfur (DS), demand for carbon (DCS), and release of sulfohydrolases (ES).

where R is the rate of release of CO_2 [μg C (g soil)$^{-1}$d^{-1}]; U_t is total uptake [μg C (g soil)$^{-1}$d^{-1}] by bacteria or fungi from all C sources predicted according to Eq. (1) and Table 1; Y_{max} is the potential growth yield (0.6 μg biomass C per μg C taken up); M is the maintenance rate [0.002 μg CO_2–C (μg biomass C)$^{-1}$d^{-1}]; and B_c is bacterial or fungal biomass [μg C (g soil)$^{-1}$]. The actual growth yield will be less than Y_{max}, the theoretical maximum, because of maintenance respiration.

Since organic substrates may contain elements in ratios different from those required by microbes and since the elements are assumed to be taken up from substrates in the ratio they exist, one or more elements may be in excess. Excess nitrogen was assumed to be released as ammonium. The rate of release, A_n [μg N (μg biomass N)$^{-1}$d^{-1}], was assumed to be inversely related to demand for nitrogen:

$$A_n = W_n * (1 - DN) * B_n, \tag{3}$$

where W_n is the maximal rate of release [0.05 μg N (μg biomass N)$^{-1}$d^{-1}], DN is DN_b or DN_f defined in Figure 2; and B_n is bacterial or fungal biomass N (μg N/g soil). According to Eq. (1) and Eq. (3), uptake and release of inorganic N will proceed simultaneously at intermediate C:N ratios.

Table 1. Parameter values and demand factors used in Eq. (1), the general expression for substrate use

Substrate	Microbial group *	Maximal uptake rate V_m [μg element (μg biomass C)$^{-1}$d^{-1}]	Half-saturation constant K_s [μg element (g soil)$^{-1}$]	Demand factor D (nondimensional)
Ammonium	b	0.1	20	DN_b (Fig. 2)
	f	0.1	20	DN_f (Fig. 2)
Nitrate	b	0.1	2	DN_b (Fig. 2)
	f	0.1	2	DN_f (Fig. 2)
Sulfate	b	0.002	4	DS_b (Fig. 3)
	f	0.002	4	DS_f (Fig. 3)
Cellulose	f	0.5	400	DC_f [Eq. (2)]
Dead microbes and products	b	0.16	1000	D = 1†
Stabilized soil organic matter	b	0.12	10000	D = 1†
	f	0.007	10000	D = 1†

* b = bacteria, f = fungi
† Microbial element ratios were assumed not to control use of these substrates, since they are good sources of C, N, and S.

Excess sulfur was assumed to be released as wastes in the form of SO_4^{2-} and organic sulphate, although there is little information available on this point. Excess sulfur is released at a rate proportional to the level of organic sulfate in the biomass according to an equation analogous to Eq. (3) for N mineralization:

$$A_s = W_s * (1 - DS) * B_s, \tag{4}$$

where A_s is rate of release of excess S [μg S (g soil)$^{-1}$d^{-1}], W_s is the maximal rate of release (d^{-1}), DS is demand for S as defined in Figure 2, and B_s is bacterial or fungal biomass S–O–C (μg S/g soil). For fungi, the maximal rate of release W_s takes values of 0.016 and 0.004 for SO_4^{2-} and organic sulfate, respectively. Corresponding values for bacteria are zero and 0.02. These parameter values were chosen in order for the model to reproduce the observed lack of S mineralization in the experiments of Saggar et al. (1981b). Bacteria are known to release large amounts of organic sulfate during growth (Fitzgerald, 1978), but there is little information about fungi.

Death

We assumed that microbes suffer no death during active growth, but that when the specific growth rate falls below 2% per day, death commences at 10% per day. The specific death rate then decreases exponentially by 3% per day as the organisms adapt to an inactive condition. Such a decrease in the death rate of bacteria is supported by data of Anderson et al. (1983), but little information is available for fungi. All dead bacteria and 95% of dead

fungi are transferred to the dead microbe compartment (Figure 1). The remaining 5% of dead fungi, representing a melanic fraction resistant to decomposition, are transferred to stabilized organic matter.

Transfer of ^{35}S isotope

Labelling the sulfate pool allows for S mineralization and immobilization to be distinguished in an experiment in which these processes go on simultaneously.

The transfer of ^{35}S was modelled by assuming that ^{35}S, when transferred into a compartment, is immediately and uniformly mixed with the S already present. As a consequence, the ratio of ^{35}S to ^{34}S in any transfer will be the same as the ratio in the source of the transfer. Although this assumption is never exactly correct, it would be difficult to build a more realistic model. A tracer model based on this simple assumption still will be useful for interpreting the data.

Every sulfur state variable was replicated for ^{34}S and ^{35}S. Transfers of ^{34}S were calculated as explained in the sections above, and then the transfer of ^{35}S was calculated as

$$^{35}\text{S flux} = {}^{34}\text{S flux} * \left(\frac{^{35}\text{S in source compartment}}{^{34}\text{S in source compartment}}\right)$$

The only exception to this scheme is the case of conversions back and forth between S–C and S–O–C in microbes, which were assumed to occur instantaneously for both ^{34}S, as explained above, and ^{35}S.

Sulfohydrolases

Plant roots, bacteria, and fungi all are capable of producing esterases and releasing them into the soil to hydrolyze sulfur esters (Fitzgerald, 1976):

$$\text{R–C–O–S–O}_3^{2-} + \text{H}_2\text{O} \xrightarrow{\text{sulfohydrolase}} \text{R–C–O–H} + \text{SO}_4^{2-}. \quad (5)$$

Most information about exoenzymes in soil (Kiss et al., 1975) is in terms of enzyme activity, rather than mass of enzyme, so that it is not possible to model exoenzyme production in terms of its energetic cost to the organism. Therefore, we represented sulfohydrolases E using arbitrary units (activity units/g soil) in a submodel that does not connect to the rest of the model via flows of matter:

$$\frac{dE}{dt} = 0.1\,(BF_c * ES + BB_c * ES) * \frac{S\text{–O–}C_t}{S\text{–O–}C_t + 1} - 0.05 * E, \quad (6)$$

where BF_c and BB_c are the biomass (μg C/g soil) of fungi and bacteria, ES is the effect of microbial C:S ratio on rate of release of sulfohydrolase (Figure 2), and S–O–C_t is the total amount of ester S susceptible to the action of the esterase. The negative term in Eq. (6) represents the inactivation or decay of exoenzyme at 5% per day. The equation embodies the assumptions that

sulfohydrolases are released at a rate proportional to microbial biomass, that release begins when C:S ratio is high enough to affect use of cellulose and occurs only in the presence of substrate (S–O–C), and that rate of release increases in a curvilinear fashion with substrate level. A further assumption is that exoenzyme production is inhibited by SO_4^{2-} levels above 2 μg S/g soil. The numerical constants in Eq. (6) were chosen to achieve a fit between model predictions and data (Saggar et al., 1981b) on levels of total and labelled sulfate.

The rate of hydrolysis [Eq. (5)], H [μg S (g soil)$^{-1}$d^{-1}], was assumed to follow the law of mass action:

$$H = 0.2 * E * H_u, \tag{7}$$

where H_u (μg S/g soil) is the amount of stabilized soil organic matter subject to the action of sulfohydrolases, E is sulfohydrolase level (activity unit/g soil), and 0.2 is the rate constant [g soil (activity unit)$^{-1}$d^{-1}].

Integration method

The model was solved as a set of difference equations, using a variable time step chosen to limit the rate of decrease of the fastest decreasing state variable to 40% per time step. Time steps ranged from 1.5 days to less than 0.05 day, and averaged about 0.6 day. This integration method represents a compromise between computing cost and accuracy of integration.

Model performance

Standard run

Figures 3–6 compare the fit of the model with data of Saggar et al. (1981b) on the Indian Head soil. This fit was achieved through iterative adjustments to parameter values in order to improve the correspondence between model and data, with constraints to restrict the values of constants to biologically reasonable values.

The model underestimates CO_2 evolution before day 20 in treatments with cellulose amendments but comes very close to the correct final values (Figure 3). The fit to the biomass data (Figure 4) is not as close as for CO_2. The major problem is that the model predicts about the same growth response to both the first and second cellulose amendments, while the data suggest a much smaller response to the second amendment. In treatment C2SO (see Figure 3 for explanation of the notation for treatments), the model predicts a slightly smaller growth response to the second amendment, as a result of S limitation, which appears not to have developed in treatment C2S1, considering the abundant supply of SO_4^{2-} at the end of the experiment (Figure 5). Nitrogen also appears not to be limiting (Figure 6). However it is conceivable that some factor not considered in the model, such as accumulation of

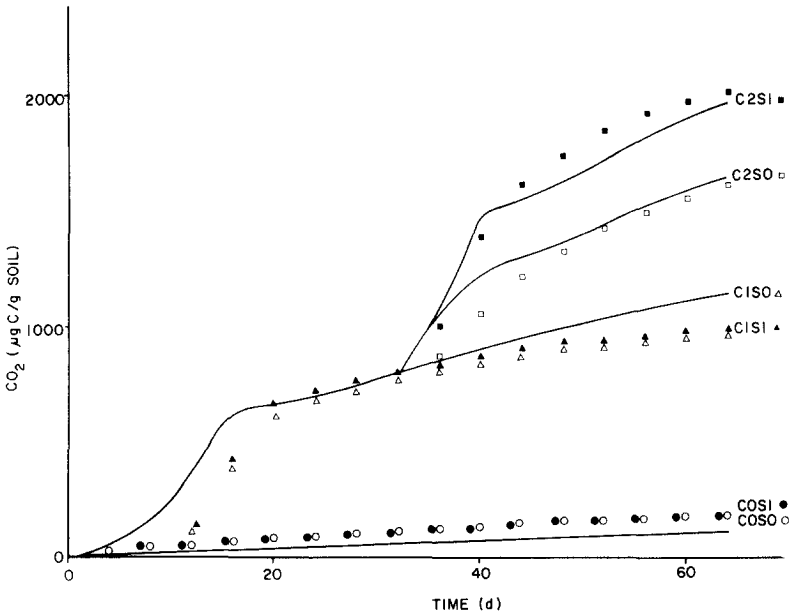

Figure 3. A comparison of data with model predictions of the effects of sulfate and cellulose amendments on cumulative CO_2 evolution. Data points from Saggar et al. (1981b). Treatment designations CO, C1, C2 indicate zero, one, or two cellulose amendments. SO and S1 indicate zero or one sulfate amendment (see text).

wastes, supply of another nutrient, or the activity of microbivorous fauna, lessened the growth response to the second amendment.

The model predicts that SO_4^{2-} falls to zero after about 50 days in the C2SO treatment, while the data indicate a residual level of one or two μg S (Figure 5). It is possible that the extraction used removes SO_4^{2-} from a pool that is not actually available to the microbes. Another discrepancy in the fit to SO_4^{2-} data is that the data indicate a slow continuous uptake of SO_4^{2-} after periods of peak activity in the cellulose-amended treatments and throughout the incubation in the unamended treatments, while the model predicts no such uptake. This may indicate that the thresholds in the demand factors used to control uptake (Figure 2) are incorrect and should be replaced with continuous functions in which SO_4^{2-} uptake continues at some low rate even at quite low C:S ratios.

Fit to the NO_3^- data is good, except that the model indicates too much of an effect of S amendment in the treatments amended twice with cellulose (Figure 6). The model assumes that all interactions between N and S are by way of C, and it may be that a direct interaction is needed to improve model performance.

The model correctly predicts the major features of both the dynamics and the treatment responses of CO_2, biomass, soil SO_4^{2-}, soil $^{35}SO_4^{2-}$, and soil

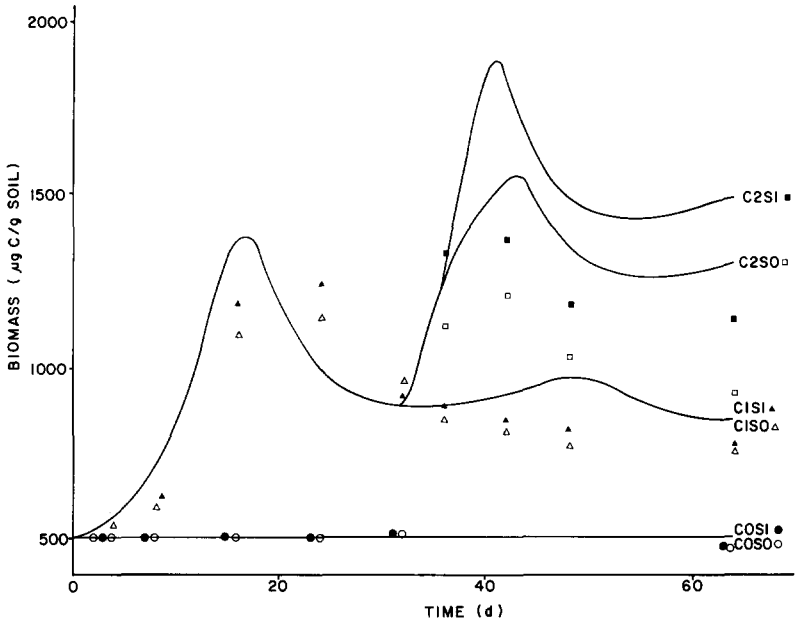

Figure 4. A comparison of data with model predictions of the effects of sulfur and cellulose amendments on biomass estimated by fumigation method. Data points from Saggar et al. (1981b). Treatment designation as in Figure 3.

NO_3^-. This is accomplished by a model that has biologically reasonable structure and without the use of any arbitrary factors to accomodate the wide range of conditions simulated. Such generally good agreement between model and data support the validity of the model, and we proceed to evaluate the ability of the model to simulate events in the Loon River soil.

Effect of soil type

The data (Saggar et al., 1981b) included two different soils representative of northern Great Plains soils with a sufficiency and a deficiency of S for agricultural production. The dynamics of CO_2, SO_4^{2-}, NO_3^-, etc., and the effects of the cellulose and S amendments were similar in the two soils, except for a delay in the development of peak rates of activity in the Loon River soil (Table 2). To test whether this delay could be accounted for simply by a difference in the initial population of cellulose decomposers, treatment C2S1 was simulated with all model parameters equal to those developed for the Indian Head soil, but with fungi initialized to one-tenth their original value. The initial value of bacteria was increased so that total microbial biomass at the start of the simulation would be the same in both the Indian Head and Loon River simulations. The model correctly predicted (Table 2) that the lag period between the first cellulose addition and the first peak was

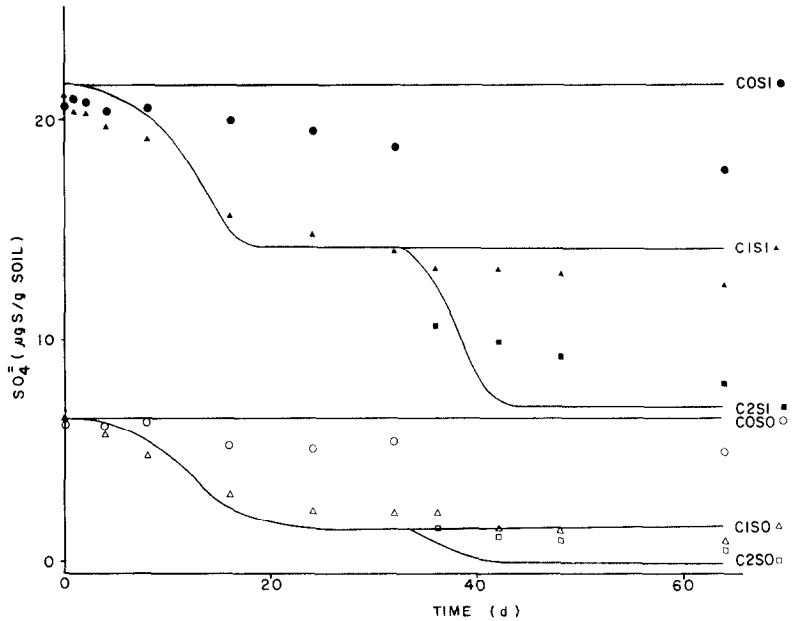

Figure 5. A comparison of data (Saggar et al. 1981b) with model predictions of the effects of sulfur and cellulose amendments on soil sulfate. Treatment designations as in Figure 3.

longer in the Loon River soil than in the Indian Head soil, that this difference between soils was less after the second cellulose addition than after the first, and that the relative increase in peak rate from the first to second cellulose addition was greater in the Loon River than the Indian Head soil. Thus, the model correctly predicted some of the qualitative differences in patterns of activity between the two soils, although the timing and magnitudes of the peaks were not predicted exactly.

Sensitivity analysis

The consequences of changing some of the assumptions in the model were tested. The objective of this exercise was to gain insight into the operation of the model and to help interpret the data.

In treatment C2S0, the model predicted that 2.0 μg SO_4^{2-}–S/g soil was made available by sulfatases. To determine the importance of this source of sulfate, treatments C2S0 and C2S1 were simulated in a version of the model eliminating the action of sulfatases. In treatment C2S1 there was no effect because sulfatases were not induced in this treatment in the original version of the model. However, in treatment C2S0, eliminating sulfatases caused the model to underestimate CO_2 output by about 20%, underestimate SO_4^{2-} levels by 2–3 μg after day 20, and underestimate N immobilization at the end of the experiment. In the standard run of treatment C2S0, one-third of the

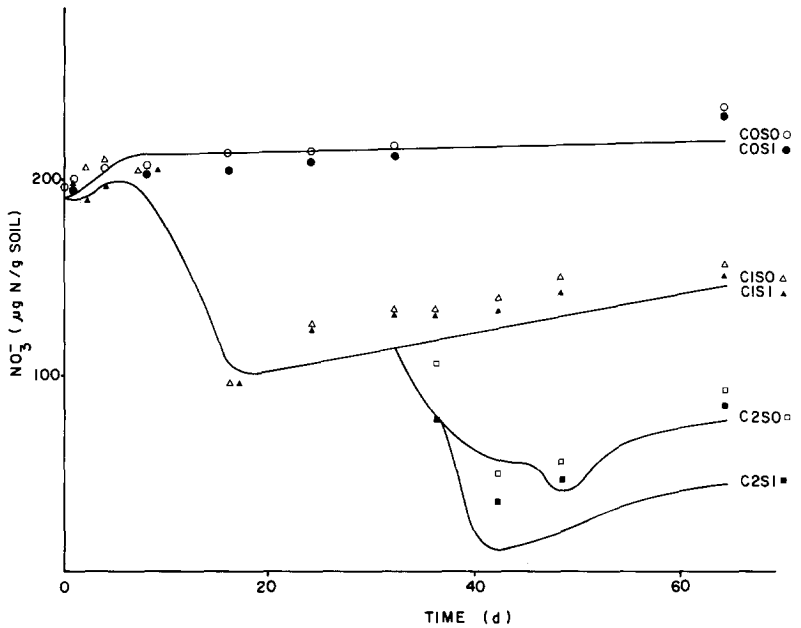

Figure 6. Comparison of data (Saggar et al. 1981b) with model predictions of the effect of sulfur and cellulose amendments on the dynamics of soil nitrate. Treatment designations as in Figure 3.

second cellulose amendment remained unused after 64 days because of S limitation, while in the run without sulfatases, two-thirds remained unused, which explains the dramatic model response to withholding so small an amount of S. $^{35}SO_4^{2-}$ was predicted more accurately in the absence of sulfatases because SO_4^{2-} was reduced to a lower level, and biomass was predicted more accurately because final biomass was not overestimated, as in the standard run. There was a dramatic decline in the specific activity of the SO_4^{2-} pool between days 10 and 20 both in the data and the model with sulfatases, while the model without sulfatases failed to show this decline. Thus, changes in specific activity provided the strongest evidence for the action of sulfatases.

Table 2. The effect of soil type (see text) on magnitudes and times of peak rates of CO_2 evolution observed by Saggar et al. (1981b) and predicted by the model. Cellulose was added on day 30

	Observed		Predicted	
Soil	Time (d)	Peak rate [μg C (g soil)$^{-1}$d^{-1}]	Time (d)	Peak rate [μg C (g soil)$^{-1}$d^{-1}]
Indian Head	15	100	13	73
	37	137	38	108
Loon River	24	48	24	70
	37	195	35	150

The temporal pattern of microbial growth in the model (fungal growth, fungal death, bacterial growth) is not supported directly by the data, but follows from the presumed superiority of fungi over bacteria in the use of cellulose, and superiority of bacteria in the use of dead microbes and products. To test the consequences of altering the two-phase growth pattern, model runs of treatments C2S0 and C2S1 were made in which the maximal death rate of fungi was reduced from 10% per day to 1%. As a consequence, total death of fungi was reduced by about 73%, final fungal biomass increased by a factor of 7 or 8, and final bacterial biomass decreased to about 48% of its former value. In spite of the large decrease in bacterial growth, other variables in the model were little affected and showed almost as good a fit to the data as before. However, with the lower death rate, the model failed to predict the observed effect of S amendment on CO_2 evolution. This failure was expressed in an underestimate of total CO_2 evolved in treatment C2S1, but not treatment C2S0. Further examination of the model output revealed that a greater fraction of the total S supply was retained in fungal biomass at the lower fungal death rate, which allowed the fungi to decompose a greater fraction of cellulose and partly to offset the smaller amount of bacterial respiration. Such relief of S limitation by reduced fungal death was effective only in treatment C2S0 without S amendment. In spite of the failure to predict the effect of S amendment on CO_2 at the lower death rate, comparable amounts of S and N immobilization and mineralization were achieved by very different balances between bacterial and fungal growth. Therefore, the good fit of the model to the data is not very strong evidence that the model correctly simulates this balance.

Discussion

An essential component of the model is the difference in chemical composition and element ratios between bacteria and fungi. In particular, an important hypothesis is that fungi store excess sulfate as ester sulfate (Fitzgerald, 1976; Saggar et al., 1981a) and therefore release a different form of sulfur as microbial metabolites in high-sulfate soils than in low-sulfate soils. This could help account for differences among sites in the composition of soil organic matter (Bettany and Stewart, 1983; Maynard et al., 1984).

An important hypothesis tested in this exercise relates to the fact that the ^{35}S dynamics and therefore the activity of sulfate in the soil solution could not be mimicked without invoking the action of esterases and the repressive effect of high soil solution sulfate concentration on esterase production, as predicted by McGill and Cole (1981). This hypothesis has received further collaborative support from experiments carried on later by Maynard et al. (1983).

We resisted the temptation to further tune the model to improve the fit to experimental data. One of the reasons for this is the difficulty of measuring sulfur in soil solution and in microbial cells. Saggar et al. (1981a)

developed a method for measuring microbial S in soils and stated that it was a preliminary approach and would have to be tested over a wide range of soils and conditions. Similarly, Saggar et al. (1981b) used the method of Voroney et al. (1981) for determining microbial N, but subsequent work on microbial N (Voroney and Paul, 1984) showed quite clearly that the recovery of microbial N using a chloroform technique depends on the C:N ratio of the microbial cell. More detailed work with microbial sulfur may also lead to modifications of the method. The availability of more accurate methods for determining sulfate in soils has depended on the automation of anion-exchange methods. These are now available and show that although the Johnson and Nishita method (Tabatabai and Bremner, 1970) for sulfate in soils (used by Saggar et al., 1981b) is accurate at high concentrations, it is subject to interference at low concentrations.

The simulation model is the first quantitative expression of our conceptual model (Hunt et al., 1983) of the importance of bond classes and esterase activity for sulfur cycling in soils. The success of the simulation model demonstrates the potential of these concepts for understanding element interactions. The model has now to be adapted to actual field conditions, where differences in sulfur concentration among horizons become important, environmental conditions are not controlled, and leaching will occur. These adaptations are not simple to accomplish, but quantitative models of interactions among three or more elements in ecosystems appear to be within reach.

Acknowledgements

Research supported by NSF research grant No. BSR-8105281, the Natural Sciences and Engineering Research Council of Canada, and SUDIC. Publication No. 437 of the Department of Soils, University of Saskatchewan. David S. Schimel, Michael B. Coughenour and David M. Swift provided useful reviews.

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