INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

SMR.780 - 71

FOURTH AUTUMN COURSE ON MATHEMATICAL ECOLOGY

(24 October - 11 November 1994)

"The Role of Soils in Global Change"

Ray R. Lassiter
U.S. Environmental Protection Agency
Athens Environmental Research Laboratory
Athens, Georgia 30605-2720
U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

These notes are excerpted from a report in preparation. Please excuse references to other sections and publications not included.

Ray Lassiter

MAIN BUILDING STRADA COSTIERA, 11 TEL. 22401 TELEFAX 224163 TELEX 460392 ADRIATICO GUEST HOUSE VIA GRIGNANO, 9 TEL.224241 TELEFAX 224531 TELEX 460449
MICROPROCESSOR LAB. VIA BEIRUT 31 TEL. 224471 TELEFAX 224600 TELEX 460392

Assumptions Forming the Basis of ***S***

In a model of a biogeochemical system, chemical transformations must necessarily be represented as net reactions that summarize a large number of intermediate reactions. It is apparent that system control via reactions that are below the resolution of the summary, cannot be represented by the model. Selection of model resolution, therefore, is guided -- in part -- by the intent to represent particular system controls. In our both our theory and model implementation, we have avoided a rigid specification of resolution in terms of specific reactions, preferring to leave open the possibility of a greater or lesser degree of summarization into net reactions, so that the effect of this aspect of system structure can be studied. Biogeochemical reactions, in general, are catalyzed by microbial populations whose size and activity depend on the concentrations of the soil chemicals, whose fluxes in turn depend on the density and activity of the populations. Hence we represent the system as consisting of the soil chemicals and the populations. In a similar sense to that of the chemical reactions being net reactions, the populations are represented as net populations, *i.e.*, more than one population may be involved in the actual transformations comprising the net reaction, but we represent it as though one population mediates the net reaction. This population is attributed the biochemical capacity to catalyze the net reaction and to respond to repressors of that capacity.

It is intended that essential microbial ecology be an outcome of this model. Specification of net chemical reactions and accompanying microbial kinetics does not explicitly specify ecological relationships. Some of the ecological interactions among microbial populations occur when substrates required by some populations are the products formed by others. These interactions will occur naturally in the coupled systems as formulated in ***S***. Symbiotic relationships can also arise naturally from such coupled systems in situations when a reaction is made to be thermodynamically feasible by a product-consuming organism. In these instances the product-producing process depends on the removal of product by the product-consuming population to maintain reactant and product concentrations that favor energy production from the process.

To create a model representing net reactions mediated by composite microbial populations, a set of strong assumptions must necessarily be made. ***S*** consists of this set of assumptions and the enabling quantities, equations and procedures. In the assumptions we try to make explicit the simplifications and abstractions made on our view of natural organic chemicals in soils to represent soil biogeochemistry. Other assumptions are made regarding soil properties, but these are not intentionally different from those usually made in models of water movement and transport of chemicals, and so are not elaborated here. The specific quantities (number of chemicals, number and specific functions of organisms) relate to the set of net reactions and populations constituting the current implementation of ***S***. The relationships are general.

i. The biogeochemical system is defined by a set of chemical reactions (reactants, products, stoichiometry (molar, electron equivalent), free energy change, microbial population mediating the reaction.)

ii. Sources of organic matter are plants (above and below ground litter and exudates), microbial cell components, microbially produced products, and by-products of microbially catalyzed reactions.

iii. All source organic material consists of a mixture of ten components (Table 1a). Each component represents a spectrum of chemicals whose properties are somewhat similar, but a component is treated in the model as if it were a specific chemical. The distribution of the chemicals in each type of source material (leaves, roots, dead microbial cells, *etc.*) is known (*i.e.*, specified).

iv. One organic material, humus, traditionally considered to be produced in the soil, is also treated as consisting of a specific chemical -- aliphatic (= "humus core") which is derived directly from (strictly, a constituent of) biomass -- and other refractory components, the exact composition of which, varies with environment.

v. Source material, upon entering the soil, is represented as separate quantities of the eleven chemicals. Nothing is implied about the location of chemicals within a soil element, nor their association with other chemicals. All decomposition dependencies are contained explicitly in the equations.

vi. Of the ten organic chemicals, five are insoluble and five soluble in water. We assume complete solubility or insolubility.

vii. Depolymerization of any biopolymer produces monomers. A transformation diagram (Figure 1) specifies the depolymerization-production couplings among the polymers and monomers for the current version of ***S***.

ix. Monomers are used by microorganisms for both synthesis and energy. Figure 2 shows the oxidation-reduction couplings among the monomers and oxidants, as well as the processes mediating the couplings for the microbially catalyzed energy transformations for the current version of ***S***.

x. The differential equation for microbial rate of change is expressed for each microbial population as a function of concentrations of substrates, inhibitors, temperature, moisture, and pH. A population consists of all organisms carrying out a given process and a single, ordinary differential equation adequately describes the rate of change of the entire population in a soil element.

xi. The set of reactions catalyzed by each microbial population for energy and synthesis is given for each population.

xii. Relative microbial uptake rates of dissolved chemicals are specified by a physically based or biochemically based function.

xiii. Production of biomass requires substrate for both synthesis and energy. Substrate consists of organic monomers and smaller molecules (for heterotrophs) and CO_2 (for autotrophs) plus inorganic chemicals (for both).

xiv. Energy is required to transform substrate to biomass. Energy used per quantity of biomass produced depends on the energetic difference between substrate and biomass.

xv. The free energy of formation of all redox reactants, growth substrate chemicals, and type of biomass is known.

xvi. Required soil properties can be obtained from soils databases, or by inference from other soil properties.

Figure 1.

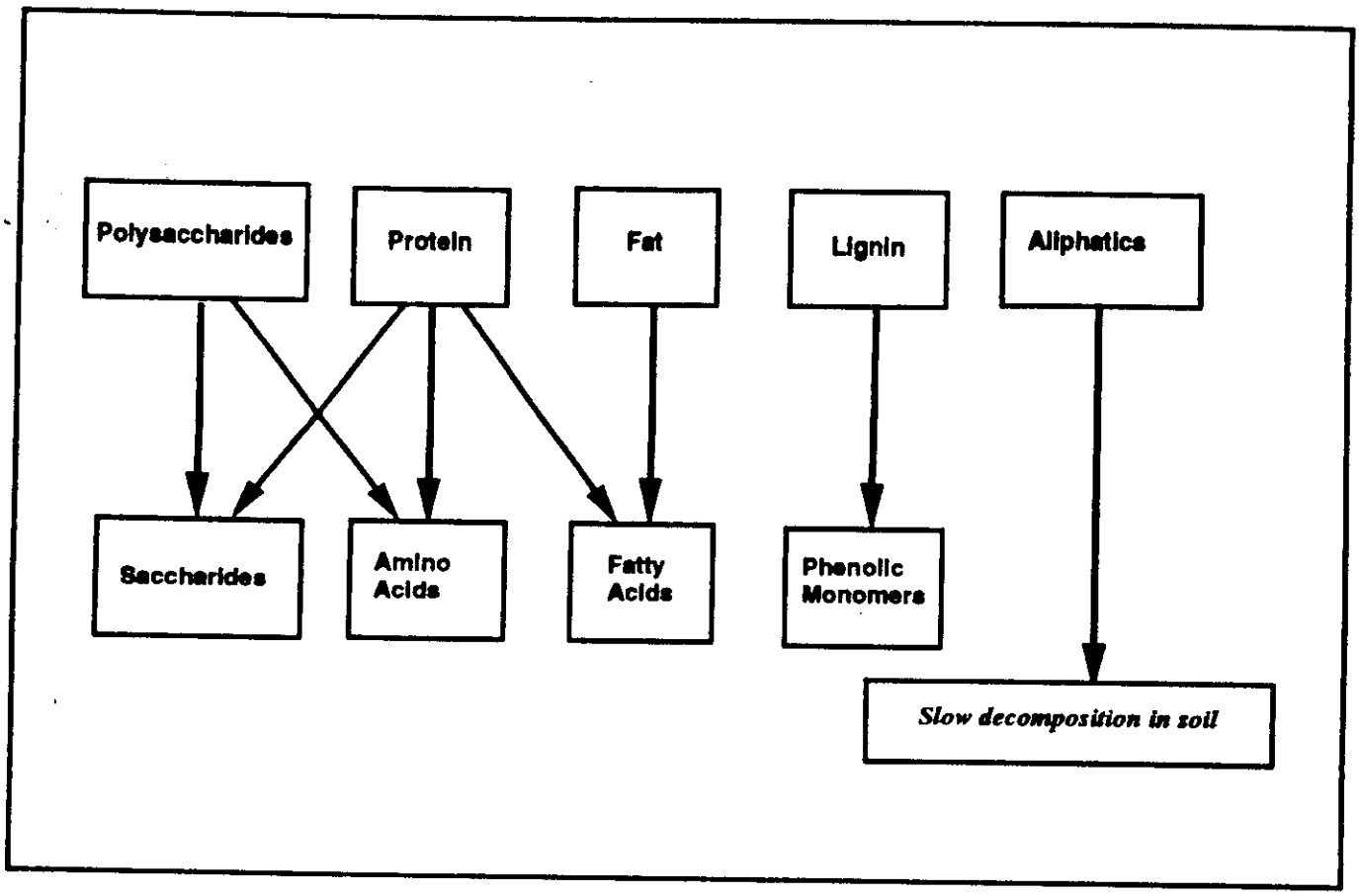
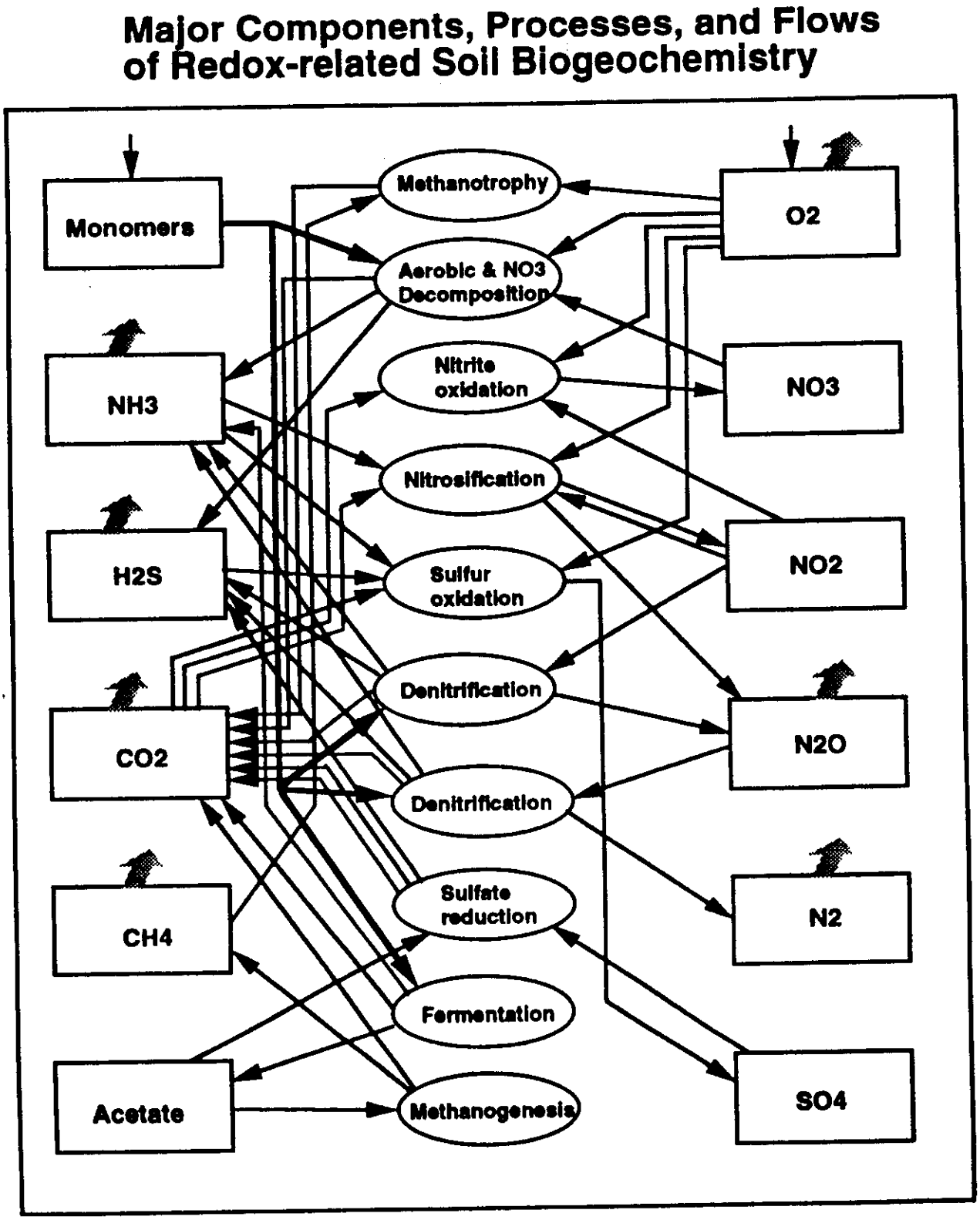

Polysaccharides
Protein
Fat
Lignin
Aliphatics
Saccharides
Amino Acids
Fatty Acids
Phenolic Monomers
Slow decomposition in soil

Figure 2.

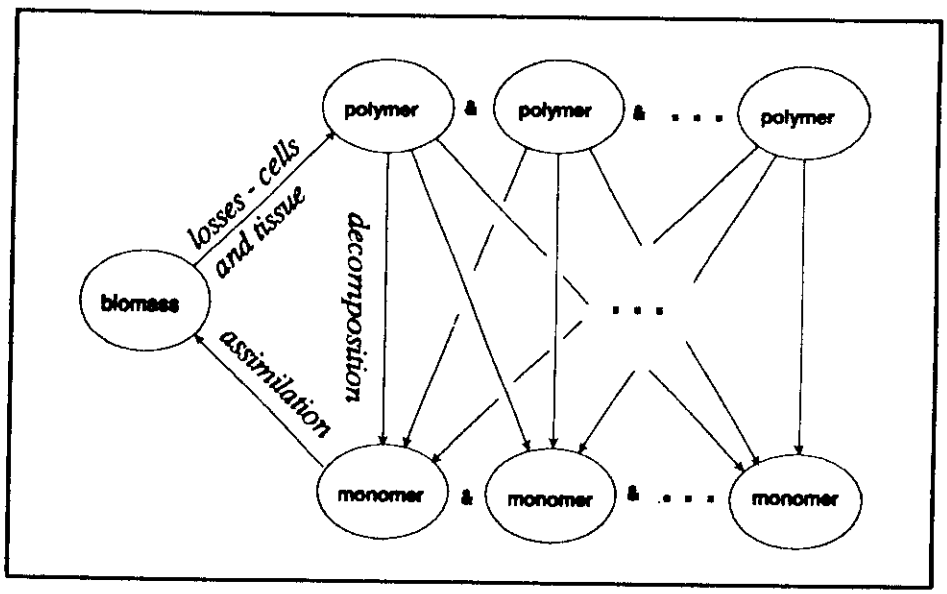

Major Components, Processes, and Flows of Redox-related Soil Biogeochemistry
Monomers
NH3
H2S
CO2
CH4
Acetate
Methanotrophy
Aerobic & NO3 Decomposition
Nitrite oxidation
Nitrosification
Sulfur oxidation
Denitrification
Denitrification
Sulfate reduction
Fermentation
Methanogenesis
O2
NO3
NO2
N2O
N2
SO4

Implementation of these assumptions in a kinetic model constitutes ***S***. For completeness ***S*** must be coupled with subsystems for exchange of energy and materials between the earth's surface and the atmosphere, and with a primary productivity subsystem. Such a system will constitute a model system of biogeochemical cycling.

A more graphic view of the biogeochemical system can be had by visualizing the chemical elements as cycling among three classes of chemical compounds: living biomass, non-living biopolymers, and monomers. Living organisms utilize monomers to create biopolymers (cell material and extracellular polymers). Production of extracellular polymer, loss of tissue, and death of cells produce non-living biopolymers. Biopolymers are decomposed into monomers primarily via extracellular enzymes of microorganisms, thereby completing the cycle. Utilization of the chemical energy stored in monomers provides the immediate source of energy to run the system. In a steady-state system, biopolymers introduced from primary producers balance entropic losses and effluxes of gases and solutes in water that passes through the system.

The process of assimilation (synthesis) is the linkage between monomers and biomass. Monomers are used for synthesis and energy to form biomass and other products. Composition of biomass and synthesized product does not necessarily reflect the composition of the substrate monomers, because some monomeric material is used for energy, and of the quantities that are used for synthesis, portions may be discarded as inorganic by-products, such as NH_3 or HS^-, or these inorganics may be obtained directly as supplemental growth nutrients. Linkages among monomer, polymer, and biomass are shown in Figure 3.

Figure 3.



Death of organisms or parts introduces polymers into the environment according to the polymeric constitution of biomass. The mixture that characterizes particular organisms is predefined in ***S*** for each type of organism (Appendix 1). When an organism dies, molts, loses roots, *etc.*, a mixture of polymers equal to both its mass and composition enters the soil.

The process of decomposition in which the polymers are broken down to monomers forms the linkage between polymers and monomers. Polymers consist of a predefined ratio of monomers, which defines their elemental composition. Decomposition of polymers introduces monomers into the environment in that ratio.

The cycle defined in the manner described accomplishes three things. First it permits conservation of mass across transformations among monomer, polymer and biomass. Second, it permits yield to be computed based on free energy changes occurring during assimilation of monomers into biomass and on the free energy of dissimilative redox reactions. Third, it removes the necessity to maintain a reservoir to deal with litter and litter decomposition. Litter, in this view, can be defined as the polymeric organic content of the topmost soil layers to be litter. Some of this polymer will have been contributed by turnover of microbial populations, but most of it will be of plant origin.

Transformations in S utilize chemical constituents dissolved in the soil water, providing substrate and energy for the synthesis of microbial mass, synthesis of extracellular organic products, and production of inorganic and organic metabolic products. The system includes the polymeric organic chemicals from higher plant residues and dead microbial cells, monomers and other chemical and biological components of the soil, and the related transformations. S is defined by equations for the rates of change of all these quantities. The rate-of-change equations are defined by their complete set of source and sink terms. The system of defining differential equations can be specified when the complete set of reactants is known. These quantities can be obtained based on a set of equations incorporating energy conservation, mass conservation for synthate (biomass and extracellular product), definition of yield, and equations that define the relative quantities of reactants that are used.

The components of the system are given in Tables 1a, 1b, and 1c.

Table 1a. System Variables[1]

Chemical	***Comment***
Biopolymer (insoluble)	
Polysaccharide	from plant and microbial sources
Protein	from plant and microbial sources
Lipid	from plant and microbial sources
Lignin	from plants
Aliphatics (= humus core)	from plant and microbial sources
Monomers (soluble)	
Saccharide	from polysaccharide
Amino acid	from protein
Fatty acid	from lipid, non-methane hydrocarbon, lignin
Phenolic monomer	from lignin
Acetate	(not a monomer, strictly) from fermentation of monomers

[1]The name of a chemical category is chosen somewhat arbitrarily after a major component of the category.

Table 1b. System Variables

Chemical	***Comment***
Inorganic chemical	
O_2	major oxidant in upper soils; diffuses into soils from atmosphere
CO_2	major greenhouse gas; dissolved and gaseous in soils; protonates as function of pH; from oxidation of all organics
NH_3	dissolved and gaseous in soils; protonates as function of pH; from amino acids and denitrification
N_2O	one of the three major greenhouse gases; dissolved and gaseous in soil; from denitrification and chemoautotrophy
NO_2^-	intermediate oxidant used by facultative anaerobes in denitrification; from denitrification and chemoautotrophy
NO_3^-	oxidant used by facultative anaerobes in denitrification; from chemoautotrophy
H_2S	dissolved and gaseous in soils; protonates as function of pH; from amino acids and sulfate reduction
SO_4^{2-}	oxidant used under anaerobic conditions without oxidized N compounds in sulfate reduction; from chemoautotrophy
CH_4	major greenhouse gas; dissolved and gaseous in soils; from acetate and $H_2 + CO_2$
H_2	general electron donor

Table 1c. System Variables

Chemical	***Comment***
Biota	
Wood rotting fungi	lignin-destroying
Fungi	depolymerizers of soil biopolymers
Facultative anaerobic bacteria	heterotroph; $NO_3^- \rightarrow NO_2^-$
Nitrite denitrifying bacteria	heterotroph; $NO_2^- \rightarrow N_2O$
Nitrous oxide reducing bacteria	heterotroph; $N_2O \rightarrow N_2$
Sulfate reducing bacteria	heterotroph; $SO_4^{2-} \rightarrow H_2S$
Fermentative bacteria	heterotroph; saccharides and amino acids $\rightarrow$ acetate
Methanogenic bacteria	acetate or H_2 and $CO_2 \rightarrow CH_4$
Ammonia oxidizing bacteria	chemoautotrophic nitrifier; $NH_3 \rightarrow NO_2^-$
Nitrite oxidizing bacteria	chemoautotrophic nitrifier; $NO_2^- \rightarrow NO_3^-$
Sulfide oxidizing bacteria	chemoautotrophic sulfur oxidizer; $H_2S \rightarrow SO_4^{2-}$
Methane oxidizing bacteria	chemoautotrophic methylotroph; $CH_4 \rightarrow CO_2$

Microbially Catalyzed Biogeochemical Transformations

Biogeochemical cycling refers to the whole suite of processes whereby chemicals are both transported and transformed. The transformations of relevance are microbially catalyzed, thermodynamically favorable, redox reactions involving organic monomers in one way or another, as well as related polymeric transformations. Transformations of organic monomers are primarily oxidations. Under anaerobic conditions oxidized forms of nitrogen and sulfur are used as oxidants and are reduced to forms that depend on the particular

reaction. When these reduced forms are transported to aerobic conditions or when local conditions become aerobic, they are returned to the oxidized forms, and this process continues cyclically. Generally these reactions are very slow by abiotic pathways, but are relatively rapid when they occur by enzyme catalysis utilized by microbiota to obtain energy for metabolism. Oxidized inorganic chemicals (*e.g.*, NO_3^- or SO_4^{2-}) can be used for growth and are reduced prior to assimilation into biomass. Upon death or loss of tissue into the soil, the reduced forms are released via decomposition, enter the biogeochemical cycling system, and under aerobic conditions are oxidized in the manner described.

Variation in the biochemical potential of organisms, *e.g.*, production of ATP per unit of free energy from substrate, has been found to be rather low in comparison to variation in their physiological performance, *e.g.*, growth, substrate utilization rates, etc. (3 - 12). Large variation in physiological performance is expected because it is modulated by variation in the energetic yields among the redox reactions utilized for energy, availability of complete growth substrates, variation in environmental factors, and repression of biochemical activity under some conditions. Representation of microbial populations and their activity at this basic level is attractive for dynamic modeling at the relatively high level of resolution used here, because it relieves some of the data requirements for performance of individual microbial species, and provides support for using a single growth equation to represent the total of all species-populations catalyzing a particular biogeochemical reaction, as we have chosen to do in this model.

The model of biogeochemical cycling in soils is based on the growth and death of microbial populations and the soil organic chemical reactions mediated by these populations for synthesis and energy during growth. Microbial growth and activity (effect on their chemical environment) are represented as processes that require substrate both as material for synthesis and to meet the energetic requirements of the synthesis process. Substrate for growth must be converted to biomass, and energetically, this entails the chemical alteration of substrate to products that are of the identical composition and at the mean oxidation state of biomass (3 - 5), a process that requires energy. Biochemically, the alteration must create the specific chemicals that comprise biomass, possibly requiring the uptake and assimilation of inorganic N and S (Appendices 2 and 3). The energetics are accomplished by different organisms in different ways (Appendix 4). In autotrophs either light or an inorganic redox reaction provides the energy to reduce CO_2 to sugars, followed by further biochemical processing to complete the transformation to biomass. In heterotrophs variable mixtures of substrate organic chemicals are oxidized with one of several possible oxidants to provide the energy to convert the substrates to biomass. One can conceive of biosynthesis as consisting of three kinds of processes: chemical reactions that build the cell's molecular composition, the polymerization of monomers into macromolecules, and physical ordering of macromolecules into structures that constitute functional biomass. Additional energy is required to create the highly improbable (from a statistical mechanics point of view), low entropy, living state. This step in biosynthesis increases the apparent mean free energy of formation of biomass over that of the mean of its pool of precursors. Development of the basis for the model of redox-based soil biogeochemistry is elaborated in Section 2.

Soil Organic Matter

Soil organic matter originates primarily as dead plant material, secondarily from animal and microbial resynthesis of existing organic material, and also from chemosynthetic fixation of CO_2 and accompanying synthesis of other inorganic substrates. Animal, fungal, bacterial, and chemical processes alter the original materials to form a variety of organic chemicals that differ in many ways, including structure, elemental composition, and

refractoriness to microbial decomposition. In this model we approximate these processes by defining a set of organic chemical classes that comprise all biota. Biota are defined, chemically, by their composition with respect to these chemicals. In principle this composition could be dynamic, but currently all biota are of fixed composition. In the process of losing biomass, exuding organic chemicals, or dying, the biota contribute to soil organic material. We represent this source of soil organic matter as fluxes of the separate soil organic chemicals.

The set of organic chemicals is defined so as to represent the spectrum of properties that determine the fate of organic chemicals in the soil. These properties include solubility, mechanism of decomposition (and hence refractoriness to decomposition), and relationship to the three major categories of monomer that drive the biogeochemistry leading to the production and consumption of greenhouse gases. Mechanism of decomposition establishes the conditions under which chemicals are decomposed and others formed, particularly formation of the monomer categories: saccharides, lipids, and amino acids, which as noted, drive the redox-based soil biogeochemistry that produces and consumes greenhouse gases. The basis of the model for the organic matter components of soil biogeochemistry is discussed in Section 3.

Soil Chemistry

Chemical and physical processes considered in S are divided into two categories: reversible and irreversible. Reversible physical processes include gas-liquid-solid phase equilibria, and the sorption of neutral molecules and exchange of positively charged ions onto soil surfaces. All the reversible processes currently represented in the model are considered to be fast, *i.e.*, their characteristic reaction or interphase exchange times are short relative to those of the irreversible (transport, microbial and diagenetic) processes. Some interphase exchanges might best be (but currently are not) represented as slow, reversible processes.

Forms of inorganic chemicals represented in the model are neutral gas-phase, neutral dissolved aqueous-phase, aqueous-phase ionized via protolysis, neutral sorbed to soil surfaces, and cation exchanged to soil surfaces (anion exchange is assumed to be unimportant in soils for our purposes). Thus ammonia, as an example, can exist in several forms including those considered to be significant in S, $[NH_3]$, $[NH_4^+]$, $[NH_4^+]_{ce}$, and $[NH_3]_g$, where the absence of subscript denotes the neutral aqueous phase form, and subscript indices, ce, and g, denote cation exchanged, and gaseous forms, respectively.

Cation exchange in soils depends on many factors including soil texture, mineral composition, ionic strength, and organic content. It is unnecessary here to represent cation exchange in the detail that would be required were pH computed dynamically. That is, knowledge of the entire suite of cations that are bound to soil is not required. Knowledge is required only of those that participate in the decomposition of naturally occurring organics and the corresponding transformation of oxidants. This places the focus on certain compounds or classes of compounds of the elements C, H, O, N, and S. Of the suite of compounds currently considered, only $[NH_4^+]$ is affected directly to any considerable degree by cation exchange. Cation exchange, therefore, can be represented in a manner that is just sufficient to permit calculation of the fractions of ammonia, rather than in a more general manner.

Biosynthesis occurs via polymerization of monomers that are obtained either directly or from anabolic processes from small intermediate molecules such as pyruvate or oxalacetate. If the cell is able to obtain the correct mix of amino acids directly from the environment, proteins are constructed with little energy spent on anabolism, and this is true similarly for the synthesis of other biopolymers when their constituent monomers are directly available. However, in the more probable case in which a biopolymer is constructed without the required mix of monomers available directly from the environment, substrate monomers are broken down to a small set of intermediate molecules and reassembled into monomers that are, in turn, used for biopolymer synthesis.

Computations within ***S*** do not make explicit use of these relationships (Equation 10) but growth rates are modified (Appendix 4) in a model that is intended to be thermodynamically consistent with these more detailed properties of microorganisms. Similarly, yield, which is expressed in one form as cell material formed per mole of ATP hydrolyzed, is computed in ***S*** from the overall free energy change of the microbial energy reaction without direct reference to ATP. We include an inefficiency factor that is a crude representation of the heat generated during electron transport, futile hydrolysis of ATP, reduction of the pH gradient by leakage across the cell membrane, and other factors. In ***S*** we take into account the net energy and mass change fluxes required to transform substrate into biomass. Energy is required to convert most substrate molecules into biopolymer, i.e., the free energy of the conversion *Substrate* → *Biopolymer* usually is positive, and although energy may be produced during some intermediate steps and consumed during others, we consider only the net energetic difference expanded by the inefficiency factor to account imperfect energy transduction.

Electron transport rate and the microbial growth expression

The electron transport rate (4), k_{max} ($eeq\ d^{-1}\ mol^{-1}$(Biomass)), is the fundamental kinetic quantity in this model. The physical meaning of this quantity is the maximal rate of consumption of energy substrate per unit of biomass, or more mechanistically, the maximal electron transport rate supported by the cellular biochemistry. McCarty (3) calculated values of k_{max} based on experimental data on aerobic and anaerobic heterotrophs, and on autotrophs. He reported a range of values of 1 - 2 $eeq\ g^{-1}$(Bacteria) d^{-1} at 298 K. This is remarkable consistency, and to a first approximation can be considered to be a constant, depending only on temperature. The maximal growth rate per unit of of biomass, μ_{max}, is given by the product -- $k_{max} Y_B$, and occurs when all factors are non-limiting, including energy substrate concentrations, growth substrate concentrations, moisture, and temperature. When any of these factors are limiting, their suboptimal conditions can be considered to be resistances to the achievement of the maximal growth potential.

We make the assumption that maximal steady state electron transport rate (*i.e.*, the transport rate that is achieved when conditions, including substrate availability, are favorable and not changing) is the *same for all bacteria*. This is a hypothesis, but an important one for simple application of our model. Organism-specific maximal electron transport rates would not alter our theory, but would increase the knowledge requirements for its application. Evidence that the hypothesis of a universal electron transfer rate is approximately correct (*i.e.*, low variance about a mean when considered across microbial taxa) is somewhat indirect, but not insubstantial. Energy for synthesis, mechanical movement, and other processes of *all* microbial cells is supplied directly by hydrolysis of ATP. In cells that use terminal electron acceptors (*i.e.*, those employing electron transport phosphorylation), ATP is formed predominantly via a reaction catalyzed by the ATP

synthetase mechanism driven by the proton motive force, which in turn is maintained by electron transport. The electron transport system is similar for all cells that carry out electron transport phosphorylation, the electron chain itself is not specific for electron donor and acceptor, and to the extent that microbial membranes are similar, electron transport rates too are expected to be similar, regardless of the electron donor and acceptor used. Hence it would appear that a basis exists for similarity of maximal electron fluxes per unit of cell for those cells carrying out electron transport phosphorylation. ATP formation via substrate-level phosphorylation also occurs, in general, via redox processes, and hence electrons are transferred. It is not clear, however, whether cells that utilize substrate-level phosphorylation are limited to the same maximal electron transfer rate as are those that utilize electron-transport phosphorylation, although McCarty (3) obtained a reasonable value of μ_{max} for fermenters using the same maximal electron transfer rate as for other organisms. Provisionally we include organisms employing substrate-level phosphorylation (fermenters) in this hypothesis[3] and depend on the low value of yield (Appendix 2) expected for the fermentation reaction to account for the lower specific growth rates observed for these organisms.

The expression for microbial growth as given in reference texts as a function of a single rate-limiting nutrient. Inasmuch as **S** is intended to function as a simulation model, we expand on that concept considerably in an attempt to reflect the various limitations that might be encountered in a global-scale simulation. We write the growth expression as the maximal growth rate times resistances potentially encountered in obtaining energy substrate and growth substrates, which we take to be independent biochemistries that might, but need not, use the same substrates for both energy and synthesis:

$$\mu = \mu_{max} \cdot g \cdot g_T \cdot B$$

with $\mu_{max} = k_{max} Y_B$ as noted above; g, the growth modulator due to suboptimal concentrations of energy substrates in the soil water; g_T, the growth modulator due to suboptimal synthesis substrates; and B, biomass concentration in the soil element. In Appendix 2 we develop g_T and its partition into components for biosynthesis and extracellular polymer synthesis; and in Appendix 4 we develop the expressions for g for the classes of energy metabolism considered in the current implementation of **S**.

Synthesis and energy reactions as used here are extremely abstract and simplified representations of reality. In reality thousands of individual processes (2) occur in serial and parallel and involve enzymes, ATP, NAD(P)H, the genome, and many other chemicals. Processing is highly coordinated, and one of the characteristics of the overall synthesis system is that the reactions are sequenced such that there are steps that involve the

---

[3]Substrate level phosphorylation occurs via redox reactions (although lyase reactions are also used (6)), and less free energy is produced per electron transferred, because of only partial oxidation. These reactions are not dependent on membrane bound carriers, and electron transport as such does not occur. Nevertheless mechanisms of electron exchange exist, and for cellular integrity, including elimination of fermentation products and maintenance of conditions favoring substrate-level phosphorylation, a membrane potential is maintained via the extrusion of H^+. These are common requirements, and, although accomplished mechanistically differently, add to the set of similarities upon which we rationalize our provisional hypothesis of the same maximal flux of electrons per quantity of cell mass for both classes of metabolism, *i.e.*, a single value of k_{max} for both electron transport phosphorylation and substrate level phosphorylation.

hydrolysis of ATP and the oxidation of NAD(P)H that make the net reaction thermodynamically spontaneous. The net of the quantities of ATP and NAD(P)H used are equivalent to the expenditure of the quantity of energy required to cause the net synthesis reactions to produce a negative free energy change. The ATP and NAD(P)H are derived ultimately from the energy reaction as described in Appendix 4. As noted above, in $\boldsymbol{S}$ we do not work at the level of detail described here, but rather deal only with net free energy changes and an efficiency factor, which includes in addition to the efficiency of energy transduction already mentioned, the degree to which the free energy for synthesis, on the average, is made negative[4].

Structure of the biogeochemical system model

Quantities of chemical substrate (reactants) are consumed and products (including biomass) formed in reactions catalyzed by microorganisms during growth. These reactions comprise most of the system biogeochemistry, and most of $\boldsymbol{S}$ is constructed in direct analogy to this view of biogeochemistry. The state variables of the model are the reactants and products of the system of reactions. Differential equations for the system quantities can be constructed for any system state for which the rates of the system of chemical reactions are known. The set of reactions is given, and what is required is to use the process models to obtain the rates at which the reactions proceed.

All microbial processes considered in $\boldsymbol{S}$ can be grouped into the two categories, energy production and synthesis, and synthesis into biomass and extracellular polymer. Process models for energy production are developed in Appendix 4, in which, k_m, the electron transport rate as limited by energy substrates is defined, and for synthesis in Appendix 2, in which, g_B, g_P,and g_T, the factors that modulate synthesis rates, are defined. Based on this categorization, separate reaction rates can be obtained for energy production, biomass production, and extracellular polymer production. Substrates are used according to their relative concentration in the soil water, with further discrimination among energy substrates based on inhibitions and competition for enzyme sites. The substrate-specific electron equivalent fluxes of the materials ($eeq\,t^{-1}$) are

energy production	e_{ij}
biosynthesis	b_k
extracellular polymer synthesis	p_l

in which $i = 1 \cdots n_a$, $j = 1 \cdots n_d$, $k = 1 \cdots n_b$, and $l = 1 \cdots n_p$. The $n's$ represent the number of substrates, with subscripts $a \Rightarrow$ acceptor, $d \Rightarrow$ electron donor, $b \Rightarrow$ biosynthesis precursor,

---

[4]Note that in the energy conservation equation the free energy for synthesis is equated to the negative of the free energy from the catabolic reaction times an efficiency factor. If this factor were considered to represent only heat losses from futile cycles of ATP plus leakage losses of $\left[H^+\right]$, etc., it would imply that energy requirements from catabolism are exactly the amount required to offset the positive free energy for synthesis. The net synthesis reaction, including energy input in the form of ATP and NAD(P)H used, would equal exactly zero, which implies equilibrium or the absence of process, *i.e.*, no change would occur in the substrate or synthate. Thus additional energy is required to favor the process. We have no basis by which to calculate this directly, so we bundle it with the other unknowns represented by φ.

$p \Rightarrow$ extracellular polymer precursor). They also define the number of chemical equations, with each equation representing a separate substrate. The number of energy equations is $n_a \cdot n_d$, the number of biosynthesis equations is n_b, and the number of extracellular polymer equations is n_p.

The usage of these quantities in constructing the system of differential equations constituting $\boldsymbol{S}$ is indicated below. Suppose we know that the following biogeochemical reactions (among others) occur and are mediated by a particular group of microorganisms whose physiology and biochemistry are similar. And from microbiological knowledge we know that they are used for energy and synthesis as noted below.

$$\nu_1^{X_1} X_1 + \nu_1^{X_2} X_2 \rightarrow \nu_1^{X_3} X_3 \quad \text{(energy production)} \qquad \textbf{(11)}$$

$$\nu_2^{X_4} X_4 \rightarrow \nu_2^{B} B + \nu_2^{X_5} X_5, \quad \text{(biosynthesis)} \qquad \textbf{(12)}$$

$$\nu_3^{X_6} X_6 \rightarrow \nu_3^{P} P + \nu_3^{X_7} X_7, \quad \text{(extracellular polymer synthesis)} \qquad \textbf{(13)}$$

where ν's are stoichiometric coefficients ($mol\ eeq^{-1}$) with subscripts referring to reaction number (arbitrary) and superscripts referring to its reactant or product, X's appearing on the LHS are reactants, on the RHS are products, B is biomass, and P is extracellular polymer that is synthesized by biomass.

Equation 11 is a biogeochemical transformation, with X_1 and X_2 perhaps representing an organic compound (electron donor) and an oxidant (electron acceptor), and X_3 possibly representing a greenhouse gas product, such as CO_2, CH_4 or N_2O. Equations 12 and 13 represent microbial removal of the environmental chemicals (X_4 and X_6) for synthesis. We wish to construct terms corresponding to these reactions in the differential equations representing rates of change of all system quantities. Reaction rates can be indicated by multiplying the substrate-specific mass fluxes by the corresponding reaction.

$$e_{11}\left(\nu_1^{X_1} X_1 + \nu_1^{X_2} X_2 \rightarrow \nu_1^{X_3} X_3\right) \qquad \textbf{(14)}$$

$$b_1\left(\nu_2^{X_4} X_4 \rightarrow \nu_2^{B} B + \nu_2^{X_5} X_5\right) \qquad \textbf{(15)}$$

$$p_1\left(\nu_3^{X_6} X_6 \rightarrow \nu_3^{P} P + \nu_3^{X_7} X_7\right) \qquad \textbf{(16)}$$

meaning that all quantities in Equation 14 change at the rate of e_{11} electron equivalents per unit of time or that X_1 changes at the rate of $e_{11}\nu_1^{X_1}$ moles per time, etc., and similarly for Equations 15 and 16. Subscripts reflect the simplicity of the example in which $n_B = 1, n_P = 1, n_a = 1$ and $n_d = 1$. The differential equation terms follow immediately.

$$\frac{dX_1}{dt} = \cdots - e_{11}v_1^{X_1} \pm \cdots$$
$$\frac{dX_2}{dt} = \cdots - e_{11}v_1^{X_2} \pm \cdots$$
$$\frac{dX_3}{dt} = \cdots + e_{11}v_1^{X_3} \pm \cdots$$
$$\frac{dX_4}{dt} = \cdots - b_1v_2^{X_4} \pm \cdots \qquad (17)$$
$$\frac{dB}{dt} = \cdots + b_1v_2^{B} \pm \cdots$$
$$\frac{dX_5}{dt} = \cdots + b_1v_2^{X_5} \pm \cdots$$
$$\frac{dX_6}{dt} = \cdots - p_1v_3^{X_6} \pm \cdots$$
$$\frac{dP}{dt} = \cdots + p_1v_3^{P} \pm \cdots$$
$$\frac{dX_7}{dt} = \cdots + p_1v_3^{X_7} \pm \cdots$$

Reactants imply sink terms and products imply source. When repeated for all the reactions in the system, the full set of differential equations will have been completely written. From algebraic solutions for e_{ij}, b_k, and p_l, values can be obtained at each point in time, and the system can proceed stepwise through computations of the system variables through time. As far as it goes, this is a close analogy to the computational approach taken in the software implementation of ***S***. When all reactions that are postulated to represent the system biogeochemistry are represented, several other population and chemical variables appear, and the set of differential equations derived from such a set constitute a model for the kinetic components of biogeochemical cycling at a point in the soil. Any full model will be considerably larger than the example, but not much more complex. The major additional complexities are hydrolysis of biopolymers to monomers, couplings of product to reactant equations, and equilibrium inorganic chemistry. Biopolymer hydrolysis rates are proportional to the total growth rates of the populations mediating the hydrolysis, given as in the differential equation for B above. Couplings are not represented in the example, but introduce no significant new complexity to the relationships. Inorganic chemicals are represented by the system, *e.g.*, by components X_3, X_5, and/or X_7, but if an inorganic component speciates protolytically, the differential equation becomes

$$\frac{dX_i'}{dt} = \cdots + e_{11}v_1^{X_{ij}} \pm \cdots \qquad (18)$$

where X_i' represents the total of all species of component i, and X_{ij} represents the j^{th} species of component i, the j^{th} species being the one liberated in the reaction. The equilibrium chemistry calculations, then, are carried out to determine the distribution of the species after the total of all species has changed by the quantity $e_{11}v_1^{X_{ij}}\,\Delta t$.

Population Mortality Rates. Mortality, m, is taken to be a function of both temperature and soil moisture. It is death of cells and is accounted as a direct biomass loss rate. Unlike maintenance, which produces only inorganic products, mortality contributes directly to the ten categories of organic matter, according to the composition of the population. But as with the maintenance rate function, the mortality rate function is an *ad hoc* formulation intended to describe the behavior over a reasonable range of temperature and moisture, and is not mechanistically related to underlying processes:

$$m(T,\theta) = b_1 e^{b_2(T - Topt)^2 (b_3 - \psi - \theta)} \qquad (33)$$

The parameters, b_1, b_2, b_3, and $Topt$, are specific to each population. $Topt$ is also a parameter in the factor that modulates biological rates as a function of temperature. When soil moisture, θ , is at saturation, $\psi + \theta = 1$. We assume this to be the least stressful condition on the microbial activity, and b_3 is selected as a value: $1 < b_3 \leq 2$, such that the mortality rate due to temperature alone can be calculated (Fig. zz).

3. Soil Organic Matter

Soil organic matter consists of an extremely wide variety of compounds. We represent soil organic matter, in keeping with our representation of other model components, according to functional categories. By association with the types of chemicals assumed to belong to each category, they are characterized by common properties of these chemicals. The categories are described in Table 1a. All organisms are assumed to consist of a subset of the categories of organic matter (Table 2). A property of each category is its elemental composition, and therefore, mass conservation on each of the elements can be used when accounting the fate of each of the categories. As the organisms die, lose leaves, limbs, *etc.*, they contribute their characteristic combination of organic matter categories to the soil organic matter. The organic matter cycle is schematized in Figure 3.

Polymeric organic chemicals are continually decomposed to produce monomers via action of fungi and bacteria. In general these processes do not produce energy directly, but microbially mediated redox reactions using monomers and other small-molecule substrates produce the energy that drives essentially all the processes occurring in the soil. Biochemical transformations accompanying the growth of heterotrophic microbial populations are based directly on the utilization of organic substrates for synthesis, as electron donors in energy reactions, and also as electron acceptors in fermentation reactions. The disposition of monomeric organic matter in the soil and its importance in biogeochemical cycling are central to the previous section.

Litter. Litter is the accumulation of recently dead and shed components of plants. No special reference to litter is required in this model, but because it is a commonly used concept, it can be viewed in the following manner. The top layer of soil can be equated to surface litter, the O_1 horizon (21). It is assumed to consist of insoluble polymers and organics in soil solution from material that has been deposited on the surface during the current year, with each year's contribution turned over annually into the second layer. The second layer, the O_2 horizon, therefore, consists of the accumulation of insoluble polymers and dissolved organics derived locally and transported from the first layer. The third and deeper layers (A and B horizons) consist of a mixture of mineral soil, dissolved chemicals, and insoluble polymers that originate in the layer from shed root parts and microbiota. For computations within S, reference is made to all layers identically, *i.e.*, to the chemical and microbial system present as mass per volume of the soil layer with reaction rates based on mass per volume of water within the soil layer. There may be differences in physical properties among any of the layers, and especially between the top two layers and those below (17).

Decomposition of organic polymers (except lignin) is assumed to occur via hydrolytic enzymes released by fungi and bacteria. There is evidence that many exoenzymes may be long-lived in the environment (52, 53), possibly protected somewhat from decomposition by other enzymes by sorbing to soil particles. For some enzymes, their environmental steady state could be nearly independent of instantaneous densities of the microbial populations from which they derive. Present level of knowledge of the exoenzyme input-output rates and factors controlling them does not provide strong support for any model as a close analogy to the natural process. We represent microbial decomposition of polysaccharide, protein, and lipid (but not lignin) as a second-order kinetic process in polysaccharide and other polymer (*i.e.*, either polysaccharide, itself, lipid, or protein). The rationale for this model is based on the observation that depolymerization enzymes have a considerable lifetime in the soil, and on our representation of all extracellular polymer as lumped into the chemical group -- polysaccharide, which therefore contains exoenzymes. We assume -- without proposing a mechanism -- that exoenzymes comprise a constant proportion of the polysaccharide group regardless of season or environmental condition. This assumption is made simply to facilitate a reasonably simple model, and is at best only a crude approximation, because of the temporal variation in sources of polysaccharide from plant and microbial sources. Thus the second-order process is assumed to be a direct interaction between extracellular enzyme (represented by a constant fraction of the polysaccharide chemical group) and either lipid, protein or, polysaccharide, itself.

Polysaccharides, proteins, and lipids. Polysaccharides comprise the largest category of soil organics. Cellulose is the predominant polysaccharide in the source material originating with plants (22, 23) constituting about one third of all CO_2 fixed by green plants. The predominant polysaccharide in soils, however, may be mucopolysaccharides originating from the continuous action of bacteria (22). Mucopolysaccharides serve to bind soil particles, influencing the textural properties of the soil.

Proteins originate from the same sources as do polysaccharides, *i.e.*, from plants and microorganisms. Many are produced as extracellular products (52, 53), but most derive from dead plant and microbial tissue. Although exoenzymes (cellulases, proteases, and lipases) generally are proteinaceous, our current model represents them as a part of the polysaccharide chemical group as noted above.

Lipids derive, as do polysaccharides and proteins, from dead plant and microbial tissue. This category represents a very diverse group in terms of the refractoriness of the macromolecule. Whereas phospholipids and triglicerides are relatively labile, waxes and resins are relatively refractory. The distinction between lipids and the category labeled "aliphatic" in terms of specific compounds represented is purposefully obscure at this time. Waxes and resins might best be considered to be part of the aliphatic category. It is not necessary, for present purposes, to be explicit in this regard. It is only necessary to quantify the composition of organisms with regard to content of the categories.

In Appendix 2 a model is derived in which growh and the production of extracellular polymer occur according to

$$G_B = k_m Y_B \frac{[\mathrm{C}][\mathrm{N}]}{(K_1 + [\mathrm{C}])(K_2 + [\mathrm{N}])} B$$

$$G_P = k_m Y_P \frac{[\mathrm{C}][\mathrm{N}]}{(K_1 + [\mathrm{C}])(K_2 + [\mathrm{N}])} B$$

The rate of change of the i^{th} organic chemical component (except lignin) in the j^{th} soil layer from n_s plant and microbial sources and being decomposed by n_B groups of microorganisms is given by

$$\frac{dC_{ij}}{dt} = \sum_{k}^{n_s} F_{ijk} - r_{pi} C_{pj} C_{ij}, \quad i \neq \text{> lignin, humus, p => polysaccharide.} \quad \textbf{(35)}$$

Values of the second-order decomposition coefficient, r_{pi}, vary considerably, especially across the i chemical categories, which range from polysaccharides that decompose relatively rapidly to some lipids that decompose extremely slowly. Values of r_{pi} are assigned to represent the relative refractoriness of the polymers, as well as to account for the fraction of the total polysaccharide pool consisting of exoenzyme. The sources, F_{ijk}, are given both by other models coupled to this model, most notably a vegetation model, and by terms from other equations, such as equations for microbial rates of change, *i.e.*, loss terms from rates of change equations for microbial populations and extracellular biopolymer synthesis rates. We choose not to write such terms explicitly at this point, however, to avoid unnecessary complexity.

Lignin. The second most abundant source material originating from terrrestrial plants is lignin (22). Lignin is an irregular polymer that decomposes very slowly in soils. Because of its high input rate to the soil and its slow turnover rate, it is desirable to represent lignin decomposition especially well in order to closely approximate quantities of soil carbon. Lignin is decomposed primarily by wood rotting fungi, the principal organism studied being the white rot fungus, *Phanaerochaete chrysosporium*. These organisms depend on a strictly aerobic environment to function, no ligninolysis being observed below an oxygen concentration less than 5% and are stimulated by high oxygen concentrations (25). In contrast to the way that other natural polymers usually are decomposed, highest rates of ligninolysis occur when fungal populations are not growing or are in decline due to C, N, or S limitation (25, 26). Experiments by Jeffries, *et al.* (26) showed that fungi at greater densities decomposed lignin more rapidly, in spite of the fact that the populations were

stationary or in decline. Recent work has implicated several enzymes secreted by fungi in the decomposition of lignin: laccases, extracellular phenol oxidases, lignin peroxidases, manganese peroxidase (27). Some of these enzymes require the presence of singlet oxygen and others hydrogen peroxide. Presence of nutrient forms of C, N, and S at usable concentrations represses the formation of these enzymes (28), derepression occurring when any one or more of these nutrients become limiting. Ligninolysis by some fungi, *e.g.*, *Dichomitus squalens*, (27) is not repressed by the presence of N and S nutrients, and hence, decompose lignin regardless of the nutrient status. This behavior, however, is apparently the exception, and we represent the process as occurring similarly to the descriptions for *P. chrysosporium* and others that decompose lignin only when in decline. Apparently no model representing ligninolysis according to this behavior has been published.

To obtain a model for ligninolysis, we assume that fungi employ a biochemical system that produces lignin degrading enzymes when it is not repressed by some form of C, N, and S. The derivation is given in Appendix 6. The equation is

$$\frac{dC_{lj}}{dt} = \sum_{k}^{n_s} F_{ljk} - \sum_{m}^{n_m} \left(\frac{r_{ml} C_{lj}}{1 + K_{ml}^{-1} g_{Bm}} \right), \quad l \Rightarrow \text{lignin} \qquad (36)$$

where r_{ml} represents the microbial-mass-specific characteristic ligninolysis rate per unit lignin concentration in the soil element when growth rate is zero. Its value is $\frac{1}{2} r_{ml}$ when g_B equals K_{ml}.

Humus. Traditionally humic substances have been considered to be comprised of three fractions: fulvic acids, humic acids, and humin. These categories are defined with reference to their acid and base solubility upon treatment with strong base followed by acidification of the solute. Humin is the portion insoluble in strong base, humic acids are soluble in the base but precipitate upon acidification, and fulvic acids are soluble in both (54). By this chemical categorization, it would appear that all soil organics are humic substances. Because of the specifics of microbial degradation of polysaccharides, lignin, etc., we identify several categories separately, and thus deviate from the categorization of humic substances based on separation techniques. Much of the recent published discussion of humus formation also departs from this traditional operational definition, postulating partial structures, precursors and formation pathways (44 - 48).

We assume that humic substances are formed by preservation of parafinnic components and other relatively refractory chemical components, accompanied by selective degradation of the labile chemical components of dead algal, bacterial, and plant tissues. The mix of biopolymers will reflect the plant sources and the properties of the environmenbt affecting decomposition. For example, no mechanism exist in *S* by which lignin can disappear from anaerobic soils. Humic substances, therefore, are defined in *S* via computational "separation techniques", *i.e.*, by whatever categories of soil organics that we might choose to call collectively "humic substances" for some immediate purpose. This corresponds most closely to the selective degradation pathway of humic substance formation (47), but is somewhat more restrictive. Selective preservation of the aliphatic components during degradation, followed by condensation of nitrogenous materials has been suggested (47), but knowledge of these mechanisms does not appear well enough developed to support mechanistic modeling. We do not represent humic substance formation as consisting of any

condensation process in the soil, but rather as a mixture of the very long-lived paraffinic constituents of biota and other remaining organic chemical constituents of the soil.

Nitrogen content of terrestrial humic acids is found in about a 10:1 to about 50:1 atomic C:N ratio (50, 51). The wide disparity in atomic ratios is probably due to the varying lignin and other structural organic chemical content of the organic mixture that is extracted as humic substances. Stevenson (52) gives an average empirical formula for humic acids (ignoring S) to be $C_{10}H_{12}O_5N$. N:S ratios range from 3:1 - 8:1. An empirical formula for humus as we might compute it, however, is expected to be more aliphatic than would be implied by Stevenson's formula, especially in moderately dry to dry soils.

Humus decomposition, however, is more problematic. Apparently there are few published discussions of humus decomposition mechanisms, especially for the parafinnic fraction that corresponds to our definition. Because of our definition of the humus core as aliphatic with nitrogen- and sulfur-containing subgroups, we can assume that it is broken down much more slowly than other categories of biopolymer. We further assume that it is broken down only in the presence of oxygen, which is required for transformations leading to beta oxidations of aliphatic chains. We represent the rate of change of humus as a variation on Equation 35, with

$$\frac{dC_{hj}}{dt} = \sum_{k}^{n_x} F_{hjk} - C_{hj} O_j \sum_{p}^{n_B} r_{ph} G_{Bp}, \quad h \Rightarrow \text{humus} \qquad (37)$$

with symbols as defined, and with $O_j = \frac{[O_2]}{K_{ho} + [O_2]}$, without specific derivation, on the assumption that O_2 is required separately from the O_2 required in growth, and its use is enzyme mediated independently of other requirements; K_{ho} is the $[O_2]$ for which humus decomposition rate is half maximal.

4. Soil Chemistry

Much of what has been discussed above is soil chemistry, albeit microbially mediated. A few other aspects of chemistry are required by ***S***, primarily equilibria among chemicals distributed among protolytic, surface-cation-bound, sorbed, and neutral species, and between the aqueous and gaseous phase. To obtain good approximations of these equilibria, we must have a representation of cation exchange, and of the effects of temperature on equilibria. The distribution of chemicals among these forms is required both because microbiota transport some of the forms and not others to a significant extent, and because gas-phase transport is of major importance to the focal prediction of ***S***, *viz.*, exchange of trace gases across the soil-atmosphere interface.

Chemical equilibria. In the current version of ***S***, pH is not computed dynamically, but is taken to be a soil property that is independent of the microbially mediated biogeochemistry. Adopting this point of view does not preclude time dependent values of pH, *e.g.*, where a seasonal variation is known. For long simulations wherein soil organic content undergoes major changes in both composition and quantity, pH conceivably could undergo corresponding changes, and dynamic simulation might become necessary. To do so, more information is needed of the mineral content of soil and perhaps other characteristics than