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"Process Model for Soil Biogeochemical Cycling"

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

Chapter 6. Process Model for Soil Biogeochemical Cycling

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Introduction

Soils properties and processes interact with the climate system via exchange of heat and radiatively important gases, most notably water vapor and greenhouse trace gases. Although exploratory research has been done, soils processes have not been widely included in global models dealing with climatic change. Wilson *et al.* (1987) found that changes in soil texture influenced the results of the Biosphere-Atmosphere Transfer Scheme to an extent equal to or greater than did changes in vegetation. Other soils properties, especially the dynamic properties that are involved with the production and consumption of trace gases have not been evaluated. Biogeochemical models that include soils processes and that are suitable for inclusion in three-dimensional global models have not yet been formulated, although considerable work in biogeochemical modeling exists, including some in a climate change context (Schimel et al., 1990; Hunt et al., 1991). Production and consumption of greenhouse gases in soils are major processes in the global budgets of these gases. The ability to estimate the quantity of this exchange as a function of appropriate properties of the environment is needed for development of earth-system models in which climate and biogeochemistry interact.

Exchange across a soil's surface depends on atmospheric and soil gas concentrations and soils properties. Hence, models to represent these important processes should be functions of soils properties, of the gradients of gas concentrations between atmosphere and soil, and should compute gas production and consumption within the soil based on fixed and transient soil properties. This work is directed toward contributing to the production of a general model of the biogeochemistry underlying greenhouse gas production and consumption that will be suitable for inclusion in three-dimensional earth-system models. A major motivation for this work is interest in evaluation of biospheric feedbacks, which will require the interaction of a climate model and a biospheric model. By *general model*, it is meant that the equations describe at the selected resolution what are believed to be the dominant processes controlling element cycling in soils, including both aerobic and anaerobic microbial transformations.

The model is formulated in terms of kinetic equations describing microbial processes in the soil with soil properties given by parameterization. Many more equations could have been included to attempt to account for even more soil chemicals. Choice of what to represent and what to omit is a somewhat arbitrary but extremely important aspect of modeling, determining exactly what the model represents. Fortunately choices of what to represent are not irreversible -- this model is still undergoing change in this regard. The intent is to arrive at a model that will reliably predict the exchange fluxes of radiatively important trace gases across the soil's surface. The approach taken is to write equations to predict production and consumption of oxidized and reduced chemical species as a function of the concentrations of oxidants, reductants, soil moisture, and temperature. In a model implementation in which the kinetic model is distributed vertically with surface exchanges of gases, influx of liquid water, and transport primarily by water movement, net production of greenhouse gases can be computed for that vertical column, including exchange across the soil's surface.

Representation of the Soil Column

The soil column is represented as a one-dimensional (vertical) object, characterized by several static properties including bulk density, texture (sand, silt, and clay content), and porosity. It also is characterized dynamically by several quantities including the mass density (mass per total volume) of new and old biopolymers, the concentrations of organic monomers, acetate, methane, and several inorganic chemical species in the soil water and bound to soil particles; and for the volatile species, their mass density in soil air. Hydraulic conductivity, gas diffusivity, and dispersion coefficients for the movement of soil chemicals also are dynamic properties inasmuch as they vary as a function of the soil matric potential in unsaturated conditions. Matric potential constrains microbial activity (activity slows with drying). Evapotranspiration is a function of the distribution of root density with depth and the gradient of atmospheric to soil water potential with depth (See Chapter 2).

Transport moves chemicals to zones where they are oxidized, synthesized into organic matter, or reduced. Most of the redox processes are mediated by micro-organisms' enzyme systems from which the organisms derive energy for life processes. These transformation processes can be visualized as individual sources or sinks of the reactant or product that is referenced. When the transformations yield products that exist partly as trace gases (carbon dioxide, methane, nitrous oxide, ammonia, and hydrogen sulfide), they move in the vapor phase with portions transferring to the atmosphere across the soil-air interface.

Back-diffusion of trace gases from the atmosphere also occurs. The rate of change of concentration of any chemical, C_t, at every point in the soil column can be represented as:

$$\frac{\partial C_T}{\partial t} = \frac{\partial}{\partial z}\left[D \frac{\partial C_T}{\partial z} - A C_T \right] - S \qquad (6.1)$$

Equilibrium among the forms and phases and the following relationships are assumed to hold true locally (within a vertical soil element):

$$D = D_W (\beta_d + \beta_i) + D_g \beta_g \qquad (6.2)$$

D_W mixing coefficient of solution phase constituents

D_g mixing coefficient of vapor phase constituents

$\beta_j = \beta_j (K_j, P_j)$ fraction of C_T in form or phase j

K_j set of parameters (equilibrium, temperature, activity, etc. coefficients)

P_j set of environmental quantities ($[H^+]$, temperature, etc.)

j $\in$ {dissolved (d), ionized (i), ion exchanged (e), sorbed (s), (g)) gaseous}

$$A = v_l (\beta_d + \beta_i - \beta_g) + \alpha \qquad (6.3)$$

v_l average liquid vertical velocity

S sum of biogeochemical transformation terms -- sources and sinks of C_T

α gas flow terms due to pressure changes.

The soils biogeochemistry model, which is the primary subject of this Chapter, relates entirely to the terms of S. The other terms are discussed in Chapters 2 and 5. The soil chemicals currently included in this model are forms of carbon, nitrogen, and sulfur. Transformations among these chemical forms are represented as occurring via kinetics of microbially mediated redox transformations in the presence of local equilibria for speciation, sorption, and ion exchange for the chemical forms and for changes between liquid and gas phases. A schematic representation of microbial kinetic processes in soils is presented in Figure 6.1.

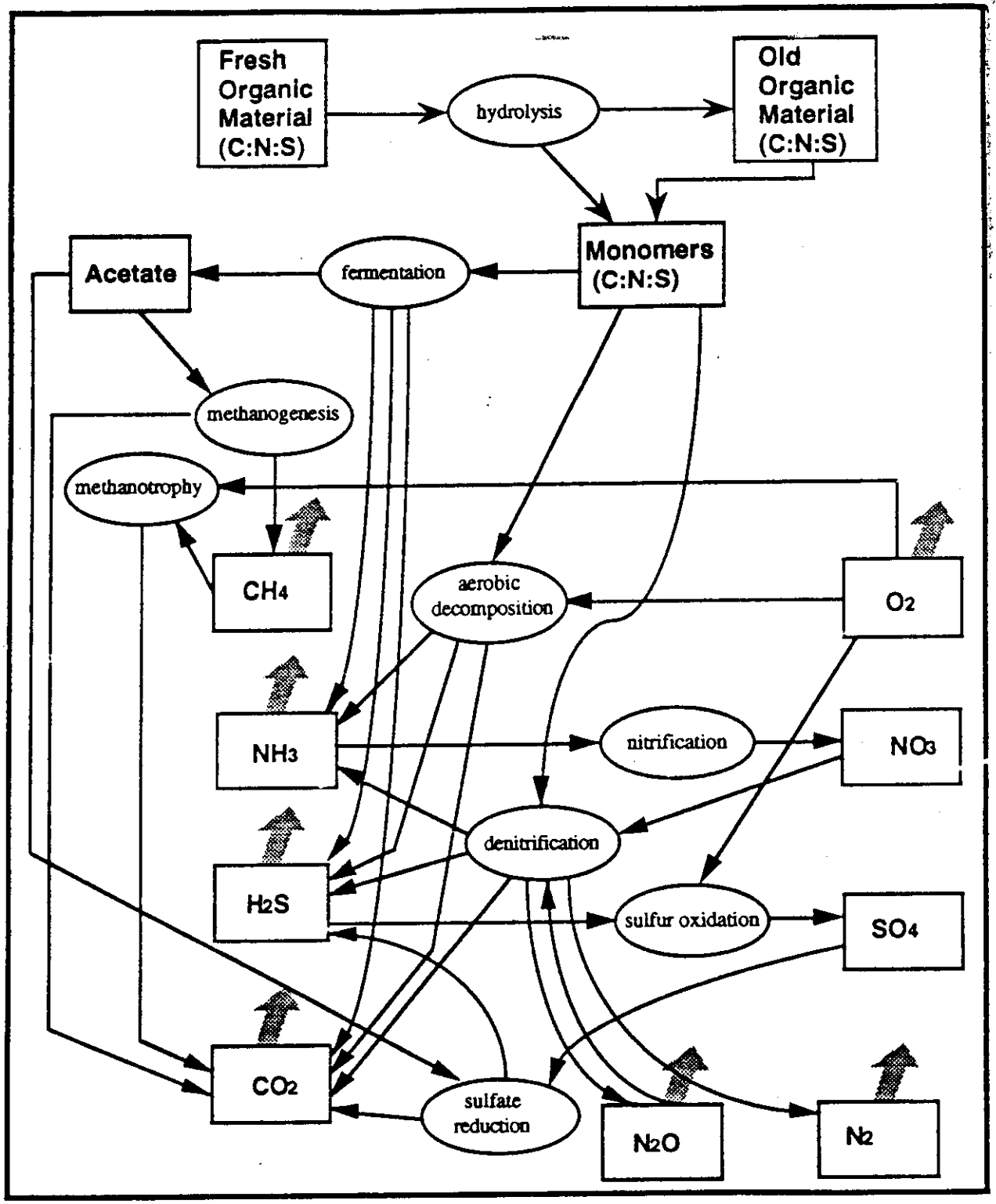

Figure 6.1. Components (boxes), processes (ovals), and reactants or products (arrows) of soil biogeochemistry model. Components that can exist in the gas phase are indicated by attached shaded arrows.

Biopolymer decomposition

The soil receives organic matter at the surface from litterfall, and in the subsurface from root exudation, sloughing and death of roots and root components, and from production of microbial biomass throughout the column. Fresh organic matter (OM1 -- a mixture of monomers and biopolymers, some readily digestible) is leached and depolymerized by microbial activity (primarily fungi under aerobic conditions) resulting in the production of free monomers (a mixture of soluble organic components) and more refractory polymers (OM2), which also are depolymerized, but considerably more slowly. The current implementation of the model contains these two categories of polymeric organic matter, as well as a pool of mixed monomers and a pool of acetate.

Current work is underway, however, to evaluate published information on humification and subsurface organic matter production (see Chapter 4 for progress on the latter subject, and Chapter 3 for the current model status for both surface and subsurface organic matter production). Current theories involve the reaction of amino acids with leachates or products of microbial decomposition, such as phenols or sugars, and subsequent condensation of the products to form dark-colored, high-molecular-weight products that are resistant to further microbial attack. These chemicals, although formed from microbial decomposition products, are not themselves formed via microbial enzyme systems, and hence are of variable composition (Paul and Clark, 1989).

Depolymerization is not a redox reaction. (It is predominantly hydrolysis.) Metabolism of the organisms carrying out the depolymerization occurs via oxidation of organic substrates by oxygen, accompanied by carbon dioxide production. Accounting of the oxygen demand and other aspects of these metabolic processes are omitted in the current model. It is quite possible that these three generic categories of organic material (fresh biopolymers, old biopolymers, and monomers) will not be adequate to represent the spectrum of turnover times needed for long term simulations. Other soils models, in part because they have been primarily concerned with the aerobic components of the spectrum of biogeochemical processes, represent many more categories of organic material (Hunt et al., 1991; Schimel et al., 1990; Hunt, 1977). In these models, however, other soil chemical processes have been represented in considerably less detail than here. Other models have incorporated specific aspects, *e.g.*, interaction of the C:N ratio and decomposition rate (Parnas, 1975). In conjunction with and following the evaluation of published information noted above, this area will undergo a re-evaluation for a more appropriate representation, particularly with respect to the production of organic matter by the root systems of vegetation and the formation of humic and other long-lived soil organics and classes of

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organic matter. In the work to date, polymeric organic matter is assumed not to exist in either aqueous or vapor phases; hence, they are not transported. Monomers and all other components are soluble, and many exist as gases. Hence, these components move within the soil.

Disappearance of each of the organic matter pools is represented as a rate process in concentration (mass per soil volume) of OM1 or OM2 multiplied by a hyperbolic factor in oxygen. Oxygen is not represented as being used stoichiometrically, because it is not a reactant in organic matter decomposition, but rather is a requirement of the fungal decomposers' growth and maintenance metabolism. The fungal metabolic oxygen demand is accounted in their use of monomers for energy. (Currently, however, use rate of monomers for energy is not coupled to depolymerization rate; it will be coupled in future implementations.) Thus, although we represent oxygen as having a modulating role in depolymerization, depolymerization is not coupled to the differential equation for oxygen via a loss term there. The depolymerization process term appears in the differential equations for OM1 and OM2 as loss terms and in the monomer differential equation as a source term. Figure 6.2 represents this process schematically.

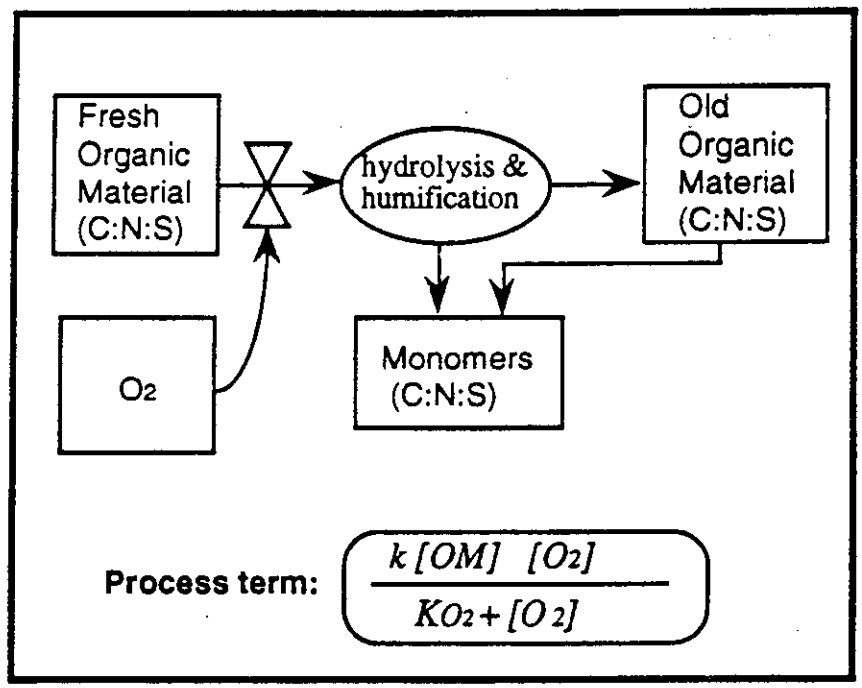

Figure 6.2. Decomposition of organic material of plant and microbial origin and production of soil organic matter and monomers.

Monomer oxidation

The monomer pool is the primary source of reduced substrates for soil biogeochemical reactions. It contains substrates for both aerobic and nitrate-based decomposition (denitrification). If oxygen is present, only aerobic decomposition occurs, because oxygen represses the enzyme systems responsible for denitrification. In wet soils, and with increasing depth, oxygen is depleted while monomer substrate remains. Under these conditions, oxidation of monomers accompanied by nitrate reduction and the production of N_2O and N_2 usually occur.

The differential equation describing the rate of change of monomer contains the disappearance terms of OM1 and OM2 as source terms, and loss terms in monomer concentration and oxidant (oxygen or nitrate). Unlike the decomposition of organic matter, oxygen (and nitrate) are reactants (oxidants) and hence are used stoichiometrically. These terms multiplied by stoichiometric coefficients appear as loss terms in the oxygen, nitrate, and monomer differential equations, and in the equations for the products as source terms. Figures 6.3 and 6.4 present the monomer oxidation process schematically for aerobic (Figure 6.3) and anaerobic (denitrification -- Figure 6.4).

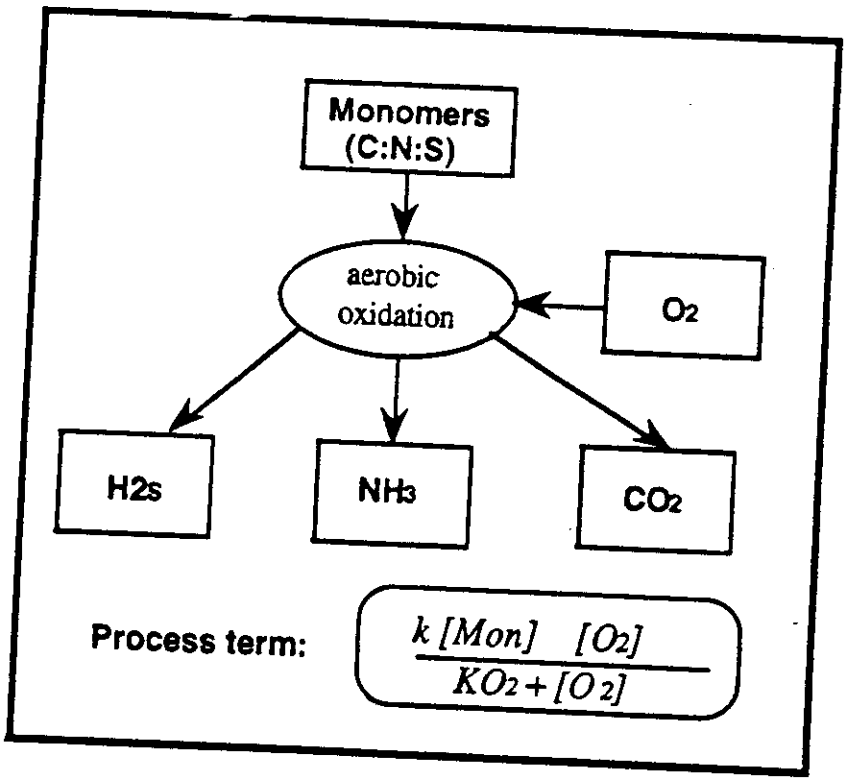

Figure 6.3. Oxidation of monomers with oxygen as the terminal electron acceptor, and the production of products according to the stoichiometric makeup of the monomeric substrate.

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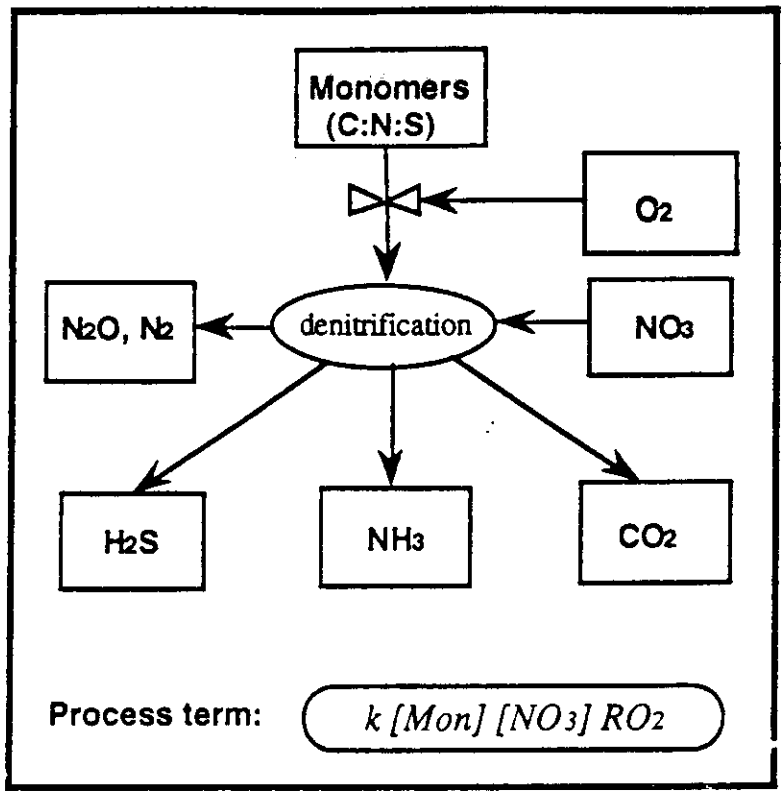

Figure 6.4. Denitrification

Fermentation

Under anaerobic conditions some monomers can be used for energy by microbial populations in redox reactions without an inorganic oxidant entering into the reaction. In fermentation, one organic molecule is oxidized via the reduction of another. The net effect is the loss of monomers and production of acetic acid and a few other low molecular weight organic acids. The net process includes hydrolytic removal of -HS and $-NH_2$ groups to produce H_2S and NH_3.

The fermentation reaction is represented as first order in monomer, but with a repression factor in oxygen that causes the rate term to approach zero rapidly as oxygen increases from near zero concentration. In general, substances that repress reactions are not used to any significant degree in the reactions, and hence, repression terms are not coupled to the differential equations of the repressants. The process term appears in the differential equation for monomers as a loss, and in the equations for acetate and other products as a source. A schematic of the process is presented in Figure 6.5.

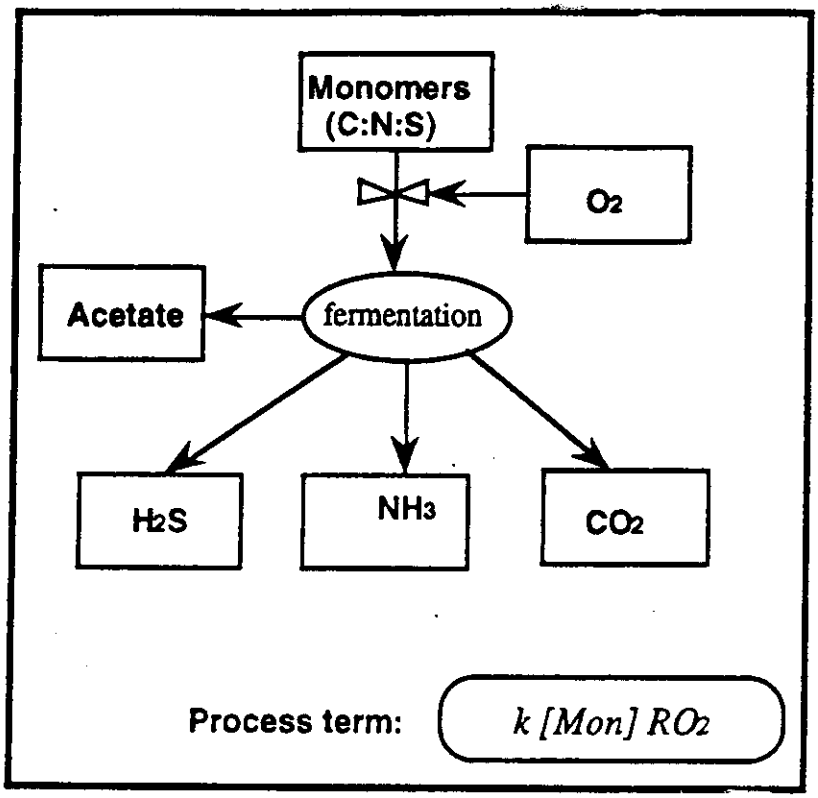

Figure 6.5. Fermentation

Sulfate Reduction

No sulfur-containing greenhouse gas is of current, direct concern to this research. Sulfate reduction, however, is crucial in the production of methane, out-competing methanogenesis for the substrate, acetate. Other components of the sulfur cycle must be represented in order to achieve a useful level of accuracy in the representation of sulfate reduction. Acetate is used as a reduced substrate in microbial energy production via a redox reaction using sulfate as the oxidant. This reaction also is repressed by the presence of oxygen.

This reaction is represented as a product of acetate concentration and a hyperbolic factor in sulfate concentration, and with a repression factor in oxygen that causes the rate to approach zero rapidly as oxygen increases from near zero concentration. Both acetate and sulfate are used stoichiometrically, and hence, terms appear with appropriate stoichiometric coefficients as losses in their differential equations and as sources in the equations for the products. A schematic of the process is presented in Figure 6.6.

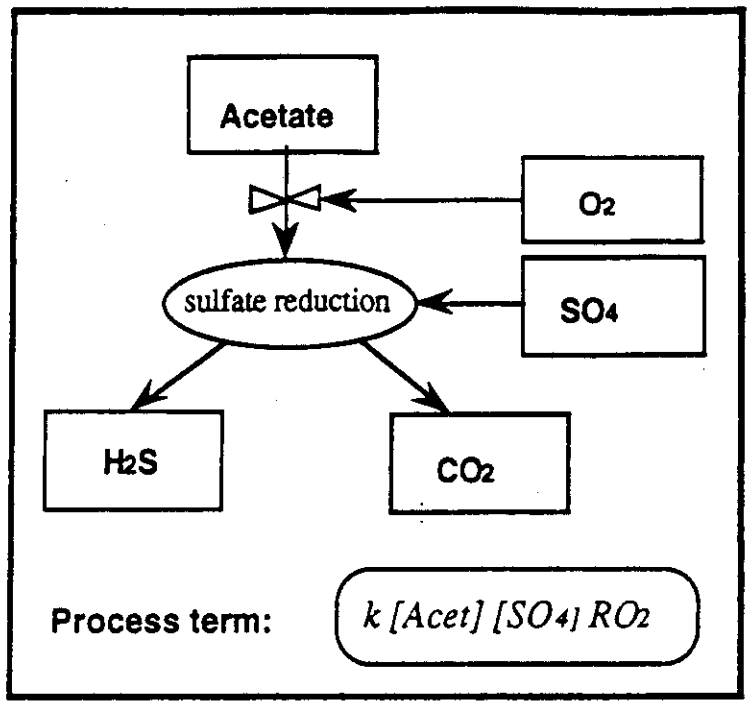

Figure 6.6. Sulfate reduction

Methanogenesis

Methanogenesis can occur as a decomposition of acetic acid into carbon dioxide and methane as well as a reduction of carbon dioxide by molecular hydrogen. Production from acetic acid is the predominant pathway in natural systems (Phelps and Zeikus, 1984). It is inhibited by the presence of nitrate (Bollag and Czlonskowski, 1973). The processes of methanogenesis and sulfate reduction are competitive for acetate. Generally, sulfate reducers have a higher affinity (a lower half saturation constant) for acetate than do methanogenic bacteria, resulting in acetate levels below the half saturation concentration for methanogens and consequent low production of methane when sulfate is present. This is sometimes referred to as inhibition, but is more appropriately represented here as competition for resources, which comes naturally out of the equations as described.

The reaction is represented here as first order in acetate, with an inhibition factor by nitrate. The process term appears as a loss in the equation for acetate and as a source in the equations for CO2, and methane. A schematic of the process is given in Figure 6.7.

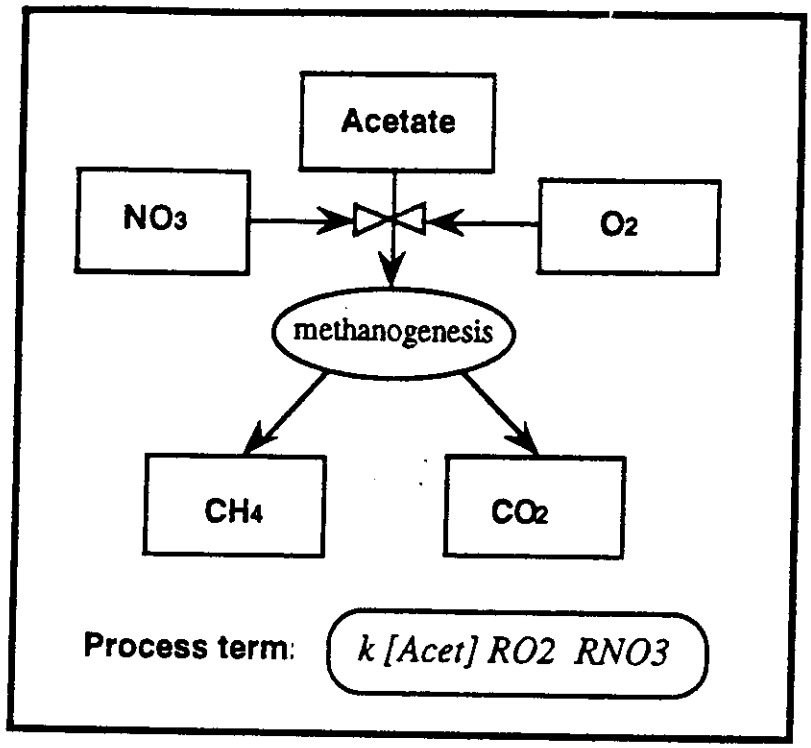

Figure 6.7. Methanogenesis. Inhibition by oxygen and nitrate are indicated, but competition for acetate is not explicitly represented here, because this competition derives from the interaction of this process with the sulfate reduction process and hence is of a higher order of interaction than this figure portrays.

Methane Oxidation

Methane production and oxidation are terminal processes for organic material in soils. If methane is produced below an aerobic surface layer of soil, it can be oxidized as it diffuses through this layer. Ammonium nitrate fertilizer has been observed to inhibit this process (Steudler et al., 1989). Observations have also suggested that sulfate reducers might oxidize methane (Ward and Winfrey, 1985), but only the aerobic pathway is currently included in this model formulation. Biosynthesis is omitted from the model, but in the methylotrophs, methane (or other source of methyl or reduced single carbon compounds) is required for growth -- biosynthesis occurs via de novo composition of cellular constituents from single carbon compounds other than CO_2.

The process term is represented as a product of methane concentration and a hyperbolic factor in oxygen concentration. Both methane and oxygen are used stoichiometrically, and the term appears with stoichiometric coefficients as a loss in the differential equations for methane and oxygen, and as a source in the equation for carbon dioxide. A schematic representation of the process appears in Figure 6.8.

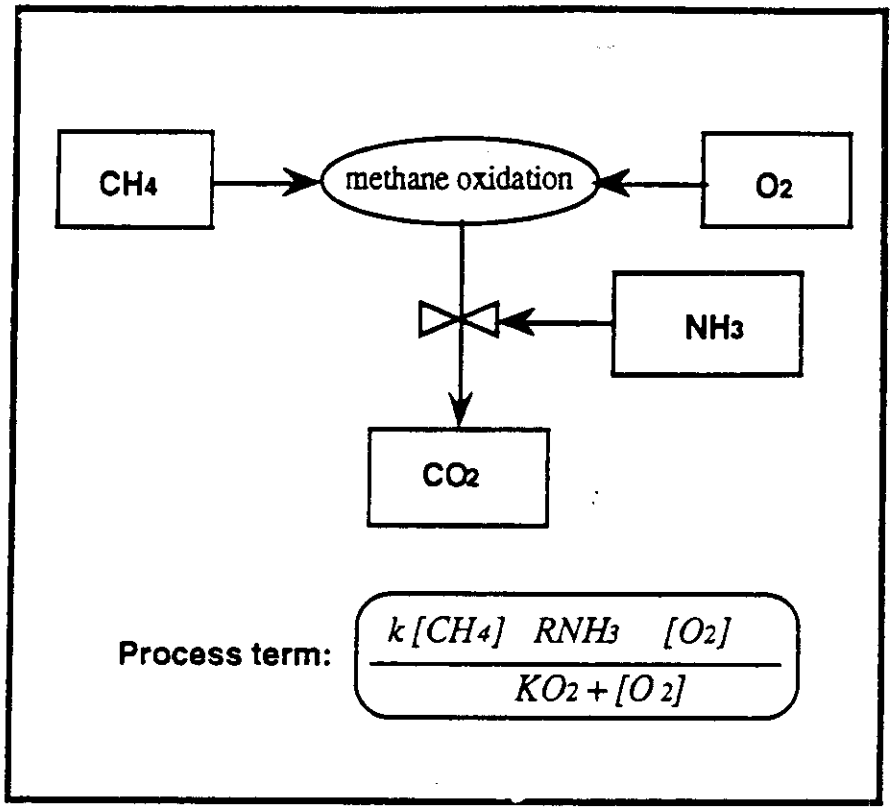

Figure 6.8. Methane oxidation (methylotrophy)

Carbon Dioxide Production and Consumption

As noted in the foregoing discussion of the separate processes and as indicated in Figures 6.1 through 6.8, carbon dioxide is produced in all the redox reactions (all processes discussed thus far except biopolymer decomposition),. Oxidation of organic compounds, in general, gives rise to carbon dioxide. Thus monomer oxidation by oxygen and nitrate, and acetate oxidation by sulfate, yield carbon dioxide. This is represented in the equations via carbon dioxide source terms and their appropriate stoichiometric coefficients. Both fermentation and methanogenesis also produce carbon dioxide and are represented similarly.

Carbon dioxide is lost by solute transport and gaseous diffusion to neighboring locations in the soil column, to the atmosphere at the surface, and into ground water below. It is lost also to microbial processes, particularly to chemosynthetic bacteria in the aerobic zones of soil. Only the terms representing transport losses are included explicitly, however, as explained below following the description of chemosynthesis and the production of oxidized inorganics.

Production of Reduced Inorganics

Several other products worthy of note in soils biogeochemistry are produced by the processes already described. Among them are ammonia, hydrogen sulfide and nitrous oxide. Hydrogen sulfide is produced during oxidation of monomers and as the reduced product from sulfate reduction. These sources are accounted in the differential equation for sulfate, as noted in the description of the individual processes. It is lost via transport and oxidation via sulfur bacteria. Ammonia is produced in soils primarily during the oxidation of amino acid and other nitrogenous monomers. It is lost via transport and chemosynthesis. Nitrate reduction produces a series of partially reduced products, including nitrous oxide, which in turn, is further reduced to dinitrogen. Nitrous oxide is also reportedly produced during nitrification (Bremner and Blackmer, 1978). Hydrogen sulfide, ammonia, and nitrous oxide all move in the gas phase, and are lost to the atmosphere at the soil's surface. All these processes and products can be accounted stoichiometrically and appear as source or sink terms in the appropriate equations. The relationships are indicated in Figure 6.1.

Oxidation of Reduced Inorganics

Chemosynthetic bacteria use oxygen to oxidize reduced inorganic molecules for energy production. Any heterotrophic pathways for these bacteria are not currently included in the model. In this model hydrogen sulfide and ammonia are the reduced inorganics considered. Hydrogen sulfide and ammonia are produced when monomers are used for energy in aerobic decomposition and in denitrification. Hydrogen sulfide additionally is produced in anaerobic zones during sulfate reduction. Gas phase transport, therefore, can be very important to the functioning of this process, because reduced inorganics produced in anaerobic zones and oxygen from the surface must be transported to the same location, if aerobic oxidation is to occur.

Chemosynthesis is named in analogy to photosynthesis, and is a primary productivity process, in the sense that synthesis of organic chemicals for biomass occurs from inorganic precursors. Thus, a carbon dioxide sink is associated with the process. As noted earlier, this carbon sink is not included here, in keeping with the implicit treatment of biotic components, on the assumption of steady state chemosynthesizer populations. These processes are represented schematically for ammonia (nitrification) in Figure 6.9 and for hydrogen sulfide in Figure 6.10.

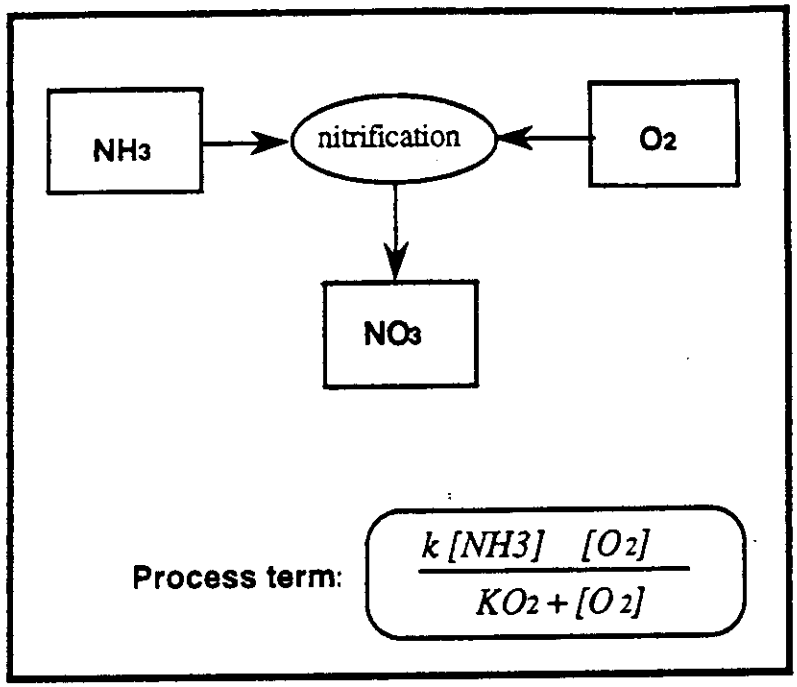

Figure 6.9. Nitrification

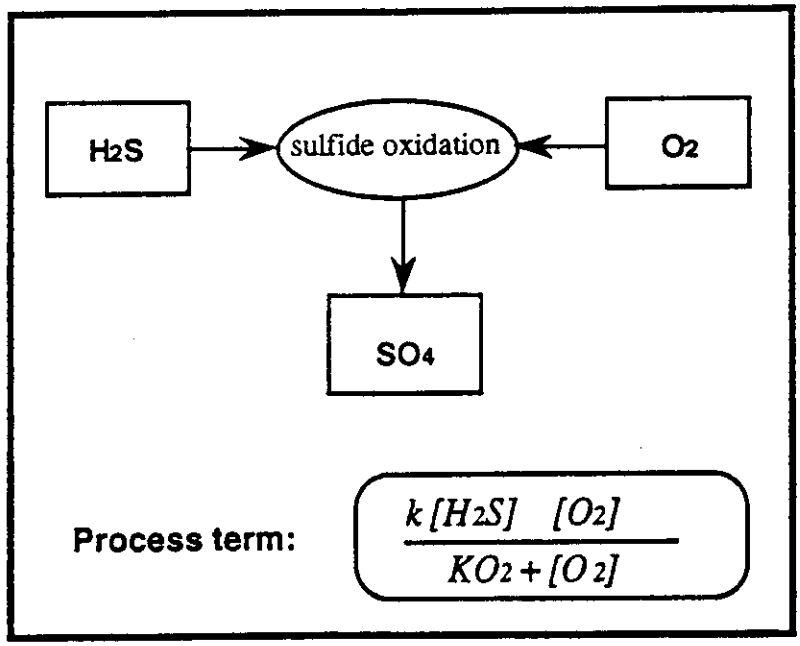

Figure 6.10. Sulfide oxidation

Rationale for Implicit Representation of Biotic Components

Explicit treatment of the microbial population groups required to carry out the reactions described would add an additional set of equations, roughly doubling the number now incorporated in the model. On the positive side, they would add a degree of dynamism and adaptiveness not now present in the model. Again on the negative side, it is doubtful that enough is known about the densities of microbial populations to check whether the population predictions are as expected for the modeled soil conditions. Without such knowledge one could not determine whether a poor prediction was due to poorly represented microbial dynamics or to some other problem. Similarly, one could not determine whether good predictions were simply fortuitous. It seems appropriate in the initial phases of this model development to include system components when an expectation of improvement is high, and not to include them otherwise. Hence the model currently represents biosynthesis implicitly, and hydrolysis and energy-producing reactions explicitly.

Chemical Equilibria

Except for hydrolysis of biopolymers, microbial reactions utilize chemicals dissolved in soil water. Many of the chemicals exist, however, in other forms and phases. We assume that at any point in the soil, local equilibrium exists between the forms and phases of the chemical. Thus if a chemical exists in two or more forms and microbial processes utilize only the dissolved form, we assume that the other forms instantaneously and continuously adjust such that equilibrium is maintained and mass is conserved. To accomplish this computationally, several chemical constants are needed: the Henry's constant for partitioning between the water and gas phase, an equilibrium constant for each aqueous ionic form (e.g., inorganic carbon exists in water as dissolved carbon dioxide, carbonic acid, bicarbonate ion, and carbonate ion and dissociation constants are needed for each of these forms), a constant to characterize cation exchange, and a constant for neutral sorption to soils solids. Mass conservation is maintained by including an equation of total mass in the simultaneous solution for the equilibria. The total itself is time-varying due to kinetic processes that are sources and sinks of the component forms.

Potential Sources of Error

Errors occur due to ignoring biosynthesis and microbial populations in the dynamics of soil biogeochemistry. Most of the errors deal with the allocation of elemental mass into the appropriate categories and locations as a function of time. Without a representation of microbial biomass, accounting cannot be done for the storage of elemental mass that is incorporated into biomass, and therefore, a mass-accounting error occurs. For moderately long simulation times this error should become negligible in a net sense. Because of turnover of the elements comprising biomass, cumulative input and output should become nearly the same. Greatest errors should occur under transient conditions where large biomass die-off and decomposition or high biosynthesis rates occur. These errors would tend to cause incorrect representation of the transient dynamics of the forms of the elements. The production of solid phase organic material below zones of input by higher plants occurs by microbial biosynthesis. It is possible that turnover of these components (via death of microbial cells) introduces significant quantities of solid phase organic materials throughout the soil profile. Under conditions approaching a steady state, another concern is accuracy of the rate coefficients, because they incorporate the steady-state magnitudes of the microbial densities.

Along these latter lines, a more general concern is the fidelity with which this particular model approximation to the system, in which major dynamic components are assumed to be static, can represent the dynamics of the system. Transient growth of microorganisms generally is found to respond nonlinearly (hyperbolically) to changes in substrate concentration. This is a response that saturates with increasing substrate concentration, whereas the model employed here assumes a linear response. For sufficiently high substrate concentration a linear response exceeds the hyperbolic. The rationale for use of the linear response model is as follows. The hyperbolic response model for the population includes a product of population density and the hyperbolic factor in substrate concentration. The saturated population growth rate must exceed the sum of all population loss rates, because its long-term survival occurs at growth rates that are less than the saturated rate. Hence the population density will increase to the level at which the resource consumption gives a growth rate that just balances the loss rates. Moreover, for low resource concentrations, the population similarly will decrease until growth rate just balances loss rates. This argues generally that the product of population density and the hyperbolic factor should change monotonically with substrate concentration. The linear model is a simple means to accomodate this argument. A full analysis of this problem is needed, but to date, it has not been carried out.

A system level source of error can occur in this model as in every highly coupled system model. An error at any point in the system will produce an incorrect component flux, which, as a source to another

process, drives that process incorrectly, and so on throughout the system. Finally, little discussion is required to identify error introduced by incorrect parameterization of soil and other fixed system properties, by the inevitable aggregation of the spatial distribution of components, and by the gross simplification, omission, and aggregation of the very complex microbial ecosystem into these few components.

Model Results

The kinetics model was first implemented for a single point, to check for completeness, mass conservation, and other general concerns. Kinetic coefficients were estimated based on published data and on colleagues' estimates of turnover times for given conditions. Stoichiometric coefficients were obtained from balanced redox reactions for the processes and were expressed as mass coefficients. Subsequently, a vertically distributed model was used as part of the model development activity to provide a spatial context for the kinetics. This model (Lassiter and Plis, in press) consisted of seven layers and utilized a rainfall pattern for the period of the run, as well as selected values of soil properties, and initial values for all the dynamic quantities of the model. No attempt was made to simulate a specific situation, but rather the model was used to check the kinetics model in a spatial context. Losses of inorganic products in the gas phase to the atmosphere tended to be small compared to losses of the dissolved phase out the bottom of the column. These observations probably are due to an incomplete representation of soil water movement. Chapter 5 reports progress toward a more general solution of the transport problem.

Discussion

The main concern of this research is development of the soils biogeochemistry model, but the ability to simulate the biogeochemistry of a real soil over any considerable time span will depend on the existence of the coupled components of terrestrial vegetation and organic matter production as discussed in Chapters 3 and 4, to fill the need for a vegetation model that predicts organic carbon input, including elemental composition, onto the surface and into the subsurface zones. Model testing can be accomplished by providing these and other quantities using measured data, but for long simulations, the vegetation model is needed. Major tasks for the current model include testing of the expressions currently representing the processes, and additional research to find the best way to represent critical processes, such as nitrous oxide production and consumption. Obtaining kinetic coefficients and other quantities is

an ongoing activity. Finally, there is the need to initiate a complementary experimental program to guide the testing and provide a firm basis for the form that the model finally takes.