

A Model of Microbial Processes Relating to Sulfur Cycling in a Peatland:  
Effects of Climate Change

Melanie Hayn  
*Cornell University, Ithaca NY 14850*

Abstract:

Peatlands contain large reservoirs of carbon and have the ability to act as sources or sinks for carbon dioxide, however the response of carbon flux to climate change and anthropogenic influences remains uncertain. Here I describe a model developed to predict the influence of climate change factors on carbon fluxes and rates of sulfate reduction in a peatland system. The model found that increased sulfate deposition to peatlands causes a large increase in carbon flux as a result of increased sulfate reduction. Climate warming causes a substantially smaller increase in flux, and increased plant uptake and atmospheric CO<sub>2</sub> concentration were not found to impact soil-atmosphere carbon exchange significantly. As a result, warmer temperatures projected for the next decade could induce peatlands to become a greater source of carbon to the atmosphere, further increasing temperature and causing a positive feedback. Control of global sulfate deposition could be an important factor in mitigating future climate change due to increased CO<sub>2</sub> in the atmosphere.

Introduction:

While peatlands cover only 5% of the terrestrial surface of the globe, they may have an important role in the global carbon budget because they store approximately a third of the world's soil carbon (Gorham, 1991; Aselmann and Crutzen, 1989). Long-term average carbon accumulation rates are typically on the order of 23gC/m<sup>2</sup>/yr (Gorham, 1995), which is equivalent to ten percent of the annual net primary production of peatland vegetation (Gorham, 1995). This implies that peatlands are functioning as a carbon sink. A recent estimate for carbon

dioxide sequestration in peatlands is 0.076Pg of carbon per year globally (Aselmann and Crutzen, 1989). This is a particularly important characteristic of peatlands today, with the mounting concerns about global warming and the increase in atmospheric CO<sub>2</sub> as a result of anthropogenic activities such as the burning of fossil fuel.

Coupled models of the atmosphere, biosphere and hydrosphere predict that climate change will impact the global climate cycle, and the ability of terrestrial ecosystems to act as a sink for carbon (ex. Cox et al, 2000). These models predict a positive feedback, where increases in carbon dioxide emissions from terrestrial sources as a result of warming contribute to further climate warming and carbon release. This is exacerbated by the increased use of fossil fuels in developing countries (Melillo, personal communication). Some models predict that in as little as 50 years terrestrial ecosystems will switch to being net sources of CO<sub>2</sub> to the atmosphere, because of a greater increase in respiration relative to photosynthesis (Cox et al, 2000). This prediction is not certain, however, and depends primarily on the sensitivity of soil respiration processes to warming (Melillo et al 2002). Under warmer temperatures, rates of microbial processes should increase (Jenkinson et al, 1991; Kirschbaum, 1995), thus releasing more CO<sub>2</sub> into the atmosphere and causing the positive feedback predicted by many coupled climate change models.

Many northern peatlands are dominated by anaerobic metabolism due to subsurface saturation and slow water turnover times. Under these conditions anaerobic microbial respiration becomes the dominant metabolic pathway. Microbially-mediated dissimilatory sulfate reduction is one means of anaerobic metabolism involving the oxidation of organic carbon to CO<sub>2</sub> though the use of sulfate as an electron acceptor (Schlesinger, 1997). Although sulfate reduction has not generally been thought to be as important in freshwater wetlands as in coastal wetlands, the sulfate pool in peatlands dominated by *Sphagnum* can turn over rapidly and

support high rates of sulfate reduction (Vile et al 2003). Because of this process, atmospheric sulfur deposition can play an important role in the total respiration of a system, and thus in the peatlands ability to act as a sink for carbon. This could be of particular importance in Asia, where emissions of SO<sub>2</sub> to the atmosphere remain high, and where the fourth largest global peatland area is located (Bridgham et al, 2000).

There are a variety of anaerobic carbon mineralization reactions possible within a peatland other than sulfate reduction. Nitrate reduction is the most favorable, but anaerobic conditions and plant uptake typically cause this process to be insignificant (Lang et al 1993). Methanogenesis is typically less energetically favorable than sulfate reduction, but is the dominant pathway in many peatlands with low sulfur inputs. However, when there is a significant input of sulfate to the peatland, sulfate reduction becomes more important to total soil respiration (Vile et al, 2003). Additionally, in sulfate reduction two moles of carbon are mineralized for each mole of sulfate reduced, compared with one mole of carbon mineralized in both aerobic respiration and methanogenesis (Conrad, 1989). Thus a shift in the importance of sulfate mineralization can have a potentially large impact on the carbon dioxide production resulting from microbial respiration, and thus has the potential to cause a shift to greater carbon mineralization rates and a net loss of carbon from the peatland. The effect of increased rates of sulfate reduction on rates of methanogenesis is currently being debated (Vile et al 2003).

When considering the impact of climate change on microbial respiration, it is important to also consider the interactions between soil chemistry and vegetation. Plants compete with microbes in the soil for essential nutrients, and plant uptake of sulfate could potentially have an impact on its availability in the soil. Vegetative biomass and thus plant uptake of sulfate could be expected to increase with either increased loading of limiting elements (N or P) or as a feedback effect of increased temperature and atmospheric CO<sub>2</sub>.

In this paper I have developed a model of a peatland system to evaluate the potential impacts of several aspects of climate change and anthropogenic influences on sulfate reduction rates and the exchange of CO<sub>2</sub> with the atmosphere as a result of changing soil respiration.

#### Model Description:

To assess the impacts of climate change and anthropogenic forcings on peatland carbon exchange and microbial respiration I constructed a model of a theoretical peatland system (Figure 1). The model peatland has a shallow peat depth (~50cm) divided into nine layers (designated by the letter j), each with a thickness of 5cm. Microbial and soil processes are the same within each layer, and interactions between the chemistry of adjacent layers occurs via diffusion. In this simplified model rates of groundwater flow are negligible, and movement of species occurs through simple diffusion. New inputs to the system come either from the atmosphere (through diffusion or deposition), plant interactions, or diffusive exchange between the bottom soil layer and the underlying groundwater. Because the soil substrate is peat, I also assume that supply of organic matter does not limit microbial processes.

To determine the important factors influencing sulfur dynamics, I examined sulfur cycling in wetlands from several different sources (Fenchel et al, 2000; Mitsch & Gosselink, 2000; Schlesinger, 1997; Stumm & Morgan, 1981). Within each soil layer in the model I have modeled the feedbacks that influence two respiration processes, aerobic respiration and sulfate reduction. Since there is some debate as to how rates of methanogenesis are affected by the rates of sulfate reduction, I assume for the purposes of the model that there is no feedback between the two and that methanogenesis is constant under conditions of the changing importance of sulfate reduction (Watson and Nedwell, 1998).

Since cycling in the soil does not take place solely with regard to one element, the model was split to account for fluxes in oxygen, carbon and sulfur. The pools of the same compound with respect to different elements are related by molar ratios. Each modeled chemical species is preceded by a letter representing which element it is represented in terms of. For example, OSO<sub>4</sub> (sulfate in terms of moles of oxygen) is four times SSO<sub>4</sub> (sulfate in terms of moles of sulfur).

The model simulates the size of the pools of sulfate (SSO<sub>4</sub>) within each layer of the soil and other compounds essential to the chemical cycling of sulfur, including hydrogen sulfide (SH<sub>2</sub>S), bicarbonate (CHCO<sub>3</sub> and OCHCO<sub>3</sub>), and oxygen (OO<sub>2</sub>). The model also simulates the soil carbon dioxide pool (CCO<sub>2</sub> and OCO<sub>2</sub>) that is influenced by sulfate reduction and aerobic respiration. For simplicity, effects of carbon dioxide concentration on microbial processes have not been incorporated into the model, since there remains some debate about the specific effects of CO<sub>2</sub> concentration on soil processes.

The rates of many of the equations in the model are dependent on the redox status of the soil. For simplicity, redox processes that depend on the presence of oxygen are represented as occurring when oxygen levels are above 0.001M by means of an oxygen parameter (m) defined as equation 1 (Table 1). Processes that only occur under anaerobic conditions occur when the oxygen concentration is below 0.001M.

Microbially mediated processes were modeled with Michaelis-Menten equations that depend on either one or both reactants in the process. The rate of sulfate reduction (equation 2, Table 1) depends only on the concentration of sulfate since organic carbon supply is not limiting (Boudreau and Westrich, 1984), and aerobic respiration (equation 3) depends only on the concentration of oxygen in the soil layer. Microbial sulfide oxidation (equation 4) depends on both the oxygen and sulfide concentrations in the soil, since both potentially limit the rates of

sulfide oxidation. Uptake of sulfur by plants (equation 6) is modeled as a saturating process that depends on the sulfate concentration in the soil and saturates at a maximum value ( $U_{max}$ ) that is dependent on the maximum growth rate of the plant. This value is constant, since I assume that vegetative growth is limited by either nitrogen or phosphorus and not by a factor within the modeled system.

Of particular importance to the implications of the model toward carbon balance is the carbon dioxide and bicarbonate equilibrium in the soil. Inputs to these pools come as products of aerobic and anaerobic respiration, and the equilibrium between the two within the soil is dependent on pH. The carbon equilibrium equation (equation 5) calculates the difference between what the concentrations of the two species would be in equilibrium and then adjusts the two concentrations so they approach these values. The equilibrium values are important because the proportion of inorganic carbon present as carbon dioxide is able to exchange with the atmosphere via surface soil, controlling the ability of the soil to retain carbon.

The microbial and chemical processes in the individual soil layers are tied together by diffusion equations. Between layers simple diffusion occurs for each solute down its concentration gradient (equations 8,9). In addition, each chemical diffuses into or out of the underlying groundwater (equation 10) following simple diffusion, which has a major influence on the chemistry of the entire soil profile. For gaseous elements, diffusion also occurs between the top soil layer and the atmosphere (equation 11), as gasses dissolve into solution according to Henry's Law. Rates of oxygen diffusion from the atmosphere into surface soil limits oxygen availability to the system, and the diffusion of this oxygen through layers of the sediment is limited by the rapid uptake in surface layers via microbial respiration.

## Parameterization:

The values of the concentrations of O<sub>2</sub>, H<sub>2</sub>S, and CO<sub>2</sub> were calculated using Henry's Law (at 20°C and 1 atm) and the average concentration of these gasses in the atmosphere (Schlesinger, 1997). These concentrations for O<sub>2</sub> and H<sub>2</sub>S were incorporated into the equations for each element (equation 11; O<sub>2</sub>=0.273MO, H<sub>2</sub>S=0.20MS) and the value for CO<sub>2</sub> was defined as a parameter (ATMeq) so that it could be manipulated. Diffusion rate parameters were chosen by fitting concentration data with personal observation of typical dissolved oxygen levels in New York peatland soils (generally zero below 10cm). This resulted in the top two or three layers of soil being oxic (on average) with the lower layers being anoxic.

A pH of 7 was chosen for the simulations based on the observation that the peatlands I've studied in New York tend to be circum-neutral. This is particularly true for the band of the northeastern US and Canada that is dominated by carbonate bedrock (Brady & Weil, 1999). I parameterized the carbonate-CO<sub>2</sub> equilibrium within the soil using equilibrium equations and K values for carbon species modeled after Cosby et al (1985) and assuming a temperature of 293K. The parameters for sulfate reduction were based on the values for saltwater systems (Rm=0.02, Boudreau and Westrich, 1984) with some manipulation. I chose the remaining parameters (Table 2) to fit with my general expectations about how peatland chemistry should behave in equilibrium based on personal observation and general principles of nutrient cycling.

I assigned values for drivers such as groundwater concentrations of nutrients based on the preliminary equilibrium concentrations obtained for the state variables in the model (Table 3). I assumed that the groundwater was enriched in most elements relative to the active microbial zone of the soil and chose values that seemed in logical proportion. Based on the preliminary equilibria I chose initial state variable concentrations that were of the same order of magnitude as

the equilibrium values to better approximate a natural state, and assigned the surface soil layer gas concentrations in equilibrium with the atmosphere (Table 4).

Analysis:

I ran the model initially in what I consider a pristine state. There was no sulfate deposition from the atmosphere, atmospheric gas levels were representative of today's average global values, and microbial processes occur in my best approximation of their natural rates. This model settled at equilibrium by 500 days, with the top 3 layers of the soil aerobic. Overall, soil column aerobic respiration rates exceeded sulfate reduction rates, and the peatland was a small source of CO<sub>2</sub> to the atmosphere.

The first factor I manipulated in the model was sulfate deposition. Prior to the addition of this term, there was no external supply of sulfate to the soil system other than internal cycling through H<sub>2</sub>S oxidation. I added 0.5M/day to the system from 500 to 1500 days, then ceased the deposition and examined its impact. The primary result of this addition was an increase in rates of sulfate reduction. Over the course of the sulfate addition, sulfate reduction rapidly became the dominant microbial pathway. This can be seen when examining the total soil respiration rates in each layer of the soil (Figure 2). In the top three layers of the soil respiration rates only increased a small amount over their pristine rates, while the total respiration in the bottom layers increased dramatically. The middle soil layers (layers 5 and 6) had larger increases than the very bottom layers because the bottom layers lost sulfate to the groundwater more rapidly than they could reduce it. Because of these increased rates of microbial respiration, carbon dioxide concentrations in the soil increased, and the flux of carbon dioxide from the sediment to the atmosphere increased (Figure 3). When I removed sulfate deposition the model returned to its pristine state, with the magnitude of carbon flux identical to its initial value.

The next scenario I investigated was increased plant uptake, either due to fertilization or change in dominant species cover. I doubled the rate of plant uptake of sulfate to investigate its impact on carbon exchange. Overall rates of soil respiration decreased as a result of the removal of sulfate from soil water, with a corresponding decrease in rates of sulfate reduction (Figure 4). Soil in layers 5-8 had the largest decrease in respiration, while surface layers had no visible change in rates. However, the magnitude of the depression in respiration was very small, on the order of  $10^{-6}$ , and did not have a significant impact on  $\text{CO}_2$  in the surface soil layer or  $\text{CO}_2$  flux from the soil (Figure 7).

Global warming had a more significant impact on carbon exchange. I worked with the assumption that microbial metabolism would double for every ten degrees of warming. I then examined the changes that would occur as a result of an increase of  $10^\circ\text{C}$  by doubling rates of aerobic respiration, sulfate reduction, and  $\text{H}_2\text{S}$  oxidation. Under these conditions, the surface soil respiration had the greatest response, showing increased soil respiration as a result of more rapid microbial processes (Figure 5), and demonstrating that under warmer conditions without sulfate deposition aerobic respiration dominates total soil respiration. We also see a corresponding increase in both surface soil  $\text{CO}_2$  (Figure 6) and  $\text{CO}_2$  flux out of the soil (Figure 7).

The final scenario I examined was the effect of increased  $\text{CO}_2$  on physical processes in the peatland. I assumed that the concentration of  $\text{CO}_2$  in the atmosphere would double, causing a doubling in the amount that is dissolved in water in equilibrium with the atmosphere. Because I didn't consider direct feedbacks of  $\text{CO}_2$  on microbial processes, this scenario did not have an effect on microbial respiration. It did however affect the amount of  $\text{CO}_2$  dissolved in the surface layer of the soil (Figure 6). Since more  $\text{CO}_2$  can be dissolved in the surface layer under conditions of increased atmospheric  $\text{CO}_2$ , a smaller amount of  $\text{CO}_2$  is actually escaping from the

soil (Figure 7). This scenario therefore decreases the ability of the peatland to act as a source for CO<sub>2</sub>.

#### Discussion:

Overall, the change in carbon dioxide flux to the atmosphere as a result of most scenarios is small when compared to the pristine (control) situation (Figure 8). To a measurable approximation (three to four decimal places), increasing plant uptake and atmospheric CO<sub>2</sub> concentrations does not make a difference in overall carbon flux from the peatland. Global warming has a larger impact, although only causes an increase of 33% over the pristine condition. Sulfate deposition, on the other hand, causes a substantial difference in CO<sub>2</sub> flux, causing the flux to be over 40 times that of the pristine state. One implication of these results is that the system's low initial sulfate concentrations were responsible for very low rates of sulfate reduction, and that the system has the potential for much higher rates of sulfate reduction than are found in the pristine state. It also shows that the anaerobic zone has the potential to be a very important factor in controlling carbon dynamics within the system.

The small response of the model to changing temperature and CO<sub>2</sub> in the atmosphere as well as to increased plant uptake show that the system is well buffered with respect to internal changes in carbon pools and recycling rates. Even under large external forcings, the system shows little change in its carbon fluxes and reservoirs. This may be partly due to the absence of methanogenesis in the model, which may also respond to changes in temperature and climate, adding to the response of sulfate reduction to climate change parameters. However, if the peatland modeled here is a representation of the sensitivity of northern peatlands to climate change, then prediction that peatlands will convert from a carbon sink to a carbon source as a result of climate change may be true. Although the magnitudes of the change in carbon flux

from peatlands in the model are small, they are represented as fluxes in moles of carbon per liter of water in the surface soil per day. Over the vast stretches of peatlands in the northern latitudes this change in flux could be dramatic. Also, one prediction of climate change models is that the northern latitudes will warm more than equatorial latitudes, potentially causing a larger change in flux than we would predict just based on changes in the global average temperature.

The model also implies that the potential importance of sulfate reduction to overall microbial processes within peatlands has been underestimated. The model in the pristine condition demonstrates low sulfate reduction rates, which is comparable to observed natural systems. In the model, large increases in sulfate flux (an order of magnitude higher than surface  $\text{SO}_4^{2-}$  levels) cause correspondingly large increases in sulfate reduction. This result suggests that sulfur cycling in peatlands is indeed an important process in the mineralization and cycling of carbon and that sulfate deposition, particularly in Asia and areas without federal regulations on sulfur emissions, can have a large detrimental impact on these systems. If we are to control the response of these wetlands to climate change, mitigating sulfur emissions around the globe would go a long way to alleviating carbon emissions from sulfate reducers. Otherwise the fluxes of carbon to the atmosphere resulting from sulfate reduction will be very high, causing substantial increases in atmospheric  $\text{CO}_2$  concentrations, and potentially contributing to climate change and adverse effects on terrestrial and aquatic ecosystems.

More research into the interactions between sulfate reducing and methanogenic microbial populations and the introduction of this relationship into the model would increase its accuracy and help us predict whether the outcomes of the model would actually occur should similar circumstances happen in the world. Another way to improve the accuracy of the model predictions would be to consider a hydrogen ion budget for the system, to assess the effect these climate changes would have on pH of the soil, which would then affect reaction rates and the

equilibrium between bicarbonate and carbon dioxide in soil water. Finally, this model applies to a peatland that has exchange with underlying groundwater, but no actual groundwater flow through it. Modeling hydrologic delivery would make this model more applicable to a variety of different peatland habitats, and thus more representative of the response of the broad area of northern peatlands to climate change.

#### Acknowledgements:

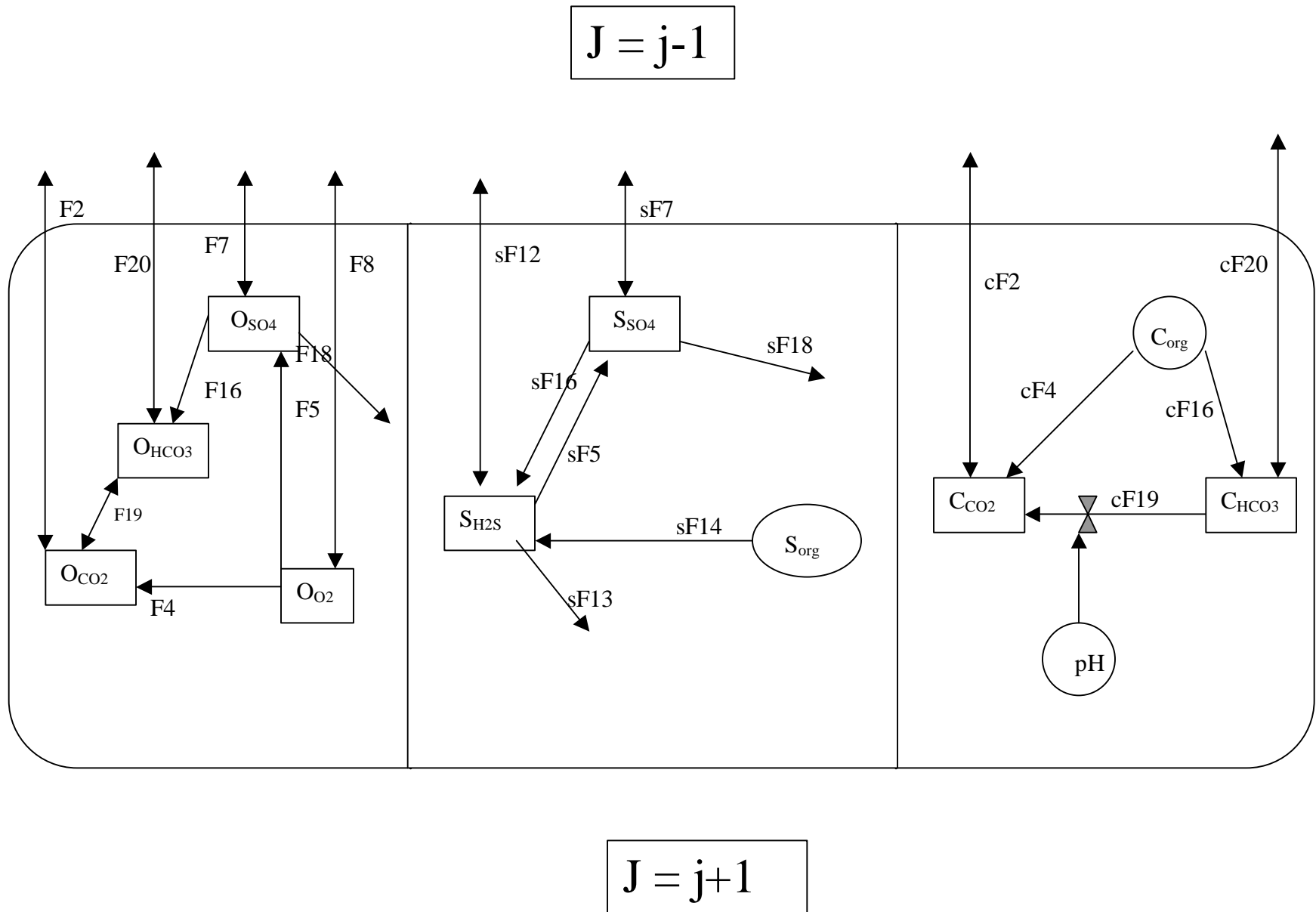
Thanks to Ed Rastetter and Bonnie Kwiatkowski for their help formulating and implementing my model, developing the model shell and code to cope with the layered soil model format, and helping me work through the various problems that arose in its development.

#### Literature Cited:

- Aselmann, I. and P.J. Crutzen. 1989. Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality, and possible methane emissions. *Journal of Atmospheric Chemistry* 8:307-358
- Brady, N.C., and R.R. Weil. 1999. *The Nature and Properties of Soils*. Prentice Hall, NJ.
- Bridgham, S. D., C. L. Ping, J. L. Richardson, and K. Updegraff. 2000. Soils of peatlands: Histosols and gelisols, in *Wetland Soils: Genesis, Hydrology, Landscapes, and Classification*. CRC, FL.
- Boudreau, B.P., and J.T. Westrich. 1984. The dependence of Bacterial Sulfate Reduction on Sulfate Concentration in Marine Sediments. *Geochimica et Cosmochimica Acta* 48:2503-2516
- Conrad, R. 1989. Control of methane production in terrestrial ecosystems, in *Exchange of Trace Gases between Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 37–58, John Wiley, NY
- Cosby, B.J., G.M. Hornberger, and J.N. Galloway. 1985. Modeling the Effects of Acid Deposition: Assessment of a Lumped Parameter Model of Soil Water and Streamwater Chemistry. *Water Resources Research* 21(1): 51-63
- Cox, P. M., R. A. Betts, C. D. Jones, S. A. Spall, and I. J. Totterdell. 2000. Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model, *Nature*, 408, 184–187.
- Fenchel, T., G.M. King, & T.H. Blackburn. 2000. *Bacterial Biogeochemistry: The Ecophysiology of Mineral Cycling*. Academic Press. San Diego.
- Gorham, E. 1991. Northern peatlands: Role in the carbon cycle and probable responses to climate warming, *Ecol. Appl.*, 1, 182– 195
- Gorham, E. 1995. The biogeochemistry of northern peatlands and its possible responses to global warming, in *Biotic Feedbacks in The Global Climate System: Will the Warming Feed the*

- Warming?, edited by G.M. Woodwell and F.T. Mackenzie. Oxford Univ. Press, NY
- Handbook of Chemistry and Physics. 1977. CRC Press, Cleveland, Ohio
- Jenkinson, D.S, D.E. Adams, and A. Wild. 1991. Model estimates of CO<sub>2</sub> emissions from soil in response to global warming. *Nature* 251:304-306
- Kirschbaum, M.U.F. 1995. The temperature dependence of soil organic matter decomposition, and the effects of global warming on soil organic C storage. *Soil Biol. Biochem.* 27:753-760
- Lang, K., M. Lehtonen, and P. Martikainen. 1993. Nitrification potentials at different pH values in peat samples from various layers of a drained mire. *Geomicrobiol. J.* 11:141-147
- Mankerscheid, R., S. Burkart, A. Bramm, and H.J. Weigel. 2003. Effect of CO<sub>2</sub> enrichment on growth and daily radiation use efficiency of wheat in relation to temperature and growth stage. *European Journal of Agronomy.* 19(3):411-425
- Melillo, J.M., P.Steudler, J.D.Aber, K.Newkirk, H.Lux, F.P.Bowles, C.Catricala, A.Magill, T.Ahrens, and S. Morrisseau. 2002. Soil warming and carbon-cycle feedbacks to the climate system. *Science* 298:2173-2176.
- Melillo J. 2003. Lecture on carbon cycling. Semester in Environmental Science
- Mitsch, W.J., and J.G. Gosselink. 2000. *Wetlands*. John Wiley & Sons. New York.
- Schlesinger, W.H. 1997. *Biogeochemistry: An Analysis of Global Change*. Academic Press. CA
- Stumm, W. & J.J. Morgan. 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. John Wiley & Sons, New York.
- Vile, M.A., and S.D. Bridgham. 2003. Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands. *Global Biogeochemical Cycles* 17(2):27-33
- Watson, A., and D.B. Newell. 1998. Methane production and emission from peat: the influence of anions (sulphate, nitrate) from acid rain. *Atmos. Environ.* 32:3239-3245

Figure 1. Simplified Model Diagram. General fluxes are shown for processes within all soil layers. Exchanges with the atmosphere and groundwater are not shown.



**Table 1. Model Equations**

For every soil layer, these processes occur:

1. Oxygen Parameter: 
$$m = \frac{1}{1 + \frac{O_2^b}{w}}$$
 (1 if anoxic, 0 if oxic)
2. Sulfate Reduction (S): 
$$sF16 = \frac{Rm * SSO4}{Ks * SSO4} * m$$
3. Oxidic Respiration (O): 
$$F4 = \frac{Oresp * O_2}{kF4 * O_2} * \lambda * m$$
4. H<sub>2</sub>S Oxidation (S): 
$$sF5 = \frac{b1 * O_2 * H_2S}{kF5 * O_2 * SH_2S} * \lambda * m$$
5. Carbon Equilibrium (C): 
$$cF19 = 10^{pH - 6.1} * CHCO_3 * 3.33 * CCO_2 * kc$$
6. Plant Uptake (S): 
$$sF18 = \frac{U_{max} * E_o * SSO_4}{U_{max} + E_o * SSO_4}$$
7. FeS Precipitation (S): 
$$sF13 = \alpha * SH_2S * m$$

For layers 2 to 9, diffusion between a layer (2-9) and the layer above (1-8) occurs for all chemical species in a layer:

$$8. GasDiffusion = \frac{DIFFaqG * (Concentration_{layer j} - Concentration_{layer j-1})}{5}$$

*Gas diffusion applies to CO<sub>2</sub> (F2 and cF2), O<sub>2</sub> (F8), and H<sub>2</sub>S (sF12)*

$$9. SaltDiffusion = \frac{DIFFaqS * (Concentration_{layer j} - Concentration_{layer j-1})}{5}$$

*Salt diffusion applies to SO<sub>4</sub><sup>2-</sup> (F7 and sF7) and HCO<sub>3</sub><sup>2-</sup> (F20 and cF20)*

For layer 9, diffusion into the soil column comes from underlying groundwater:

$$10. Diffusion = \frac{DIFFaq(SorG) * (Concentration_{groundwater r} - Concentration_{layer j})}{5}$$

Diffusion carries the same flux designations as above.

For layer 1, exchange of gaseous elements between the water and the atmosphere:

$$11. \text{AtmExchange} = \frac{\text{DIFFatm} * \text{Concentration}[\text{layer}][i] - \text{Conc}[\text{ATMeq}][i]}{5}$$

Occurs for CO<sub>2</sub> (cF2,F2) O<sub>2</sub> (F8) and H<sub>2</sub>S (sF12)

Derivatives:

$$d\text{CCO2dt}[j] := -cF2[j] + cF2[j+1] + cF4[j] + cF19[j]$$

$$d\text{CHCO3dt}[j] := -cF20[j] + cF20[j+1] + cF16[j] - cF19[j]$$

$$d\text{SSO4dt}[j] := -sF7[j] + sF7[j+1] - sF18[j] - sF16[j] + sF5[j] + (\text{Sdep} * \text{SdepP}[j])$$

$$d\text{SH2Sdt}[j] := -sF12[j] + sF12[j+1] + sF16[j] - sF5[j] + sF14\text{driver} - sF13[j]$$

$$d\text{OO2dt}[j] := -F8[j] + F8[j+1] - F5[j] - F4[j]$$

$$d\text{OCO2dt}[j] := 2 * d\text{CCO2dt}[j]$$

$$d\text{OSO4dt}[j] := 4 * d\text{SSO4dt}[j]$$

$$d\text{OHCO3dt}[j] := 3 * d\text{CHCO3dt}[j]$$

Table 2. Parameters, descriptions, and their initial values.

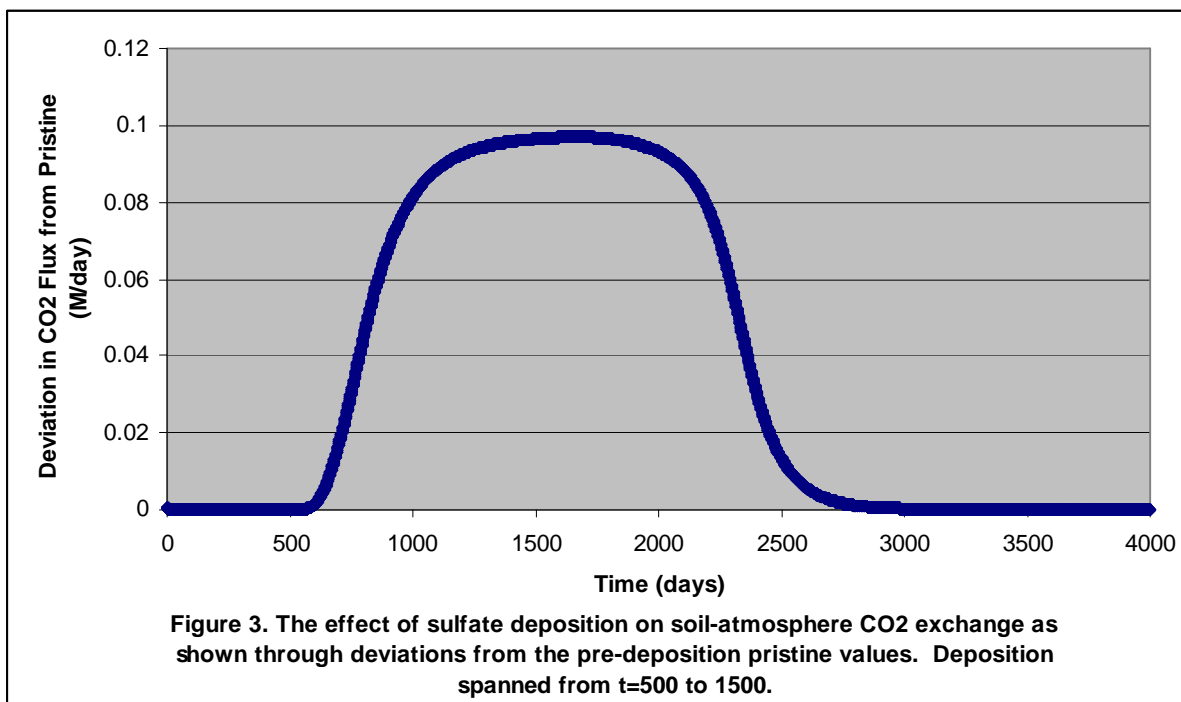
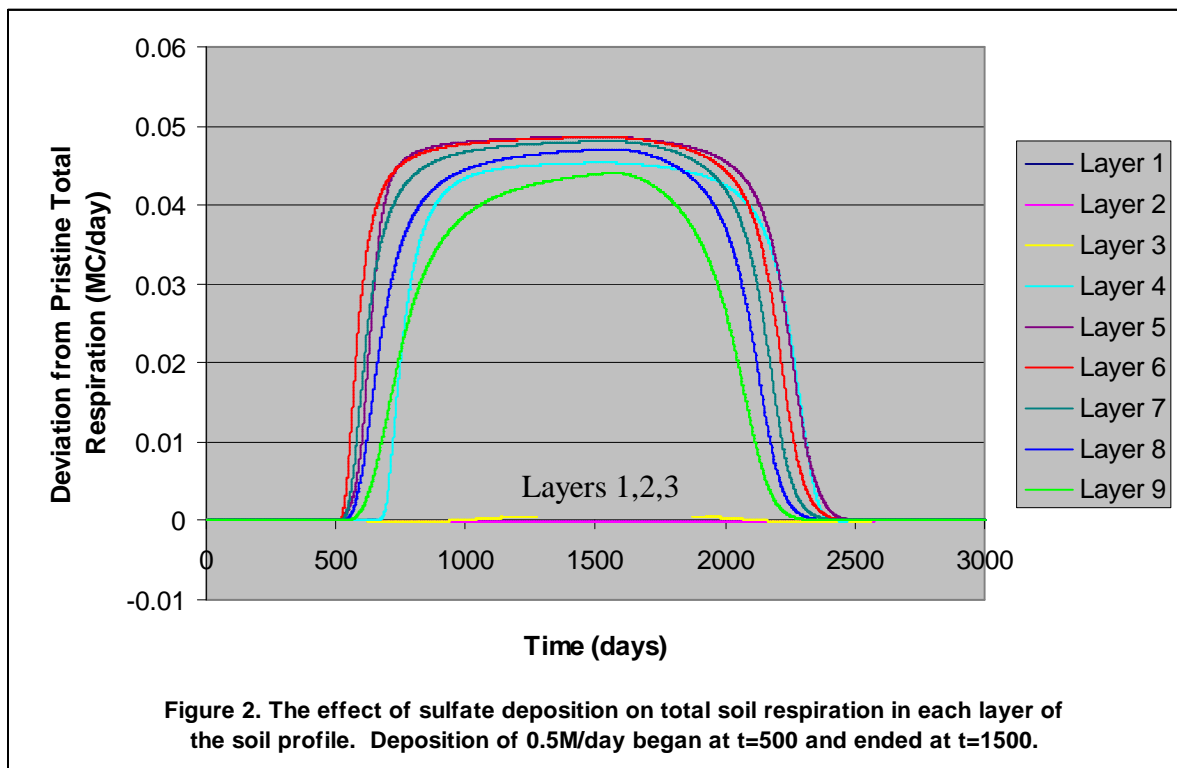
<u>Parameter</u>	<u>Description</u>	<u>Initial Value</u>	<u>Units</u>
Oresp	Oxic respiration constant	0.001	day <sup>-1</sup>
b1	H <sub>2</sub> S oxidation constant	0.01	day <sup>-1</sup>
alpha	FeS ppt rate constant	0.001	day <sup>-1</sup>
kF5	H <sub>2</sub> S Oxidation Half Saturation	0.1	moles S/L
kF4	Respiration Half Saturation	0.1	moles O/L
kc	Carbon Equilibrium Rate Constant	0.1	day <sup>-1</sup>
Rm	Max SO <sub>4</sub> <sup>2-</sup> reduction	0.025	moles S/L/d
ks	SO <sub>4</sub> <sup>2-</sup> red half saturation	0.45	moles S/L/d
Umax	Max S uptake	0.01	moles S/L/d
Eo	limited S supply rate	0.05	day <sup>-1</sup>
DIFFaqG	Diffusion constant for gasses	0.5	day <sup>-1</sup>
DIFFaqS	Diffusion constant for salts	0.3	day <sup>-1</sup>
DIFFatm	Diffusion constant for atmospheric exchange	0.5	day <sup>-1</sup>
ATMeq	Concentration of CO <sub>2</sub> in equilibrium with atmosphere	0.00121	moles C/L
w	oxygen parameter	0.001	unitless
b	oxygen parameter rate exponent	10	unitless

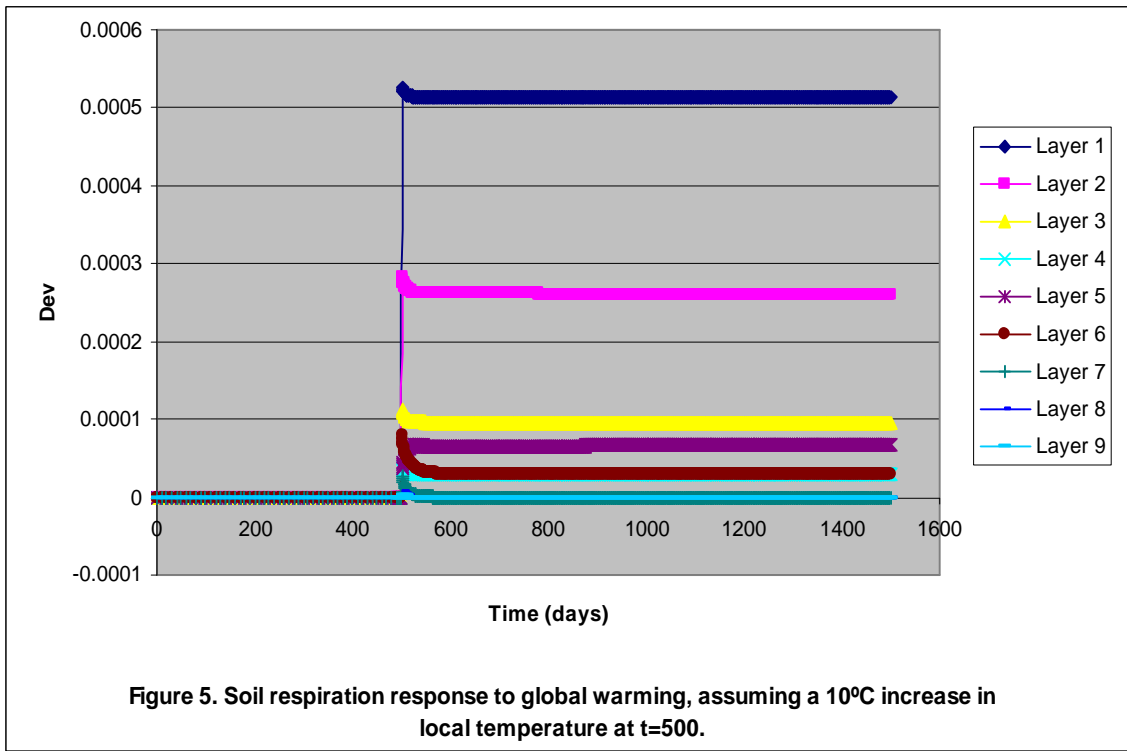
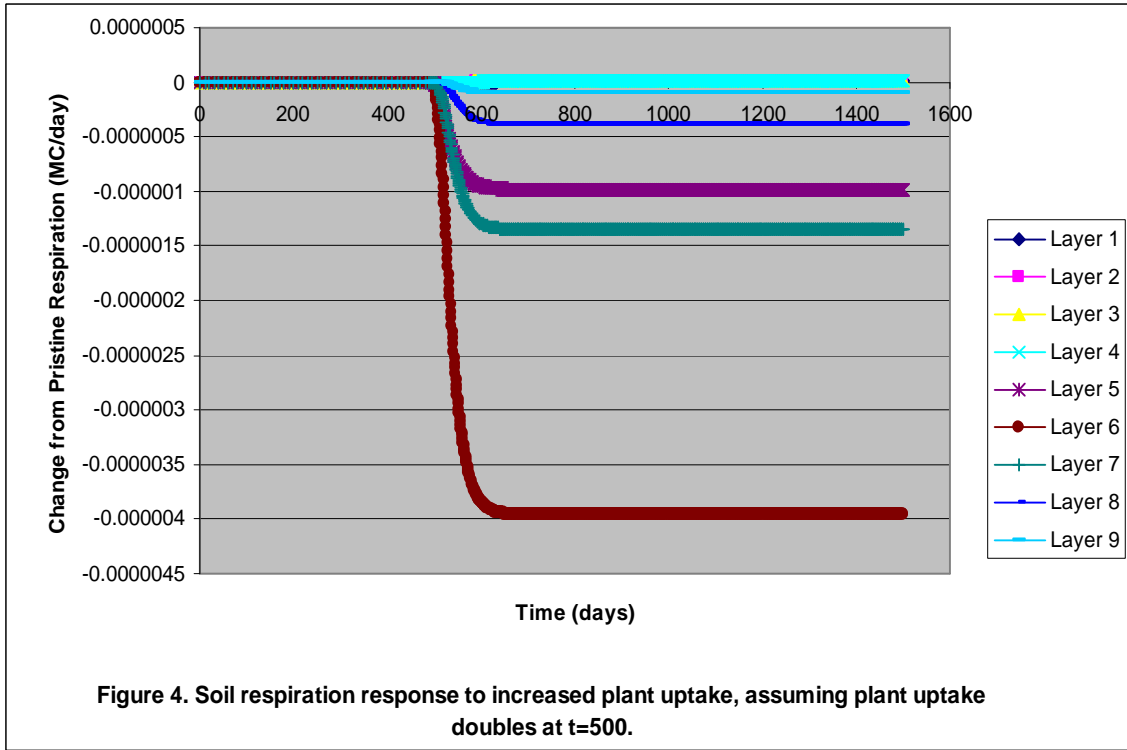
Table 3. Drivers, descriptions, and their initial values.

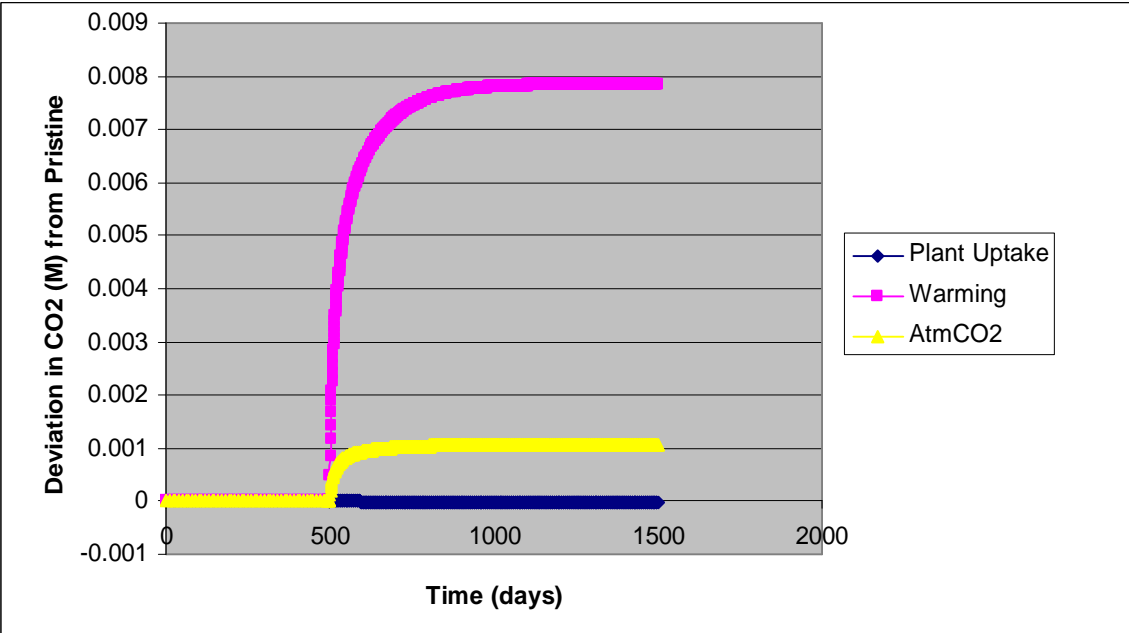
<u>Driver</u>	<u>Description</u>	<u>Initial Value</u>	<u>Units</u>
Sdep	Atmospheric Sulfate Deposition	0	moles S/L/d
sF14driver	Organic S Oxidation	0.001	moles S/L/d
pH	pH	7	-log[H <sup>+</sup> ]
gH2OCHCO3	Groundwater HCO <sub>3</sub> <sup>2-</sup> C	0.1	moles C/L
gH2OCCO2	Groundwater CO <sub>2</sub> <sup>-</sup> C	0.1	moles C/L
gH2OSH2S	Groundwater H <sub>2</sub> S <sup>-</sup> S	0.5	moles S/L
gH2OSSO4	Groundwater SO <sub>4</sub> <sup>-</sup> S	0	moles S/L
gH2OOCO2	Groundwater CO <sub>2</sub> <sup>-</sup> O	0.2	moles O/L
gH2OOSO4	Groundwater SO <sub>4</sub> <sup>2-</sup> -O	0	moles O/L
gH2OOO2	Groundwater O <sub>2</sub> <sup>-</sup> O	0	moles O/L
gH2OOHCO3	Groundwater HCO <sub>3</sub> <sup>2-</sup> -O	0.3	moles O/L

Table 4. State Variables and their initial values.

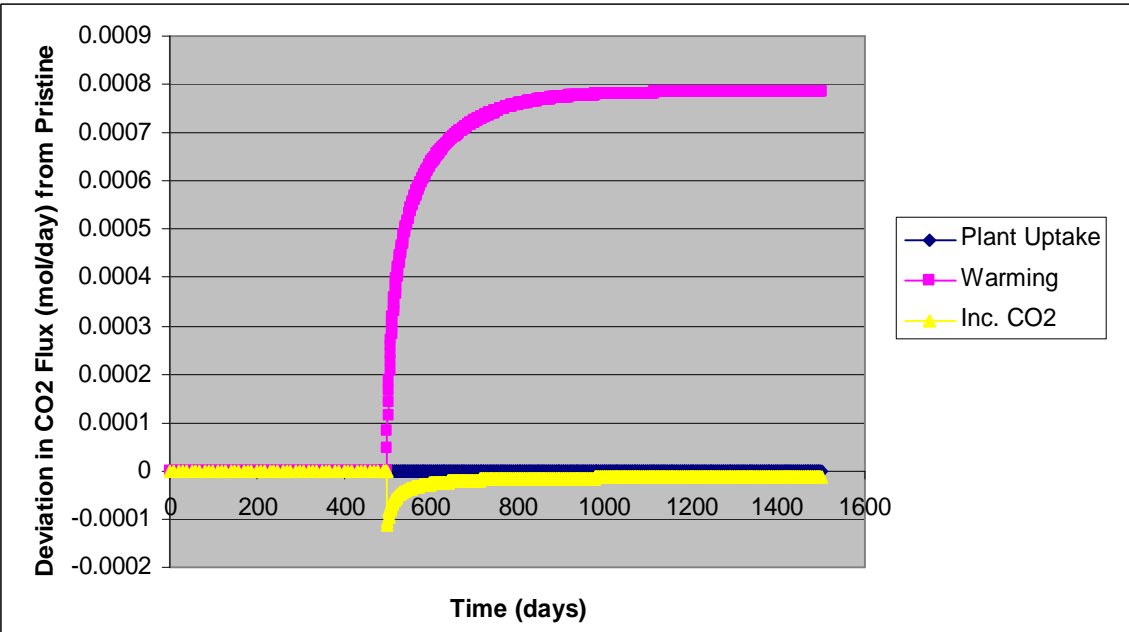
<u>State Var.</u>	<u>Initial Value</u>	<u>Units</u>	<u>State Var.</u>	<u>Initial Value</u>	<u>Units</u>
CCO21	0.0012	moles C/L	OO21	0.1117	moles O/L
CCO22	0.041	moles C/L	OO22	0.0401	moles O/L
CCO23	0.055	moles C/L	OO23	0.0129	moles O/L
CCO24	0.067	moles C/L	OO24	0.0039	moles O/L
CCO25	0.079	moles C/L	OO25	0.0013	moles O/L
CCO26	0.09	moles C/L	OO26	0.00084	moles O/L
CCO27	0.101	moles C/L	OO27	0.00062	moles O/L
CCO28	0.112	moles C/L	OO28	0.00042	moles O/L
CCO29	0.118	moles C/L	OO29	0.00021	moles O/L
CHCO31	0.0093	moles C/L	OCO21	0.0024	moles O/L
CHCO32	0.0138	moles C/L	OCO22	0.082	moles O/L
CHCO33	0.0181	moles C/L	OCO23	0.11	moles O/L
CHCO34	0.02227	moles C/L	OCO24	0.134	moles O/L
CHCO35	0.02633	moles C/L	OCO25	0.158	moles O/L
CHCO36	0.03035	moles C/L	OCO26	0.18	moles O/L
CHCO37	0.03401	moles C/L	OCO27	0.202	moles O/L
CHCO38	0.03832	moles C/L	OCO28	0.224	moles O/L
CHCO39	0.048	moles C/L	OCO29	0.236	moles O/L
SSO41	0.03447	moles S/L	OSO41	0.13788	moles O/L
SSO42	0.02381	moles S/L	OSO42	0.09524	moles O/L
SSO43	0.01353	moles S/L	OSO43	0.05412	moles O/L
SSO44	0.00677	moles S/L	OSO44	0.02708	moles O/L
SSO45	0.002972	moles S/L	OSO45	0.011888	moles O/L
SSO46	0.000924	moles S/L	OSO46	0.003697	moles O/L
SSO47	0.000268	moles S/L	OSO47	0.00107	moles O/L
SSO48	0.00007680	moles S/L	OSO48	0.000307	moles O/L
SSO49	0.00002043	moles S/L	OSO49	0.0000817	moles O/L
SH2S1	0.2393	moles S/L	OHCO31	0.02883	moles O/L
SH2S2	0.2897	moles S/L	OHCO32	0.04129	moles O/L
SH2S3	0.3405	moles S/L	OHCO33	0.05244	moles O/L
SH2S4	0.3855	moles S/L	OHCO34	0.06782	moles O/L
SH2S5	0.4221	moles S/L	OHCO35	0.07798	moles O/L
SH2S6	0.4493	moles S/L	OHCO36	0.09205	moles O/L
SH2S7	0.4699	moles S/L	OHCO37	0.10204	moles O/L
SH2S8	0.4851	moles S/L	OHCO38	0.11595	moles O/L
SH2S9	0.4951	moles S/L	OHCO39	0.14401	moles O/L







**Figure 6. Effect of pertterbations on CO2 in surface soil layer**



**Figure 7. Effect of perturbations on CO2 Flux to Atmosphere from soil column. Values are deviations in CO2 flux from the pristine values.**

