AN EXPLORATORY PROPOSAL FOR CARBON STORAGE

Increasing Carbon Storage within Soils By Controlling Key Microbial Respiration Processes

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Limiting increases in atmospheric greenhouse gases will likely be achieved by a variety of advances that both limit their production and increase their consumption. Integrating sequestration objectives into traditional agricultural practices has the potential to provide dramatic short-term (10 to 100 y) offsets in carbon emission. Managed wetlands such as rice paddies, in particular, represent a promising distributed carbon sink. Presently, rice production occupies an area of approximately 1.5 x 10^{12} m^2 globally and, with an average carbon content of 4%, accounts for approximately 60 Gt of carbon within the upper 1 m of soil (IRRI, 2006). Therefore, if the averaged carbon content within the upper meter were increased by even just 10% (4 g-C / Kg-soil), the sequestered carbon would offset an entire year of anthropogenic greenhouse gas production. Increasing carbon storage can be achieved by ensuring that anaerobic microbial respiration dominates during both cropping and fallow periods by sustaining periods of water inundation, but will also require limiting methane (methanogensis, resulting from extreme anaerobic conditions) and nitrous oxide emissions, the production of which could offset any gains in limiting carbon dioxide formation. Through control of water levels, periods of inundation, and rates of both flooding and draining, we are investigating whether specific iron(III) minerals can be maintained that will ensure anaerobic microbial metabolisms with minimal methanogenesis. The objectives of our project are (i) to examine current organic carbon and iron mineral phase contents within existing wetlands under different historic management practices and (ii) to conduct a pilot study were we control the operative microbial metabolisms to limit carbon mineralization rates (relative to aerobic rates) while restricting methane production.

Wetlands are characterized by high primary productivity (Brinson et al. 1981) which, when coupled with seasonally-variable water saturation, can lead to disparate carbon pathways leading to CO_2 or CH_4 flux to the atmosphere and organic and inorganic carbon sequestration (Figure 1). These divergent outcomes are primarily controlled by water saturation, a parameter manipulated in as rice paddies. Iron(III) oxides are unique among the anaerobic respiratory processes in that energy yields vary dramatically depending on the specific mineralogical form of iron; for example, a progression from ferric hydroxide to hematite decreases the energy yield by nearly 25%. Under conditions of limited oxygen delivery to soils, iron commonly serves as a dominant contributor to microbial respiration. However, the quantity of iron within a given soil is often fixed, so a sustained coupling of carbon oxidation to iron reduction necessitates redox cycling of iron. Hydrologic regimes that produce seasonal wetting and drying, such as rice paddies, can provide the driver for iron cycling; during drying iron species undergo oxidation, during wetting periods iron species undergo reduction. Thus iron cycling has the potential to both limit carbon oxidation and limit methane release (by acting as a subsurface oxidative agent and a competing electron acceptor in microbial respiration). Rattering (2000) and Sahrawat (2004) demonstrated the potential for iron oxides to limit methanogenesis and a strong correlation has been established between the extent of the overlying iron oxide-rich zone and methane oxidation (Fiedler 2000; 2004). Thus, by manipulating both the period and rate of cycling between wet and dry periods, the proportion of each pathway and the mineralogical form of iron oxide can be dictated—potentially giving rise to large variations in carbon storage.

Our project was initiated in January 2007 and we are in the early stages of data collection on a series of experiments. We are presently conducting a series of soil manipulation studies where hydrologic or chemical conditions are adjusted to optimize carbon storage while minimize methane emissions. Effectively, we are trying to create conditions where carbon oxidation is linked overwhelmingly to Fe(III) respiration. Within the Mekong Delta of Cambodia, we are using 12 L vessels, to which we are adding approximately 10 Kg of soil, to examine how water inundation period or Fe amendment alters both carbon mineralization and methane production rates. We have introduce three different iron minerals (ferrihydrite, goethite and hematite), which produce thermodynamic respiratory yields varying by 25%, to soils in separate vessels, with each treatment conducted in triplicate. The soil vessels, with and without rice, are then subject to the following conditions (i) permanent inundation throughout the annum, (ii) three periods of drainage and flooding coinciding with harvesting and replanting, with water level changes occurring rapidly, (iii) three periods of drainage/flooding with slow drainage (2 week period), and (iv) three periods of drainage/flooding with pulsed water cycles during drainage. The latter two treatments are intended to form more crystalline Fe(III) phases (e.g., hematite) that while lead to the slowest carbon mineralization rates while still limiting methanogenesis. Within the different treatments, we are measuring the net daily efflux of CO_2 and CH_4 from the soil. In order to track the depth of soil respiration linked to various electron acceptors, we are also conducting gas profile measurements in combination with the measure of dissolved constituents (NO_3^-, Mn^{2+}, SO_4^{2-}, and H_2S). We are also measuring total carbon, Fe(III) content, and Fe(III) mineralogy throughout the course of experimentation. To further aid in determining the rate of carbon oxidation within each treatment system, we are also performing differential decomposition measurements. To each soil treatment, we are adding 10 g of ground rice hulls encompassed within a nylon-mesh bag (100 μm openings) that are embedded at

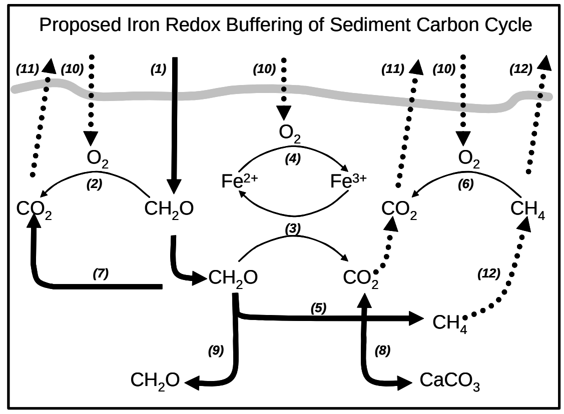

Figure 1. Carbon in wetland sediments can be released as gas (CO_2 and CH_4) or sequestered (as organic or inorganic carbon) in the sediments.

Processes and Reactions

(1) Solid and aqueous transport of organic carbon

(2) Carbon oxidation by oxygen:

$$CH_2O + O_2 \Rightarrow CO_2 + H_2O$$

(3) Carbon oxidation by ferric iron:

$$CH_2O + 4Fe(OH)_3 \Rightarrow CO_2 + 4Fe^{2+} + 8OH^- + 3H_2O$$

(4) Iron oxidation by oxygen:

$$4Fe^{2+} + O_2 + 10H_2O \Rightarrow 4Fe(OH)_3 + 8H^+$$

(5) Methanogenesis:

$$2CH_2O \Rightarrow CO_2 + CH_4$$

(6) Methane Oxidation:

$$CH_4 + O_2 \Rightarrow CO_2 + 2H_2O$$

(7) Fermentation

$$2CH_2O_{(complex)} \Rightarrow CO_2 + H_2O + CH_2O_{(simple)}$$

(8) Inorganic Sequestration

$$CO_2 + Ca^{2+} + H_2O \Leftrightarrow +CaCO_3 + 2H^+$$

(9) Organic sequestration

(10) Oxygen gas flux

(11) and *(12)* Carbon dioxide and methane gas flux.

varying depths in the soil. We then extract the bags at varying times during the incubation and measure changes in carbon content.

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Appendix 1, Biographical Information

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Activities and Research Interests

Scott Fendorf is an associate professor of soil and environmental biogeochemistry in the School of Earth Sciences. His research focuses on the chemical and biological processes that control the elements such as iron, manganese, arsenic, uranium, and chromium within soils, sediments, and surface waters. Over the past decade, he and his research group have detailed the pathways of iron cycling with a particular emphasis on bacterial reduction of iron(III) minerals. He has published more than 100 papers, organized a series of symposia/workshops, and given numerous invited presentations on this subject area (including a recent address to the National Academy of Sciences on "molecular aspects of soil processes" relevant to the "future directions of soil science research").

Education:

1992 Ph.D. in "Soil & Environmental Chemistry", University of Delaware. Advisor, Donald L Sparks
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Professional Experience:

Assistant Professor, Soil Science Division, University of Idaho	1993-1998
Associate Professor, Soil Science Division, University of Idaho	1998-1999
Pacific Northwest Laboratory Affiliate Staff Scientist	1994-present
Adjunct Professor, Chemistry Department, University of Idaho	1997-1998
Affiliate Faculty, Stanford Synchrotron Radiation Laboratory	1999-present
Affiliate Faculty, Interdisciplinary Graduate Program in Environment and Resources	2005-present
Assistant Professor, Stanford University	1999-2002
Associate Professor, Stanford University	2003-present
Associate Chair, Dept. of Geological and Environmental Sciences	2006-present

Selected Publications (>100 total):

Ginder-Vogel, M. A., C. Criddle, and S. Fendorf. 2006. Thermodynamic constraints on the oxidation of biogenic UO_2 by Fe(III) (hydr)oxides. Environ. Sci. Technol. 40: 3544-3550.

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EDUCATION

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PROFESSIONAL EXPERIENCE

Assistant Professor, *Geosciences, Boise State University*	July 2004-Present
Visiting Scholar, *Geological and Environmental Sci., Stanford University*	2002-Present
Assistant Research Professor, *Desert Research Institute*	2002-2004
Graduate Faculty, *Hydrological Sciences, University of Nevada, Reno*	2003-2004
Post Doctoral Fellow, *Geological and Environmental Sci. Stanford University*	2000-2002

SELECTED PUBLICATIONS (>25 Total)

Mayer, K.U., Benner, S.G., and Blowes, D.W. 2006 Application of the reactive transport model MIN3P to a reactive barrier treating acid mine drainage. Contaminant Hydrogeology, 85, 3-4, 195-211.

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