AN EXPLORATORY PROPOSAL FOR CARBON STORAGE

Increasing Carbon Storage within Soils By Controlling Key Microbial Respiration Processes

Investigators

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Abstract

Managed wetlands, in particular rice paddies, represent a promising distributed carbon sink that may help to offset presently increasing levels of atmospheric carbon dioxide. Wetlands are characterized by high primary productivity which, when coupled with seasonally-variable water saturation, can lead to disparate carbon pathways producing CO_2 or CH_4 to the atmosphere and organic and inorganic carbon sequestration. These divergent outcomes are primarily controlled by water saturation, a parameter manipulated in agriculturally managed wetlands such as rice paddies. Under conditions of limited oxygen delivery to soils, iron commonly serves as a dominant contributor to microbial respiration. Ensuring that iron(III) serves as the dominant sink for electron flow from organic carbon ensures a slow rate of metabolism and minimal methane or nitrous oxide emission, both potent greenhouse gases. Here we illustrate through iron amendments and controlled flooding that methane flux can be regulated and carbon storage increased within soils under rice producing conditions. Further, we show that methane production is dependent upon the degradation state of rice straw added to soil. Collectively, our results demonstrate the both carbon storage and decreased methane efflux from soils can be achieved within soils.

Introduction

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 1.5×10^{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

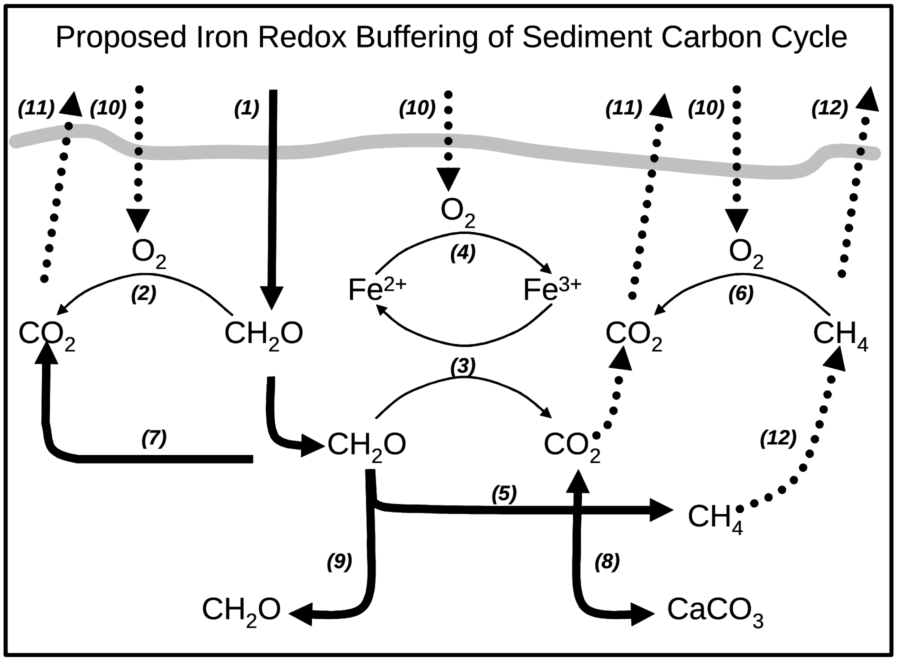


Figure 1. Carbon in wetland sediments can be released as gas (CO_2 and CH_4) or sequestered (as organic or inorganic carbon) in the sediments. Processes and reactions denoted are: (1) Solid and aqueous transport of organic carbon; (2) Aerobic carbon oxidation: $CH_2O + O_2 \Rightarrow CO_2 + H_2O$; (3) Carbon oxidation by ferric iron: $CH_2O + 4Fe(OH)_3 \Rightarrow 4Fe(OH)_3 + 8H^+$; (4) Iron oxidation, $4Fe^{2+} + O_2 + 10H_2O \Rightarrow 4Fe(OH)_3 + 8H^+$; (5) Methanogensis, $2CH_2O \Rightarrow CO_2 + CH_4$; (6) Methane oxidation, $CH_4 + O_2 \Rightarrow CO_2 + 2H_2O$; (7) Fermentation, $2CH_2O$(complex) => $CO_2 + H_2O + CH_2O$(simple); (8) Inorganic sequestration $CO_2 + Ca + H_2O \Leftrightarrow CaCO_3 + 2H^+$; (9) Organic sequestration; (10) Oxygen gas flux; (11, 12). Carbon dioxide and methane gas flux.

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 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.

Results

We conducted two primary experimental trials to determine the potential for rice paddy hydrology manipulations to decrease methane efflux while increasing carbon storage relative to aerobic conditions. Our experiments are predicted on rice production within the Central Valley of California, utilizing soil of various classifications and under different states of production. Soils were collected from rice paddies of Richvale, CA and with different rice straw amendments. A high clay content (Vertisol) rice paddy soil was collected after a fallow period and two subsequent experiments were conducted. First, we performed a microcosm incubation of the soil under varying states of water saturation and iron oxide treatments; second, we examined the impact of rice straw amendment under active rice production within greenhouse studies, again examining water saturation and iron oxide treatment.

Respiration and Methane Production from Iron and Carbon Amended Soil Incubations

Soil, collected from Richvale, CA after a fallow season, was air-dried and sieved through a 8-mm soil sieves. Soils received varying iron amendments: a control having no iron addition, 10 g ferrihydrite (a short-range order ferric hydroxide) per Kg soil, or 10 g/Kg goethite (a crystalline ferric oxyhdroxide). Organic carbon additions were made in select treatments as either glucose (50 g/L soil water) or rice straw addition (30 g/Kg). Soils were maintained either with standing water or after gravimetric water drained from soil (termed ‘field capacity), and all experiments were performed in triplicates.

Six hundred grams of soil were mixed with iron and transferred to an incubator and water was added. Soils were incubated for 5-week periods at 20 C; exodunous carbon additions were made after these incubations and the soil processes monitored for another 5-week period. Gas samples were taken from the soil microcosms on a weekly basis to assess the flux CH_4, and CO_2. Microcosms were enclosed in 1.9 L screw-lid canisters equipped with an open sampling port on the side. After fifteen minutes of equilibration, 6 mL of gas was sampled using a 10-mL gas chromatography syringe. Samples were measured for CH_4 and CO_2 within 24 h after sampling. Methane and CO_2 were measured on a Shimadzu 14A Gas Chromatograph equipped with FID and ECD (Ni63) detectors.

Changes in gas production were not significant under any conditions within first 27 days due to a lack of labile carbon, despite a total carbon content of 1.1% (Figure 2), owing to a preceding fallow period. As a consequence, iron additions, as noted in Figure 2 for ferrihydrite, had a limited influence on carbon transformation.

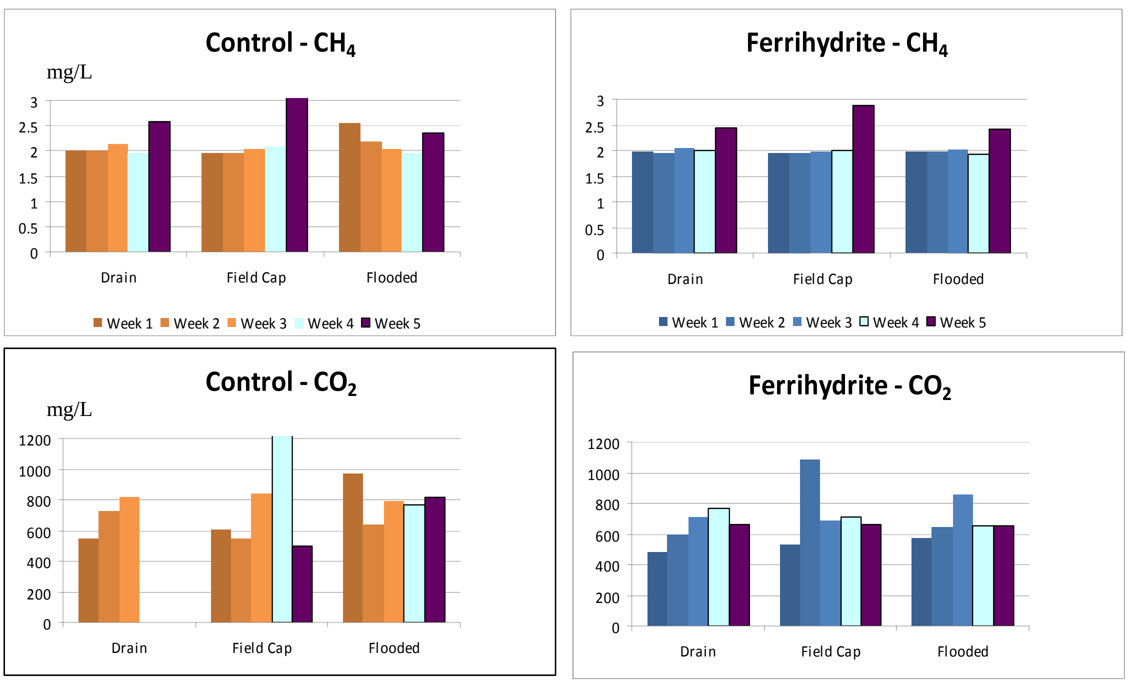


Figure 2. Iron(III) oxide (as ferrihydrite) impact on emission of CH_4 and CO_2 within fallow rice paddy soils at different moisture levels. Limited effect of iron or moisture content was noted on methane or carbon dioxide production.

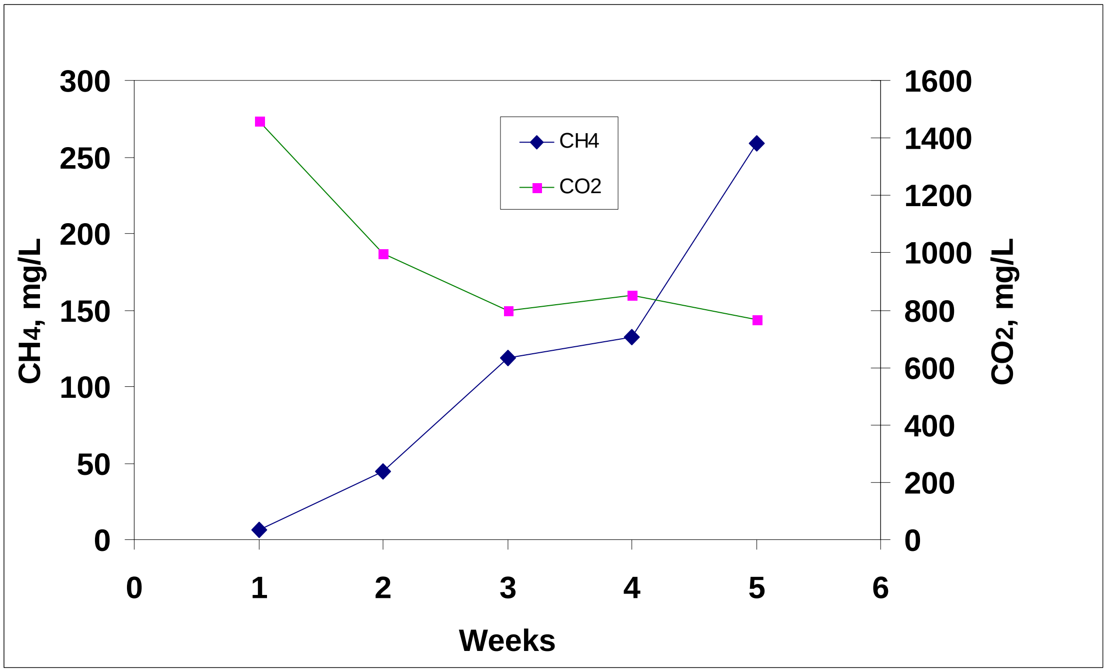


Figure 3. Change in the emission of CH_4 and CO_2 with time after addition of glucose or rice straw.

In contrast to the limited gas efflux for fallow soils, carbon amended soils underwent rapid respiration, inclusive of methanogenesis (Figure 3). Iron had a mixed impact on both the extent of respiration following a 5 week incubation and on the extent of methane efflux (Figure 4). Goethite, a well crystallized iron oxyhydroxide, addition to the soil did not significantly influence the production of methane and carbon dioxide, while, in contrast, ferrihydrite addition did significantly reduce methane and carbon dioxide when compared with the control (Figure 4). Ferrihydrite has both a greater surface area and

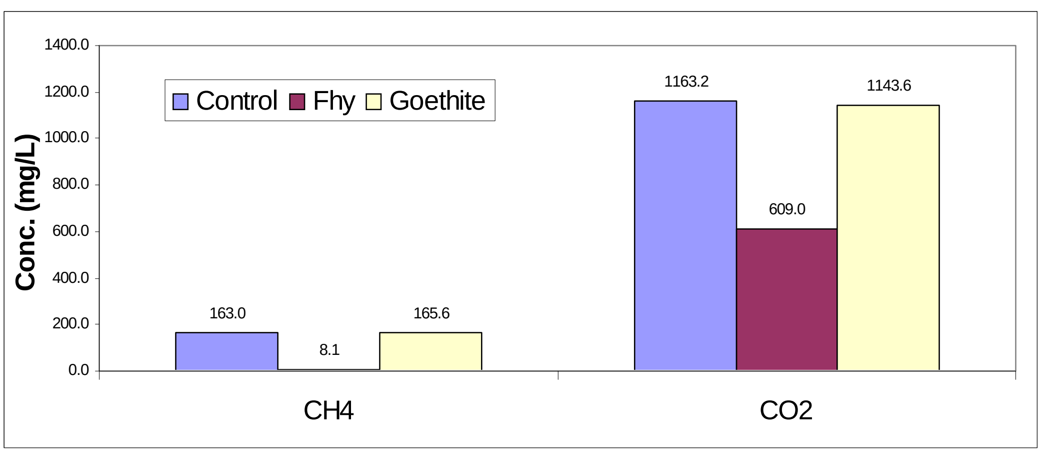


Figure 4. Impact of adding Fe-bearing minerals to soil on gas production after glucose or straw amendment.

redox potential than goethite, and thus is generally ascribed to be more available to the microbial community for respiration. Accordingly, it is reasonable to conclude that it would suppress methane production most extensively, as observed here where methanogenesis is almost completely inhibited over the 5 week incubation.

Respiration and Methane Production from Iron Amended Rice Cultivated Soils

A greenhouse mesocosm experiment was established to examine methane and carbon dioxide efflux from carbon and iron amended rice paddy systems (Figure 5). Soil (13% sand, 32% silt, 55% clay; total C content = 1.1%) was collected from a rice field in Richvale of the central valley in California. The field was fallowed for one growing season before soil collection. The soil was air-dried and sieved through an 8-mm mesh.

Figure 5. Mesocosm experimental system for methane and carbon dioxide production in rice paddy soils.

Mesocosm conditions were partitioned into three experimental permutations and two controls (Table 1). Permutations and controls were subdivided into units planted with rice or those left unplanted.

Mesocosms consisted of 21 by 26 cm (width/height) buckets with bottom drain plugs, and were filled with about 6 kg of dry soil pre-mixed with 100 g of rice straw (chopped to ~ 7 cm length). Iron (III) oxides were mixed into the soil prior to straw addition for permutations 1 and 2. Soil was packed into the buckets for a depth of 20 cm, and ceramic suction lysimeters (Soil Moisture, Santa Barabara, Ca) were inserted at

Table 1. Outline of experimental permutations (EP) and controls (Ctrl). All mesocosms were run in triplicate.

	EP 1	EP 2	EP 3	Ctrl 1	Ctrl 2
Ferrihydrite[1]	No	Yes	No	No	No
Goethite[1]	No	No	Yes	No	No
Wet/Dry cycle	Yes	No	No	No	No
Flooded	Variable	Yes	Yes	Yes	No
Rice[2]	Yes/No	Yes/No	Yes/No	Yes/No	Yes

[1]Fe-oxides were mixed into the soil for a final concentration of 0.1% Fe (m/m, Fe to dry soil)
[2]Rice – "yes/no" indicates that the permutation or control consisted of 3 mesocosms with and without rice (total of 6 units).

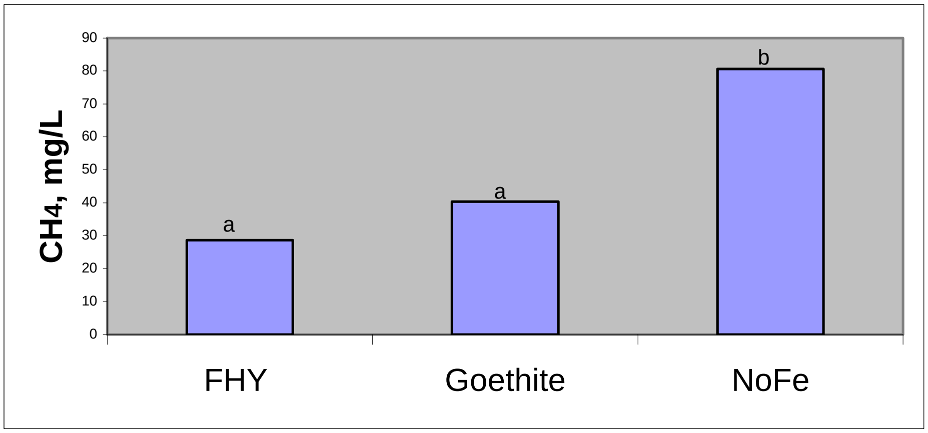
depths of 5 and 15 cm from the soil surface. Nylon lysimeter tubing was run through the side of the buckets, fitted with lure-lock connections, and plugged to prevent oxygen diffusion into the mesocosm (Figure 5). Five germinated rice seeds were planted three days after flooding the mesocosms. Water levels were held constant at 4 cm depth for flooded mesocosms by replacing transpired or evaporated water with deionized water. Replicates for control 2 were watered as needed in order maintain plant growth. Greenhouse temperature (15.5 C low, 32 C high) and light (12-hour photo period) were controlled for the duration of the experiment. Mesocosms were managed for 151 days (10/4/2007 to 3/3/2008), upon which all of the buckets were drained and allowed to dry. Mesocosms from permutation 1 were drained when methane flux started to increase (day 43) and flooded 7 days later. Buckets were also weeded on a regular basis.

Weekly gas and water samples were taken. Flux chambers (22.2 cm in length) were constructed from 7.6 cm diameter plastic tubing and caps. Lure-lock fittings were inserted in the cap to vent the chamber and allow sampling access. For gas sampling, flux chambers were placed on the soil surface, in between plants where necessary, and allowed to equilibrate for 15 minutes. Gas-tight syringes were used to take 6 mL of gas from each chamber. Pore-water samples were taken by using 60 mL syringes to apply suction to the lysimeters. The first 3 mL of sample was discarded. The following 6 mL of sample was immediately filtered (0.20 µm) and acidified with concentrated hydrochloric acid for measurement of Fe(II) and Mn(II). Methane and CO_2 were measured on an FID and methanizer-equipped Shimadzu 14A Gas Chromatograph. Total dissolved Fe and Mn were measured on an inductively coupled plasma optical emission spectrometer.

As noted for the non-rice growing experiments described above, addition of Fe-minerals significantly decreased methane production. Here, however, both ferrihydrite and goethite appreciably decrease methane release, with ferrihydrite having a more pronounced impact (Figure 6). Soil respiration, as noted by carbon dioxide efflux, was greater with ferrihydrite addition than for goethite, a result expected based on the microbial availability of this iron form.

In comparison to soil incubated without rice, those having active plant communities increased both soil respiration and methane production. Although aquatic plants induce near-root aeration, as noted by decreased dissolved concentrations of Fe(II) and Mn(II) (not shown), increased root exudation of dissolved organic carbon stimulate methanogensis—along with total respiration.

Similar to iron amendment, cycling through a soil drainage event also decreased methane emissions from soil. Inundation of oxygen and regeneration of both Mn(IV) and Fe(III) oxidants limits methanogenesis (and promotes methane oxidation), yielding results comparable to iron addition. On the basis of flooding-draining conditions giving similar results to iron amendments, it appears that simple hydrologic manipulation of rice paddies has the capacity to limit methane production while maintaining slow respiration characteristic of anaerobic soils. The combined result of short drainage pulses is thus regeneration of iron(III) minerals that inhibit methane production while maximizing carbon storage within soils.



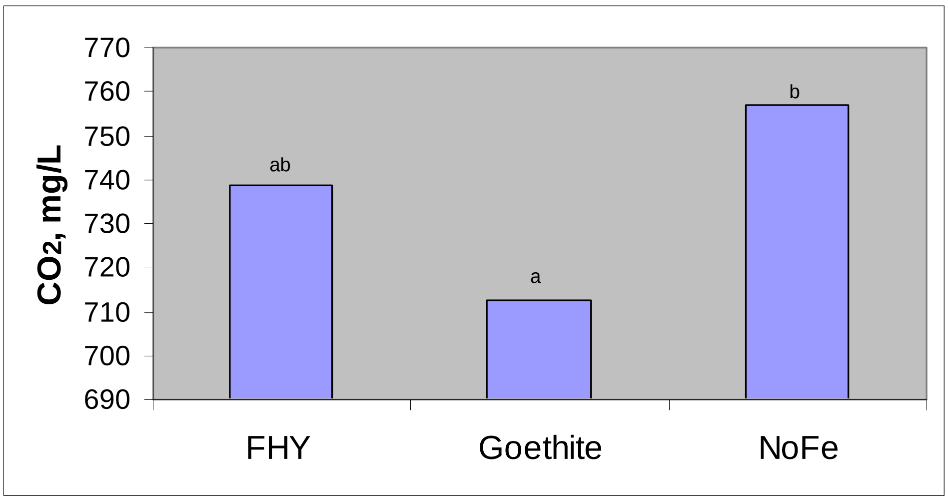


Figure 6. Influence of addition of Fe (hydr)oxides on CH_4 and CO_2 emisisons from soil after a 155 d incubation. The addition of goethite significantly reduced the CO_2 emission while ferrihydrite (FHY) did not have significant influence on the CO_2 emission. Note that bars with the same letter above mean they are statistically similar at $p = 0.05$.

Progress and Future Plans

Our pilot research project has yielded several interesting findings that are highly relevant to mitigating short-term climate forcing. First, iron oxide mineral amendment to soils, or regeneration through short pulsed drainage events, has the capacity to decrease methane efflux from rice paddies by more than 50% relative to continuous flooding conditions. A simple, short-term (3 d) drainage of high clay content soils regenerates the iron oxide content through aeration and subsequently inhibits methane production. Given that rice production accounts from greater than 10% of global methane emissions (yielding approximately 22 time greater heat insulation than carbon dioxide on a comparable molar basis), decreasing this value by 50% would have direct and immediate impacts on climatic forcing. Second, current approaches for limiting methane production, such as new rice cultivars grown under unsaturated soil conditions, result in high carbon dioxide efflux owing to enhance microbial respiration under aerated (aerobic) soil conditions. Through short pulsed drainage events or iron oxide additions/regeneration, total carbon respiration is maintained at rates of continuous flooding. In combination, our findings suggest that a hydrologic management scheme appears viable for minimizing methane production while maximizing carbon storage in soils under rice production.

In addition to iron oxide impacts on carbon cycling, either through direct addition or hydrologic manipulation, we also note the importance of considering carbon quality on methane production. Although containing 11 g C/Kg, soils residing in a fallow state (no carbon additions) for a single growing season effectively have no methane production (comparison of Figures 2 and 3). Thus, if rice straw can be partially degraded prior to incorporation within soil, it is possible to limit methane production independent of flooding conditions.

On the basis of our findings, we believe there is great potential to develop a strategy that decreases methane efflux from rice paddies by well more than half (potentially up to 90% reduction in emissions) while maximizing carbon storage. Our current premise is that a simple hydrologic strategy can be developed at the field scale, with a global perspective, for pulsed drainage under otherwise continuous flooding. Timing and duration of the pulses will be dependent on the soil texture (clay content), iron content, and growth factors (temperature and organic carbon levels). Further, we believe it is possible to provide a managed rice straw decomposition step whereby methane is intentionally generated but captured, providing both an energy source and a labile carbon deplete residual suitable for soil incorporation; the two-step process would nearly eliminate methane production independent of flooding conditions but would maintain a carbon storage placement in soils (also providing vital nutrients and soil physical amendment).

While we are complete the final stages of our experiments and calculating the global ramifications, we will be working toward a full GCEP proposal that seeks to explore specific management techniques, including pulsed flooding and two-stage rice straw decomposition, for maximizing carbon storage in soils while minimizing methane production. Our pending investigations would partner with rice growers in the Central Valley of California, low-lands of Thailand, and in China, to develop both a viable carbon. A large concern of our research will be not only to develop means to offset climate forcing, but to also ensure sustainable rice production. Thus, our studies will also deal with nutrient cycling under the proposed scenarios. In sum, our aim is to develop a rice management strategy that serves as a technology for decadal increases in soil carbon storage and minimization of methane emissions.

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