Influence of Iron (Hydr)oxide Mineralogy on Soil-Sedimentary Methanogenesis

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The net efflux of methane from soils and sediments is controlled by numerous physical and biogeochemical processes, many of which remain loosely constrained or enigmatic. Poorly crystalline and metastable soil-sedimentary iron (hydr-)oxides, such as ferrihydrite, are known to inhibit methanogenesis through enabling dissimilatory metal-reducing microbes (DMRB) to out-compete methanogens. However, iron (hydr)oxides with greater thermodynamic stability impart less of an inhibitory effect owing to the lower energy yield afforded DMRB's, particularly with increased metabolite (Fe^{2+} and HCO_3^-) activities. It has been hypothesized that (semi)conductive iron (hydr)oxides may mediate direct interspecies electron transfer (DIET) between DMRB and methanogens, facilitating methane production.[1,2] We tested this hypothesis by inoculating slurries of hematite (Fe_2O_3), goethite (FeOOH), and ferrihydrite ($Fe(OH)_3$) with wetland sediment, and measured methane production, soluble Fe(II), and solid-phase Fe(II)/Fe(III) using a residual gas analyzer mass spectrometer (RGA-MS) and spectroscopic methods respectively. High levels of methane and low concentrations of Fe(II) were produced in hematite and goethite treatments relative to controls, while abundant Fe(II) and minimal methane was produced in the ferrihydrite treatment. While this data supports the iron (hydr)oxide-DIET hypothesis, we are performing further experiments using isotopically-labeled acetate to discern whether this process is operative. Finally, additional experiments are performed to isolate reduction-oxidation processes; using a potentiostat, the electrical potential of hematite is poised at values representative of methanogenic conditions to test whether methanogens may accept electrons from hematite. This research has important implications for understanding methane emissions from iron oxide-rich soils and can be used to inform models for global methane emissions.

[1] S. Kato, K. Hashimoto, K. Watanabe, *Environ. Microbiol.* **14**, 1646–1654 (2012). [2]A. E. Rotaru *et al.*, *Appl. Environ. Microbiol.* **80**, 4599–4605 (2014).