Evaluating Trace Metal Limitations on Methane Fluxes in Terrestrial Ecosystems

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The greenhouse gas methane (CH_4) is produced in terrestrial ecosystems by subsurface microbial carbon cycling under anaerobic conditions. Its formation is localized at terrestrial-aquatic interfaces such as wetlands, permafrost soils, and soil microenvironments where oxygen is limited and organic carbon is available. Global climate models predict higher CH_4 emissions from wetlands in the future because of an increase in inundated area and the enhancement of CH_4 production as temperature increases. The large radiative forcing induced by increasing atmospheric CH_4 concentrations makes it is critical to understand the environmental controls on CH_4 production.

Global models of methane biogeochemistry assess CH_4 fluxes at the grid cell level by accounting for microbial respiration rates and how these rates are affected by temperature, pH, and soil redox state. Temperature is a major control on CH_4 production, and recent work has shown that methanogenesis in terrestrial ecosystems displays a high activation energy, indicating that increasing temperature will result in a substantial increase in CH_4 emissions from wetlands. However, it has also been shown that this relationship over predicts the temperature response of CH_4 production in many systems, suggesting that other substantial limitations on methanogenesis are present. A potentially important limitation that has been largely overlooked is trace metal availability. Methanogens are unique in having high enzymatic requirements for trace metals (e.g., Ni, Co, Zn, and Mo). Laboratory studies, primarily involving pure cultures of methanogens or anaerobic bioreactors, have shown that limited availability of trace metals inhibits methanogenesis, but such limitations have not been investigated in the field.

We hypothesize that trace metal limitations are important controls on CH_4 fluxes in terrestrial ecosystems. To test this hypothesis, we have characterized the properties, CH_4 production potential, and speciation of trace metals in wetland soils from field sites in Missouri and Florida. Surface waters in these wetlands are low in trace metals, typically <0.05 μM, well below the 1 to 5 μM concentrations shown as optimal for methanogenesis in pure culture studies. Regional river waters and groundwaters, potential water sources for the wetlands, show similar suboptimal dissolved metal concentration. Initial microcosm studies reveal that the wetland soils from our sites show methanogenic activity when maintained under anoxic conditions. Assays of lipid biomarkers indicate the presence of substantial bacterial and archaeal communities, including marker indicative of methanogens. Solid phase characterization reveals trace metal concentrations in the soils on the order of 1 to 10 μg/g. Spectroscopic studies suggest that the native metal content is largely associated with minor detrital components (e.g., silicate minerals). Soils from both locations show a substantial binding capacity for metals that maintains low dissolved concentrations (<0.05 μM) except upon addition of exceptional metal loads. Soils from the Missouri site have greater binding capacity, and spectroscopic measurements show that metals added to these soils bind to thiol groups on organic matter. Binding occurs primarily to carboxylate groups in the Florida soil, accounting for its lower capacity for metals. These initial studies indicate that trace metal availability in the wetlands systems under investigation is far below optimal levels and suggests that methanogenesis at these sites may be trace metal limited.