The role of iron complexation in the production of reactive oxygen species and CO_2 in arctic soil waters

ADRIANNA TRUSIAK[1], LIJA A. TREIBERGS[1], GEORGE W. KLING[2], VINCENT NOËL[3], JOHN R. BARGAR[3], ROSE M. CORY*[1]

[1]Earth and Environmental Science, University of Michigan, Ann Arbor, MI, 48109, USA, (*correspondence: rmcory@umich.edu)

[2]Ecology and Evolutionary Biology, University of Michigan, Ann Arbor, MI, 48109, USA

[3]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratoy, Menlo Park, CA, 94025, USA

Interactions between iron and organic carbon (C) in soils influence the fate of soil C. These interactions may be particularly important in the Arctic where thawing of the permafrost soils allows tremendous stores of organic C to be converted into carbon dioxide (CO_2) on relatively short time scales, thus providing a positive and accelerating feedback to climate change. Evidence suggests that dark, abiotic iron redox cycling results in the oxidation of dissolved organic C (DOC) to CO_2, and that this process depends on iron's association with DOC. Specifically, aeration of anoxic or low oxygen soil waters containing 230 ± 58 µM reduced ferrous iron (Fe(II)) produces 1.7 ± 0.6 µM hydroxyl radical (•OH). •OH is a highly reactive oxidant of DOC, oxidizing DOC to CO_2 in over half of the soil waters tested. We hypothesized that the variability in the amount of •OH and CO_2 produced during Fe(II) oxidation depends on the association of iron with DOC (i.e., iron-DOC complexation). To test this hypothesis, we characterized iron-DOC complexation in solutions of DOC extracted from arctic streams amended with Fe(II) spanning the range of naturally occurring Fe(II) concentrations in arctic soil waters. We used synchrotron based X-ray analysis (XAS and EXAFS) to assess the oxidation state of iron, to constrain the chemical composition of the complexes, and to measure amount of iron complexed to organic C versus free iron. EXAFS showed substantial complexation of Fe(II) to arctic DOC, on the basis of comparison to free Fe(II) and Fe(II)-DOC reference spectra. The complexation of iron and DOC in relation to •OH and CO_2 produced upon Fe(II) oxidation supports the hypothesis that with increasing Fe(II)-DOC complexation there is increasing yield of •OH and CO_2 produced during Fe(II) oxidation. Understanding the role of iron-DOC complexation on the biogeochemical reactions that convert organic C to CO_2 may be critical for predicting the fate of thawed permafrost C.