Effects of sodium borohydride reduction and dioxygen concentration on the photochemical properties of humic substances

NEIL V. BLOUGH*,[1], KELLI GOLANOSKI[1], YI ZHANG[1], AND ROSSANA DEL VECCHIO[1,2]

[1]Department of Chemistry and Biochemistry University of Maryland College Park MD United States (*correspondence: neilb@umd.edu)

[2]Earth System Science Interdisciplinary Center University of Maryland College Park MD United States

Previous results have demonstrated that the reduction with sodium borohydride of Suwannee River humic and fulvic acids, a commercial lignin, and a series of solid phase C18 extracts from fresh, estuarine, coastal and offshore waters of the middle Atlantic bight produces a preferential loss of long wavelength (visible) absorption and enhanced, blue-shifted emission [1], consistent with a previously proposed electronic interaction model [2,3]. Here the effects of this reduction on the photosensitized oxidation of 2,4,6-trimethylphenol (TMP) and on the photoproduction of hydrogen peroxide is examined. For unreduced samples, the initial rate of TMP loss (R_{TMP}) increased with decreasing [O_2] concentration over the range from 1.2 mM to ~ 50 µM; below [O_2]~50 µM , R_{TMP} decreased precipitously, with no observable loss under N_2. Borohydride reduction substantial reduced R_{TMP} at all [O_2]. These results are consistent with the (aromatic ketone) triplet sensititization model of Canonica and co-workers [4,5]. In contrast, borohydride reduction only slightly decreased the intial rates of hydrogen peroxide production and similar dependencies of the initial rates on [O_2] were observed with both reduced and unreduced samples. Preliminary work, however, indicates interesting differences in peroxide yields between these samples under conditions in which they are first irradiated under N_2 followed by the introduction of O_2 at increasing delay times.

[1] Ma *et al.* (2010) *Environ. Sci. Technol.* **44**, 5395-5402. [2] Del Vecchio and Blough (2004) *Env. Sci. Tech.* **38**, 3885. [3] Boyle *et al.* (2009) *Environ. Sci. Technol.* **43**, 2262-2268. [4] Canonica *et al.* (1995) *Environ. Sci. Technol.* **29**, 1882. [5] Canonica *et al.* (2000) *J. Phys. Chem. A* **104**, 1226-1232.

Amendment of mill tailings for *in situ* treatment of mine drainage

D.W. BLOWES[1], M.B.J. LINDSAY[1], A.H.M. HULSHOF[1], C.J. PTACEK[1], P.D. CONDON[1] AND W.D. GOULD[2]

[1]Dept. Earth and Environ. Sci. Univ. Waterloo., ON, Canada, N2L 3G1 (blowes@uwaterloo.ca; matt.lindsay@uwaterloo.ca; ptacek@uwaterloo.ca)

[2] CANMET - Mining and Mineral Sciences Laboratories Ottawa, ON,K1A 0G1 (dgould@nrcan.gc.ca)

Field studies conducted at two mill-tailings impoundments suggest that amendment of sulfide-rich tailings with small masses of organic carbon has the potential to provide passive treatment of pore water through microbially-mediated sulfate reduction, metal-sulfide precipitation and alkalinity production. At the Kidd Creek Metallurgical Site, Timmins, Ontario, fine-grained mill tailings containing 15 – 20 wt. % sulfide minerals and 8 wt.% carbonates, were amended with 20 vol. % organic carbon in the form of pulp and paper sludge or wood chips. At the Greens Creek Mine, Alaska, mill tailings containing 34 wt. % pyrite were amended with 5 or 10 vol. % organic carbon as varied mixtures of peat, spent brewing grain and municipal biosolids. Increased populations of sulfate-reducing bacteria (up to 10^6 cells g^{-1}), and increased alkalinity concentrations were observed at both sites. These changes were accompanied by decreases in pore-water concentrations of SO_4, Zn and other metals as a function of time and relative to control cells. Mineralogical investigations indicate the precipitation of secondary Fe-S and Zn-S phases. However, increases in dissolved Fe and As concentrations were observed near the onset of the Greens Creek field experiments. Combined, these experiments demonstrate the potential for tailings drainage management using organic carbon amendments, but also indicate that care must be taken to limit the inadvertent release of dissolved constituents due to the reductive dissolution of Fe(III) and SO_4–bearing phases.