Flavins, redox potentials and reactive oxygen species

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Flavins are a major class of redox-active exudates secreted by microorganisms under both aerobic and anaerobic conditions [1]. Here we present evidence that flavins may (1) control redox potential (E_H) measurements even at very low, sub-micromolar concentrations, and (2) catalyze the oxidation of As(III). The experimental data were acquired in controlled experiments using both commercially available flavins and natural compounds released by *Shewanella oneidensis* MR-1. Time series E_H values were obtained with a conventional Pt electrode.

In a series of experiments of increasing biogeochemical complexity, the successive addition of groundwater solutes, aqueous metabolites (O_2, nitrate and lactate), bacteria (*S. oneidensis* MR-1) and goethite resulted in a redox cascade with E_H values ranging from +500 to -350 mV (SHE). Between +300 and -300 mV, low concentrations of flavins secreted by *S. oneidensis* MR-1 controlled the response of the Pt electrode [2]. The observed E_H range coincided with the measured difference in E_H between the oxidized and reduced forms of flavins. We thus propose that flavins, and other redox-active exudates, help explain the relatively low E_H values recorded under nitrate-reducing conditions in water-saturated environments.

Our experimental data further provide evidence that reduced flavins are able to generate reactive oxygen species, such as H_2O_2, and possibly oxygen radicals, when exposed to O_2. Flavins may therefore significantly promote the mineralization of organic compounds and the oxidation of reduced metals and metalloids [3, 4]. In support of this hypothesis, we present preliminary evidence that the addition of reduced flavins to aerated solutions greatly accelerates the oxidation of As(III) to As(V).

[1] Marsili *et al.* (2008) *PNAS* **105**, 3968-3973. [2] Markelova *et al.* (2017) *Env. Chem.* doi: 10.1071/EN17158. [3] Bae & Lee (2013) *GCA* **114**, 144-155. [4] Massey (1994) *J. Biol. Chem.* **269**, 22459-22462.