

## Hydroquinone-mediated redox cycling of iron and concomitant oxidation of hydroquinone under acidic conditions

C. JIANG, S. GARG, T. D. WAITE\*

School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia (chao.jiang@unsw.edu.au, s.garg@unsw.edu.au, \*correspondance: d.waite@unsw.edu.au)

Interactions of 1,4-hydroquinone with soluble iron species are studied over a pH range of 3–5. Our results show that Fe(III) is reduced by 1,4-hydroquinone in acidic conditions, generating semiquinone radicals ( $Q^{\cdot-}$ ) that can oxidize Fe(II) back to Fe(III). The deprotonated form ( $Q^{\cdot-}$ ) of semiquinone radicals oxidizes Fe(II) more rapidly than the protonated form ( $HQ^{\cdot}$ ), resulting in an increase of oxidation rate of Fe(II) with increase in pH as the speciation of  $Q^{\cdot-}$  changes with pH.  $O_2$  plays an important role in iron redox transformation by rapidly oxidizing  $Q^{\cdot-}$  to form benzoquinone (Q), while its role in directly oxidizing Fe(II) is negligible at the pH range examined. The results are compared with those obtained in our previous studies of iron–Suwannee River fulvic acid (SRFA) interactions in acidic environment and support the hypothesis that hydroquinone and semiquinone moieties plays an important role in iron redox transformation in natural waters. However, the steady-state semiquinone concentrations in SRFA solutions are 2–3 orders of magnitude greater than in solutions containing pure 1,4-hydroquinone as the semiquinone radicals generated in pure hydroquinone solution are rapidly oxidized by dioxygen, while the semiquinone radicals generated in SRFA solution are resistant to oxidation by oxygen. As a result, semiquinone moieties in SRFA play a more important role in iron redox transformations than the simple quinones such as 1,4-hydroquinone. This has a dramatic effect on the cycling of iron between the +II and +III oxidation states, resulting in iron turnover frequencies in solutions containing SRFA being 10–20 times higher than those in solutions of 1,4-hydroquinone.