Diel iron cycling in acidic rivers of southwestern Spain

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Background

In June 2006, diel sampling was conducted on the Tinto, Odiel, and Agrio Rivers of Huelva Province, Spain. These rivers are highly acidic due to acid rock drainage from massive sulfide deposits of the Iberian Pyrite Belt (Cánovas et al., 2007). Variables quantified included streamflow, temperature, pH, Eh, photo-synthetically active radiation, and concentrations of dissolved and total metals, anions, Fe(II)/Fe(III), and As(III)/As(V).

Results

Average 24-h pH values were 2.36, 2.30, and 3.04 at the Tinto, Agrio, and Odiel Rivers, respectively. Both pH and streamflow were essentially constant with time in each river. The only solute that showed a robust diel concentration cycle in all three rivers was dissolved Fe(II). Concentrations of Fe(II) at mid-day were 1.8 to 28 times higher than concentrations in the early morning (pre-dawn). The daytime $m_{Fe(II)}$ increases were most likely caused by photoreduction of dissolved or solid-phase Fe(III). The night-time $m_{Fe(II)}$ decreases were attributed to biologically catalyzed re-oxidation of Fe(II) to Fe(III). First-order rate constants of (2 to 7) x 10^{-5} sec^{-1} for the bacterial oxidation of Fe(II) were estimated from the observed decreases in $m_{Fe(II)}$ during the night. Maximum rates of bacterial Fe(II) oxidation (estimated to be > 3 µmol/L/h) occurred at mid-day. This amount of Fe(II) oxidation can support a growth rate of over 10^6 cells/L/h for *At. ferrooxidans*, the dominant procaryote in the Tinto River (López-Archilla et al., 2001).

Conclusions

Photoreduction plays a key role in biogeochemical cycling of Fe in the Tinto and neighboring rivers, and it has not been reported in previous geochemical and ecological studies of this extremely acidic and Fe-rich environment (e.g., Amils et al., 2007). Further work is needed to quantify the relative rates of Fe(II) production by photoreduction and by heterotrophic Fe(III)-reducing bacteria. The results of this study have implications for the primitive life that may have existed in acidic aqueous environments on early Earth or other planetary bodies such as Mars.

Cánovas C.R. and 4 others (2007) *Sci. Total Environ.* **373**, 363-38.

Amils R. and 10 others (2007) *Planetary Space Sci.* **55**, 370-381.

López-Archilla A.I., Marin I., and Amils R. (2001) *Microb. Ecol.* **41**, 20-35.