

Nitrate-Dependent Oxidation of Fe-Sulfides in Naturally Bioreduced Zones of Floodplain Sediments Driven by Seasonal Groundwater Fluctuations

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The Rifle floodplain is located adjacent to the Colorado River in western Colorado. The floodplain consists of Quaternary fluvial sediments overlying an impermeable layer of the Eocene Wasatch Formation. Within the Quaternary sediments are small deposits of plant organic matter that create hotspots of subsurface microbial activity. A vadose depth-discrete unsaturated zone monitoring well at the site intersects one of these hotspots situated just above the baseflow water level. This hotspot contains framboidal pyrites with high concentrations of associated uranium [1]. During spring/early summer snowmelt, the groundwater level rises above baseflow flooding the bottom section of this well. Over the past 3 years, samples of soil gas and pore water for analyses of the chemical and isotopic compositions have been taken every 2-4 weeks from the intervals in this monitoring well. During normal baseflow, oxidizing conditions exist and nitrification of residual organic matter builds up high concentrations of nitrate in the porewater (up to 5-10 mM). When the water table rises, the deeper levels within the well become inundated with groundwater and conditions quickly become anaerobic. This leads to denitrification of the porewater nitrate creating a pulse of N₂O (to ~40 ppmv) in the pore gas above the groundwater. Accompanying this period of elevated groundwater and denitrification, the sulfur isotope compositions of pore water sulfate shift to significantly lower $\delta^{34}\text{S}$ values (from $> -10\text{‰}$ to $< -30\text{‰}$), indicating oxidation of the pyrite in the organic hotspot. In addition, there is an increase in concentration of Fe⁺² and U in the porewater, indicating that the framboidal pyrites in the hotspot sediments are being oxidized concurrent with denitrification of the porewater nitrate. This pattern is repeated annually and provides strong evidence that nitrate-dependent sulfide oxidation is occurring in these naturally-occurring bioreduced zones.

[1] Qafoku *et al.* (2009) *Environmental Science & Technology* **43**, 8528-8534.