



Stable sulfur, oxygen and carbon isotopes unravel the importance of bacterial sulfate reduction in passive mine water treatment systems

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Anaerobic passive vertical flow systems (VFS) are designed to raise pH and alkalinity and lower metal loads of net-acidic mine waters. Successful treatment depends on a balance of chemical and biogeochemical processes, with bacterial sulfate reduction (BSR) often assumed to be a key component, raising alkalinity and generating sulphide to precipitate iron and other chalcophile elements. Here, we study the importance of BSR in two VFS in NE England, comprising manure and limestone and designed to remediate net-acidic drainage from an abandoned coal mine and waste rock dump. The waters have pH = 4.2-6.7, alkalinity = 0-125 mg L⁻¹ CaCO₃ eq, iron = 10.5-177 mg L⁻¹ and sulfate = 248-1887 mg L⁻¹. Comparison of influent and effluent chemistry over a 1.5 year period shows that the VFS removed 77-93% iron and 21-35% sulfate (S:Fe removal ratio = 2.5-2.8), and increased pH and alkalinity by 1.2-1.8 units and 160-170 mg L⁻¹ CaCO₃, respectively. The occurrence of BSR is indicated by S isotopic data. Effluent sulfate and sulfide sulfur isotopes were fractionated compared to mine water sulphate by $\Delta^{34}\text{S}_{\text{SO}_4} = 2.43\text{-}31.6\text{‰}$ ($\alpha = 1.0166\text{-}1.078$), $\Delta^{34}\text{S}_{\text{H}_2\text{S}} = 31.0\text{-}58.0\text{‰}$ (VFS 1) and $\Delta^{34}\text{S}_{\text{SO}_4} = 1.3\text{-}3.7\text{‰}$ ($\alpha \approx 1.0095$), $\Delta^{34}\text{S}_{\text{H}_2\text{S}} = 10.7\text{-}51.5\text{‰}$ (VFS 2). Initial results indicate, fractionations between influent and effluent sulfate in the range of 3.6-14.3‰ ($\Delta^{18}\text{O}_{\text{SO}_4}$; $\Delta^{34}\text{S}_{\text{eff-infl}}$: $\Delta^{18}\text{O}_{\text{eff-infl}} < 1:1$), and low $\delta^{13}\text{C}_{\text{DIC}}$ in one VFS, significantly lower ($\leq 15\text{‰}$ lower) than limestone $\delta^{13}\text{C}$ ($\approx 1.8\text{‰}$), suggesting anaerobic microbial respiration being the dominant bicarbonate source. These data indicate that BSR is indeed taking place with potentially significant contribution to bicarbonate. Despite clear evidence for BSR, solid phase geochemistry shows that only 5% of the iron removed in the reactive substrates occurred as sulphide (pyrite), suggesting - against expectations - that BSR plays a minor role in the removal of iron. It seems likely that most hydrogen sulfide is re-oxidized to elemental sulphur and perhaps sulphate through reductive dissolution processes with iron(III)hydroxides, observed in abundance in the sediment. The importance of BSR is thus more for alkalinity generation than iron removal, with important implications for the longevity of passive treatment systems.