

Assessing Anoxic Biodegradation via Sulphate Reduction Using Sulphate Stable Isotopes

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Many plumes of organic pollutants in groundwater are characterized by anoxia in the plume core. Under these conditions, sulphate is often the most significant available electron acceptor and sulphate reduction the dominant or only pathway for biodegradation of organic pollutant species. Studies of sulphur and oxygen isotopic compositions of sulphate have the potential to yield information on the extent to which sulphate reduction contributes to biodegradation. This contribution outlines the theoretical framework for interpretation of sulphate isotopic compositions in groundwater systems, compares bacterial sulphate reduction in polluted and unpolluted systems and highlights the useful information on biodegradation which may be gained from isotopic studies of sulphate. Bacterial sulphate reduction may be approximated by the reaction: $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \Rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$ Usually, sulphate both the light ^{32}S and ^{16}O isotopes are preferentially reduced and residual sulphate becomes enriched in ^{34}S and ^{18}O . However, different mechanisms account for this effect in each case. The sulphur isotope fractionation is a kinetic effect, due to faster reaction of sulphate molecules containing the more weakly-bonded ^{32}S atoms. Enrichment of ^{18}O in residual sulphate occurs because the sulphate reduction process catalyzes isotopic exchange between sulphate and water molecules (Fritz et al. 1989); at equilibrium at environmental temperatures, sulphate is strongly enriched in ^{18}O compared to water. Most natural systems are initially at disequilibrium, containing sulphate which is ^{18}O depleted compared to equilibrium. Thus, during sulphate reduction, residual sulphate accumulates ^{18}O via isotopic exchange with water molecules. In natural systems sulphate reduction frequently occurs in old, deep confined groundwaters and large enrichments in ^{34}S and ^{18}O occur in sulphate. Instantaneous sulphur isotope fractionations between SO_4^{2-} and H_2S are very large (60-70‰), too large to result from simple kinetic fractionation. These large sulphur isotope fractionations (and highly ^{18}O -enriched sulphate) are thought to result from approach toward isotopic equilibrium over long periods of redox cycling of sulphur (Rye et al. 1981; Bottrell et al. 2000). Sulphate reduction has been studied in a highly contaminated plume of coal tar-derived phenolics. Two dissolved sulphate reservoirs have been identified with distinct oxygen isotope ratios. These consist of the natural groundwater sulphate ($\delta^{18}\text{O} = 3\text{-}5\text{‰}$) and the pollutant (plume) sulphate ($\delta^{18}\text{O} = 10\text{-}12\text{‰}$). In all cases the oxygen isotope data show simple mixing behaviour

across the plume margin. The sulphur isotope data also show a mixing trend but at one sample site this has been modified by enrichment in $^{34}\text{SO}_4$ at the plume margin. $^{34}\text{SO}_4$ enrichment is inversely correlated with sulphate concentration and coincides with the appearance of hydrogen sulphide in solution. This indicates that the enrichment in $^{34}\text{SO}_4$ is the result of bacterial sulphate reduction. $\delta^{34}\text{S}$ analysis of the hydrogen sulphide has yielded an instantaneous enrichment factor (ϵ) of -9.8‰ for present day sulphate reduction. This agrees with a long-term estimate for ϵ of -10.4‰ based on a plot of $\delta^{34}\text{S}$ vs. $\ln[\text{SO}_4]$, showing that sulphate reduction has taken place under similar conditions throughout the history of the plume. In this case sulphate reduction appears to have taken place via a unidirectional "single pass" reaction, giving a small, kinetic fractionation for sulphur and inhibiting isotopic exchange between sulphate and water, hence no enrichment of sulphate $\delta^{18}\text{O}$ is associated with sulphate reduction. Under these conditions, a Rayleigh model can be used to obtain an estimate of the pre-reduction sulphate concentration profile with depth from the sulphur isotope profiles. The difference between the pre-reduction and present profiles gives a mass balance for sulphate consumption from which organic carbon mineralization via sulphate reduction can be calculated. Sulphate $\delta^{18}\text{O}$ data from a second plume are used to illustrate how sulphide reoxidation at the margin of a plume can be identified. Under these conditions calculation of extent of sulphate reduction from isotopic profiles will be an underestimate as (some) sulphide has been reoxidized and recycled. Importantly, these data also show that sulphide as well as pollutant organics has acted as an electron donor and must be accounted for when assessing biodegradation via nitrate or oxygen reduction. Application of simple principles regarding kinetic and equilibrium fractionations can result in successful interpretation of complex isotopic profiles and yield details of redox processes and importance (or not!) of sulphate reduction as a mechanism of biodegradation.

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