Application of stable oxygen and sulphur isotope analyses to evaluate sulphate inputs from fertilizers and pyrite oxidation

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The Swan Coastal Plains of Western Australia are experiencing increasing environmental pressure from the intensification of farming and agriculture. This pressure is frequently associated with both fertilizer application and irrigation practices. The intensive agricultural use of this region started relatively recently ($\sim$150 years ago), but the cumulative anthropogenic impacts on surface water, groundwater and estuaries are substantial in a number of catchments. Loads of nutrients and sulphates in the surface waters are increasing, as is the salinity of groundwater in aquifers used to extract water for irrigation. However, the specific contributions of several sources (i.e., direct fertilizer applications and fertilizer infiltration into groundwater, land use changes or global climate changes in rainfall patterns) to the observed degradation of water quality remain unclear.

Traditional hydrochemical techniques are inadequate when evaluating the relative contributions of inputs from different sources. Therefore, as a complement to conventional monitoring and load mass balance calculations, we have identified the relative potential inputs of sulphates from different sources by stable isotope analyses of water molecules, $\delta^2H(H_2O)$ and $\delta^{18}O(H_2O)$, and sulphate ions, $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$. We compared the stable isotope compositions of water samples with signatures of precipitation, fertilizers and naturally occurring pyrite, and we modelled potential pyrite inputs at 41 locations.

In general, the $\delta^{18}O(H_2O)$ values were higher in agricultural areas (usually $<$-4.0 ‰) than in bushlands, forest plantations and some wetlands located in upper parts of the catchments (usually $<$-4.5 ‰) . Water in wetlands and in other areas with sulphur-depleted environments, where bacterial sulphur reduction may occur, had $\delta^{34}S(SO_4)$ $>$20 ‰ . In areas with expected Acid Rock Drainage, the $\delta^{34}S(SO_4)$ varied between $\sim$10 and $\sim$16 ‰ whereas the majority of natural areas had signatures of $\sim$12 ‰ . The highest SO_4 concentrations were linked with moderate $\delta^{34}S(SO_4)$ of 7–12 ‰ . Most samples (20) had signatures suggesting a moderate to very high input of sulphur from pyrite oxidation. Many samples (10) were also characterised by signatures typical of sulphur-reducing environments associated with local wetlands. The remaining samples (11) with relatively high TDS and SO_4 concentrations had signatures suggesting some inputs from fertilizers.

Our results confirm that naturally occurring pyrite oxidation can significantly elevate the level of sulphates in groundwater, and this oxidation needs to be considered in mass balance calculation models for agriculture pollutants. The major challenge is to clarify the ambiguous $\delta^{34}S(SO_4)$ signatures resulting from overlapping values of pyrites and fertilizers in areas where different types of fertilizers are used. However, to a large extent, this challenge can be addressed using $\delta^{18}O(H_2O)$ and $\delta^{18}O(SO_4)$ for modelling the inputs from acid rock drainage.