

Seasonal variations in microbial carbon cycling in freshwater wetland sediments identified through rate assays, lipid biomarkers, and porewater geochemistry

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Freshwater wetlands account for about 25% of the annual methane emissions to the atmosphere. A potential positive feedback exists between global warming and the production of this powerful greenhouse gas in sediments. This study explored seasonal variations in the dominant pathways (e.g. methanogenesis) of terminal metabolism in coastal, freshwater wetland sediments from three distinct biogeographic provinces. Through geochemical profiles, microbial rate assays, and lipid biomarker analyses, we assessed seasonal variability in the biogeochemical functioning in coastal Florida, Georgia, and Maine. We evaluated the role of temperature and other seasonal factors on rates and pathways of methane production and consumption, as well as sulphate reduction, acetogenesis, and acetate oxidation, through radiotracer rate assays. Intact polar membrane lipid analyses revealed distinct microbial communities at the three sites which varied with season and depth. The combination of microbial activities, sediment porewater geochemistry, and lipid biomarker analysis provides insight into seasonal fluctuations in microbial-mediated carbon mineralization in freshwater sediments.

Tracing sedimentary pyrite oxidation during managed aquifer recharge

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Oxidation of sedimentary pyrite is often one of the main drivers affecting groundwater quality during managed aquifer recharge [1, 2]. In cases where this leads to the depletion of the sedimentary buffering capacity, groundwater acidification and particularly the associated mobilisation of heavy metals and metalloids (e.g. arsenic) can significantly deteriorate groundwater quality [3, 4]. Data and techniques that allow for a detailed identification and quantification of the mineral reactions are therefore crucial to assess and predict such adverse water quality changes.

The present study examines the feasibility of using stable sulphur isotope analysis as a supporting tool for tracking and characterising pyrite oxidation processes during an aquifer storage and recovery experiment in Perth, Western Australia. During the experiment pyrite oxidation was triggered by the injection of potable aerobic water into a well characterised heterogeneous, anaerobic aquifer. Stable sulphur isotope signals ($\delta^{34}\text{S}$) were analysed for sedimentary sulphur species and for aqueous sulphate concentrations in both the ground- and the injectant water in addition to extensive hydrochemical monitoring.

The collected data, including the $\delta^{34}\text{S}$ value was interpreted by geochemical and reactive transport modelling. The models were specifically adapted to incorporate all reactions and isotope fractionation processes that affect the evolution of $\delta^{34}\text{S}$ in the groundwater and the sediments.

The observed $\delta^{34}\text{S}$ data from the monitoring wells indicate that the released sulphate is characterised by a successively changing $\delta^{34}\text{S}$ signal during the injection phase. These observed $\delta^{34}\text{S}$ trends are thought to result from a highly variable $\delta^{34}\text{S}$ composition of the pyrite, which was most likely caused by isotopic fractionation associated with the sulphate reduction that occurred during and/or after the deposition of the sediments.

[1] Prommer & Stuyfzand (2005) *EST* **39**, 2200–2209.

[2] Descourvieres *et al.* (2010) *Appl. Geochem.* **25**, 261–275.

[3] Jones & Pichler (2007) *EST* **41**, 723–730. [4] Wallis *et al.* (2010) *EST* **44**, 5035–5041.