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Redox reactions of dissolved organic matter contribute to anaerobic sulphur cycling in peatland soils

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Sulphate reduction rates in wetland soils typically account for a large fraction of the anaerobic electron flow, despite small pool sizes of sulphate in the pore waters. The study's objective was to test the hypothesis that recycling of sulphur occurs and that redox-reactions of dissolved organic matter (DOM) are involved in the recycling process.

To examine the recycling process we used peat mesocosm from two peatlands in Ontario, Canada and subjected them to sulphur deposition and vertical water flow of about 2 mm/day. Depth profiles of DOC and sulphate concentrations were determined and vertical mass balances calculated. In addition we determined ^{34}S sulphate profiles of pore waters. Batch experiments with addition of H_2S to solutions of standard peat humic acid (Pahokee Peat, IHSS) were used to determine whether H_2S was oxidized by humic acids, and what the reaction products were. Enrichment with ^{34}S at intermediate depths, constant sulphate concentrations with depth and absence of oxygen suggested that sulphate reduction and anaerobic sulphate release concurrently occurred. In the batch experiments two apparent reactions of H_2S with DOM were observed. In the fast initial reaction, H_2S was oxidized mostly to elemental sulphur and secondarily to sulphate (Fig. 1). Production of thiosulphate was not observed. In a slower reaction step H_2S was further consumed and the sum of dissolved inorganic forms of sulphur in the pore water decreased.

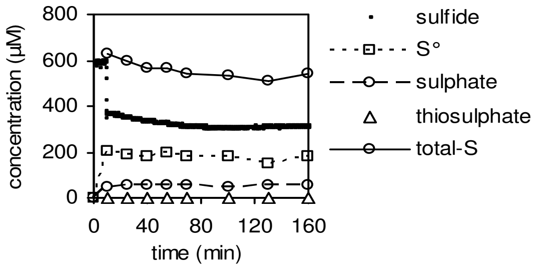

Figure 1

This was interpreted as H_2S being incorporated into the organic substance. No systematic relationship between pH and the oxidation process was found. Overall the results suggest that dissolved organic matter is involved in an anaerobic sulphur cycle allowing for high rates of sulphate reduction in sulphate-poor peatlands.

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Microcosm studies of microbially mediated arsenic release from contrasting Cambodian sediments

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Microbially mediated dissolution of hydrated ferric oxides accompanied by oxidation of organic matter is widely considered to be the dominant mechanism responsible for arsenic release into highly reducing groundwaters in Bengal and elsewhere. The typically higher organic carbon (OC) and arsenic contents of muddy sediments compared to those of coarser sandy sediments suggests that, under relevant biogeochemical conditions, the former may exhibit much higher arsenic release rates. We report here the results of microcosm experiments designed to test this theory.

Sediments were obtained from drilling into a shallow arsenic-rich aquifer in Cambodia. The groundwaters and sediments exhibited marked similarities to shallow arsenic-rich aquifers in West Bengal and Bangladesh. A typical muddy sediment (SY9) and a sandy sediment (SY28) were used in this study. The measured arsenic and OC contents of SY9 were markedly higher than for SY28. The sediments were mixed with sterile synthetic groundwater under the following conditions: (i) aerobic; (ii) anaerobic; (iii) anaerobic with added acetate as proxy electron donor; and (iv) anaerobic with added acetate and AQDS, an electron shuttle humic acid analogue. Changes in the solid and aqueous phase speciation of arsenic were monitored by XAS and IC-ICP-MS respectively.

Substantive arsenic release, mostly as As(III), was only noted under anaerobic conditions, with the highest release noted for SY9. Microbially mediation of this release is indicated by the lack of arsenic release in the sterile controls. Analysis of 16S rDNA amplified from the microcosms by PCR using broad specificity primers was used to identify the dominant indigenous microbial communities.

Addition of acetate under anaerobic conditions resulted in accelerated arsenic release in SY9 but not in SY28. The acetate added to SY9 was nearly quantitatively oxidised whereas that in SY28 was not. These are surprising results because of the higher OC content of SY9 but we speculate that this reflects greater bioavailability of the OC in SY28; this sample being obtained from a highly permeable unit more susceptible to the ingress of surface derived OC.

Addition of AQDS increased arsenic release in both sediments. We suggest that this is due to its action as an electron shuttle or by inhibition of arsenic sorption. In either case, this result suggests the importance of humic acids in controlling arsenic release in shallow alluvial aquifers in Cambodia and in similar environments, such as Bengal.