

Detailed spatial and temporal investigation of methane oxidation

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Methane attenuation in a crude oil contaminated aquifer was studied through a variety of techniques to determine spatial and temporal changes in competing electron donors and sources of electron acceptors. High resolution direct push sampling was used in combination with multivariate cluster analysis to delineate the methane plume and discrete geochemical regions within the plume. Isotopic results confirmed that methane attenuation was through microbially mediated oxidation, and further indicated that oxygen transport across the water table through gas bubble entrapment and recharge lead to aerobic methane oxidation. Flux-based mass balance calculations estimated that the flux of electron acceptors across the water table, including oxygen, could account for only a portion of the observed methane loss, indicating that an alternate electron acceptor within the aquifer was present. Long-term trends in 0.5 M HCl extractable iron from core samples taken within the methane-oxidation zone show a significant decrease in ferric iron within the sediment. Mass-balance calculations indicated that other sources of reduced carbon within the aquifer, including BTEX and non-volatile dissolved organic carbon, are insufficient to account for the observed loss in ferric iron within the sediment. The results suggest that near the water table aerobic processes contributed to methane oxidation, while within the anaerobic core of the plume, methane oxidation was likely linked to iron reduction.

Stability of glutathione and bioavailability of mercury-glutathione complexes in aquatic systems

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Low-molecular weight biogenic thiols such as glutathione (GSH) are known to play important intracellular roles, namely as antioxidants or as metal complexing agents. These thiols have also been reported extracellularly in the environment, and they could alter mercury (Hg) complexation and bioavailability towards microorganisms, due to the high affinity of Hg for S-donor ligands. Glutathione photodegradation rates were determined in both fresh- and brackish waters at different wavelengths during laboratory incubations. Photo-oxidation of GSH followed pseudo-first order kinetics, with half-lives ranging from 4 to 30 h in natural freshwater, and from 1.5 to 7 h in saltwater, with shorter half-lives in UV-irradiated surface waters than in dark treatments. The addition of Hg (II) protected GSH from oxidation by Cu (II) in the dark, but not under UV radiation. We conclude that UV-induced photo-oxidation is a key process altering the fate of GSH in natural waters. In addition, we report that the formation of stable GSH-Hg complexes increases the bioavailability of Hg towards bacteria, as shown under oxic conditions using a whole-cell bioreporter. We hypothesize that thiol moieties of two glutathione molecules bind Hg²⁺ to form a structure similar to oxidized glutathione that can be accidentally taken up by cells via glutathione transporters. In aquatic environments, such Hg-thiol complexes could represent an important fraction of the pool of Hg bioavailable to microorganisms and contribute to the contamination of aquatic foodwebs.