

## Methane oxidation in a crude oil contaminated aquifer

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At a crude oil spill site near the town of Bemidji, MN hydrocarbons have been degrading through methanogenesis for greater than 20 years. The methane rich groundwater plume extends only ~100 m downgradient from the floating oil body despite groundwater flow rates of about 20 m per year. To date the mechanisms of methane attenuation are poorly understood. A field investigation was conducted in July 2007 to investigate the potential for aerobic oxidation of the methane, and particularly for enhanced oxygenation of the aquifer through entrapment of air bubbles near the water table.

The field work involved the development and deployment of a direct push profiler specifically designed 1) to collect gas samples from the vadose zone and groundwater samples in one direct-push hole, 2) to collect samples very close to the water table, and 3) to collect samples from deep aquifers while preserving sample integrity for dissolved gases. The profiler facilitates the investigation of gas exchange processes across the water table and the sharp geochemical gradients typical of this interface.

Decreases in dissolved CH<sub>4</sub> accompanied by a shift in δ<sup>13</sup>CH<sub>4</sub> to heavier values indicate that methane attenuation is through microbially mediated oxidation. Q-PCR analysis of the pMMO gene extracted from aquifer sediment shows a significant population of aerobic methanotrophs up to 0.5 m below the water table indicating the potential for aerobic oxidation of methane at this depth. Several parameters are used to quantify the contributions of various processes to the introduction of O<sub>2</sub> into the groundwater, including; N<sub>2</sub> for bubble entrapment, O<sub>2</sub> gradients for diffusion, and other geochemical tracers for infiltration of recharge water.

Results of this study demonstrate the importance of processes near the water table with respect to contaminant attenuation and shed light on processes responsible for methane oxidation in contaminated aquifers.

## Development of coupled GC/ICPMS for analysis of δ<sup>34</sup>S in individual organic compounds

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Sulfur (S) is a key component of many biogeochemical processes and records. Specific redox transitions of sulfur are linked to large stable-isotopic fractionations, and the record of those fractionations is potentially preserved in great detail by organosulfur compounds. Organic sulfur is the second largest pool of reduced S after pyrite in most sedimentary rocks. Unfortunately, measurements of δ<sup>34</sup>S in organosulfur compounds are relatively scarce due to analytical difficulties, and there is currently no analytical route to sulfur-isotopic analysis of *individual* molecular species. The geochemical record of organic S thus remains poorly explored and underutilized. To help remedy this, we are developing instrumentation and methodology for the compound-specific analysis of <sup>34</sup>S in volatile and semivolatile organic molecules. Our approach is the direct coupling of gas chromatography (GC) with multicollector inductively-coupled plasma mass spectrometry (ICPMS). This approach provides several important benefits relative to conventional isotope-ratio mass spectrometry (IRMS), mainly because the plasma ion source generates atomic S<sup>+</sup> ions for direct analysis. Although <sup>16</sup>O<sub>2</sub><sup>+</sup> is a significant isobaric interference for <sup>32</sup>S<sup>+</sup>, the high mass resolution of the Neptune ICPMS is sufficient to separate the two. For aqueous solutions of SO<sub>4</sub> or organic sulfur, we are able to obtain ~0.2‰ (1σ) precision down to 0.3 ppm sample size. We have also modified the sampling inlet (torch, injector and heated transfer line) of the ICPMS to allow for gas analysis, and studied instrument performance using simulated 'GC' peaks of dimethylsulfide in He. Precision of measured <sup>34</sup>S/<sup>32</sup>S ratios is typically < 0.2‰ (1σ) for concentrations as low as 5 nmol S. This is within a factor of 3 of statistical ion-counting limits, and we predict that precision should be ~0.75‰ for samples containing only 0.5 nmol S. For a typical organosulfur analyte (e.g., C<sub>10</sub>-C<sub>30</sub> thiols) 5 nmol S would equate to 870-2280 ng (total mass) of each analyte, within the capacity range of thick-film capillary GC columns. Thus analysis of the most abundant organosulfur components already appears feasible. Further improvements in sensitivity of up to 1 order of magnitude may be possible with further refinements. We hope to present compound-specific δ<sup>34</sup>S measurements for sedimentary organic compounds at the meeting.