Arsenic methylation in the bedrock aquifer of the Willamette Basin, Oregon, USA

SCOTT C. MAGUFFIN[1] AND QUSHENG JIN[1]

[1]1272 University of Oregon Eugene, OR, USA

Groundwater arsenic contamination is a significant threat to human health in many regions of the world. In aquifers, arsenic typically exists as arsenate or arsenite. Methylated arsenic, such as monomethylarsonate (MMA), dimethylarsinate (DMA), and trimethyarsenate, are less abundant and often overlooked as potentially significant species of arsenic. Identifying biogeochemical processes that control arsenic speciation is critical for developing remediation strategies and for predicting the mobility of arsenic in groundwater.

We analysed arsenic speciation in the bedrock aquifer of the Willamette Basin, Oregon, USA. Our results show that arsenite is the main species, with concentrations up to several parts per million (ppm); DMA is the main methylated species, with concentrations up to 20 ppb. Significantly, the concentrations of DMA correlate linearly with those of arsenite. Based on these observations, we hypothesize that in the aquifer 1) methylated arsenic species are produced from inorganic arsenic by prokaryotic methylation; and 2) prokaryotic methylation can be a significant process in the cycling of arsenic.

To test our hypotheses, we incubated aquifer sediments in reactors and monitored arsenic speciation over time. We also included sterlized sediments as a biological control. We observed the accumulation of MMA and DMA in all but the sterilized control. To determine the *in situ* rate of arsenic methylation, we conducted a push-pull test in the bedrock aquifer. Based on the field observations, we calculated that DMA accumulated at a rate of 1 to 3 ppb per day. Because DMA is produced and consumed simultaenously, this value represents the minimum rate of DMA production in the aquifer.

Our results demonstrate that DMA is produced *in situ* at a significant rate by indigenous aquifer prokaryotes. The results suggest that arsenic methylation is an important factor in evaluating the occurence and mobility of arsenic in groundwater. Because of the volatility of many methylated arsenic species, arsenic methylation may also constitute a significant pathway in the global cycling of arsenic.

Structure, dynamics, and spectroscopy of metalloproteins from methanogenic and hydrocarbonoclastic microbes

JOHN S. MAGYAR[1]*, WEI TING CHEN[1], CHRISTINA L. CLEVELAND[1], PAUL B. HARVILLA[1] AND VICTORIA F. OSWALD[1]

[1]Barnard College, Columbia University, New York, NY 10027, USA

(*correspondence: jmagyar@barnard.edu)

The increasing scarcity of conventional, easily accessible petroleum sources leads to an increasing dependence on hard to reach petroleum in deep, cold offshore waters. These extraction processes lead to significant environmental challenges, including unprecedented spills in deep water. Here, we report progress toward an understanding of molecular adaptations for life at low temperatures, based on our study of cytochrome *c* from *Colwellia psychrerythraea*, a psychrophilic, hydrocarbonoclastic marine bacterium responsible for a large portion of the early bioremediation of the 2010 *Deepwater Horizon* oil spill in the Gulf of Mexico. Although surface oil spill bioremediation is well-established, the biogeochemistry of deep marine oil spills is not yet well understood. An understanding of psychrophilic metalloprotein dynamics and thermodynamics is essential to a full understanding of biogeochemical cycling in these environments.

Further insights into microbial metal uptake processes are gained from our parallel studies of a putative metalloregulatory protein from the methanogenic archaeon *Methanocorpusculum labreanum*. We suggest that this protein is involved in regulation of nickel uptake, which is essential for methanogenesis. In addition, we have determined that this protein is an iron-sulfur cluster-binding flavoprotein, suggesting a role in electron transfer processes as well.

For both *Colwellia* and *Methanocorpusculum*, we have used genomic information to identify specific proteins of interest. The genes are either synthesized chemically or amplified from genomic DNA by PCR and cloned into *E. coli*. The proteins have been overexpressed and purified, and we are currently characterizing them by a wide variety of spectroscopic and other techniques, including UV-vis absorption, circular dichroism, fluorescence, atomic absorption and NMR spectroscopies; X-ray crystallography; differential scanning calorimetry; electrochemistry; and analytical HPLC.

www.minersoc.org
DOI:10.1180/minmag.2013.077.5.13