Arsenic speciation and stable isotope chemistry in an arsenic contaminant plume at a landfill site

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A groundwater plume beneath a capped landfill in North-Central Massachusetts contains dissolved arsenic concentrations exceeding 15,000 ppb in some locations. Disposal of solid wastes at the landfill spanned nearly a century with little documentation of the material disposed. The source(s), fate, and transport of arsenic in the landfill aquifer have been studied extensively; however site characterization has yet to be fully defined. The primary source of the arsenic is not believed to be directly from the landfill based on several lines of evidence, including naturally derived arsenic mobilization due to reducing conditions created by in-situ bioremediation at a nearby airfield (less than 0.5 miles), the existence of extremely high arsenic concentrations in sediment (8,500 ppm) in the bordering marshland, and prior studies performed at the site including arsenic leachate potential from landfill and aquifer materials [1]. Potential natural sources include a layer of peat located beneath the landfill believed to be a part of a historic marshland, previously insoluble iron hydroxides within the glacial sands, and/or bedrock due to oxidation of sulfides containing arsenic.

Arsenic species, including inorganic As(III) and As(V) as well as organic monomethyl arsenic acid (MMA) and dimethyl arsenic acid (DMA), along with groundwater parameters such as pH and redox conditions may provide information as to where the arsenic is primarily originating from and how it is transported through the aquifer. Furthermore, the analysis of stable isotopic ratios of groundwater from different zones of the landfill with varying arsenic concentrations will aid in the delineation of probable arsenic sources, the mobilization processes, and arsenic transport modes within the aquifer. The role of strong redox gradients and the various redox ladder reactions involving water are likely to create characteristic isotopic signatures which might lead to a better understanding of biogeochemical processes within and beneath the landfill waste pile and also assist with future remidiation of the aquifer.

[1] United States Army Corp of Engineers (USACE) (2010) *Five-Year Review Report for Former Fort Devens Army Installation , Devens, Massachusetts* 1,053p.

FORAMINIFERAL ISOTOPES IN THE SEA-ICE ENVIRONMENT

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The only abundant planktic foraminifer in cold environments, *Neogloboquadrina pachyderma* left coiled (Np), is generally seen as a deep dwelling species forming its shell along the pycnocline. This may be true in the North Atlantic Ocean but can be challenged in the Arctic Ocean and sea-ice environment in general. Np occurs in sea-ice brine bubbles, especially near the base of the ice characterized by higher temperature and food availability [1]. It also occurs in cold and shallow waters where salinity is ≥ 34 and/or potential density ≥ 27.25 [2]. In sea-ice environment, Np-δ^{18}O often shows negative offset vs. isotopic equilibrium for calcite precipitated at mid-pycnocline depth. In the Arctic Ocean, the offset ranges -1 to $-3‰$ in the Western Arctic and there is a negative size-dependent isotopic gradient between light/small and heavy/large shells, which is opposite to what is observed in subarctic seas [3-5]. In sea ice, freezing of low δ^{18}O sea-surface waters produces isotopically-light brines that either concentrate in the sea-ice itself or sink deeper in the water column. *In vitro* experiments by Spindler [1] have shown that formation of new Np-shell chambers still occur in salinities of up to 58. A simple Rayleigh distillation equation governs the ^{18}O-content of brines. From a mean Arctic surface water (S ~ 30; $\delta^{18}O_{WATER}$ ~ -1‰ vs. VSMOW), brines with salinity of 34-58 and temperature of -2 to -3.5°C [6] have δ^{18}O ranging - 0.2 to -1.5‰, which may thus account for large Np isotopic offset. The brines sinking in the water column may partly accumulate along the pycnocline with the underlying saltier and warmer North Atlantic water carrying Np-tests and alive specimens. When dominant, Np is by itself a good indicator of polar water and sea-ice. When isotopic offsets vs. equilibrium increase, a longer seasonal duration of sea-ice cover may be inferred. A proxy calibration is not totally out of reach, but remains difficult because of highly variable conditions within sea-ice environment. In any case, the specific adaptation of Np to sea-ice has to be taken into account for the interpretations of paleo-records. It results in unreliable stratigraphy of $\delta^{18}O_{Np}$-records from deep-Arctic cores [7] whereas the large amplitude shifts towards exceptionally light $\delta^{18}O_{Np}$-values, which accompanied Np abundance peaks in the glacial North Atlantic, are more likely a response to the spreading of sea-ice rather than the direct impact of glacial ice meltwater on salinity [8].

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[6] Golden *et al*. (2007) *Geophysical Research Letters* **34**
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[8] Hillaire-Marcel and de Vernal (2008) *Earth and Planetary Science Letters* **268**, 143-150