

Dating groundwater in Québec using noble gases, U and stable isotopes and major elements

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The Quebec government has recently launched an ambitious program to quantify the Province's groundwater resources. In this framework, a multi-isotopic study involving noble gases, U and stable isotopes and major elements was initiated in the Bécancour River catchment basin, Central Québec, with the goal of dating groundwater and identifying flow paths. This basin is particularly interesting because this same area is a target for shale gas exploitation. This basin extends from the Appalachian Mts. down to the St. Lawrence River. Unconfined and partially confined sandy aquifers of Holocene age (Champlain sea) are mainly recharged in the mountains but also receive some local recharge in the plain.

A preliminary survey using noble gases along with stable and U isotopes was carried out along two transects, one parallel to the main flow direction, the second perpendicular to it. A plot of $^{20}\text{Ne}/^4\text{He}$ vs. $^3\text{He}/^4\text{He}$ ratios clearly points to the occurrence of three water bodies with distinct helium isotopic signatures.

Modern waters from shallow wells (5-7 m depth) show nearly atmospheric He and Ne concentrations ($^{20}\text{Ne}/^4\text{He} = 3.5$) as well as $^3\text{He}/^4\text{He}$ ratios close to 1.1 Ra, where Ra is the atmospheric $^3\text{He}/^4\text{He}$ ratio. These waters are extremely young, with ages ≤ 10 years. Groundwater localized in the north-eastern border of the basin shows tritogenic ^3He excesses up to 1.80×10^{-13} ccSTP/g. Using the Ottawa tritium decay curve from IAEA, which is valid for central Québec [1] and measured ^3He content in groundwater, leads to a first-order estimation age of ~19-21 yrs old.

The third water body contains large amounts of radiogenic ^4He , up to 4.48×10^{-5} ccSTP/g. These amounts are three orders of magnitude higher than the atmospheric background. A simple *in situ* U-Th- ^4He age model [2] yields ages varying between 2 and 22 Ma, an age range that is older than the age of the aquifers themselves. The well with the highest ^4He content is located in the proximity of the recharge area and U and stable isotopes as well as major elements suggest freshly recharged water. A possible mechanism for water ageing is related to vertical transport of radiogenic ^4He by: (1) a diffusive crustal basal flux; (2) upward advection of ^4He -rich fossil brines from the basement through fault pathways; or (3) upward degassing of methane from the Utica shales carrying ^4He .

[1] Murphy et al. (2011) *Hydrogeology* **19**, 195-207. [2] Torgersen and Clarke (1985) *Geochimica Cosmochimica Acta* **49**, 1211-1218.

In situ colonization of HgS mineral by sulfur-oxidizing bacteria and the enhancement of HgS weathering

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Soils and sediments, where mercury (Hg) can exist as Hg sulfide minerals (HgS), represent major reservoirs of Hg in aquatic environments. Due to their low solubility, primary and authigenic HgS (eg. cinnabar and metacinnabar) have historically been considered insignificant sources of soluble Hg(II) to the environment. Recently however, HgS solubility was shown to be greatly enhanced in the presence of a natural microbial consortium [1]. Mechanisms for this enhanced solubility have yet to be assessed. Further, bacteria capable of colonizing HgS surfaces in the environment have not been identified, yet their association with the mineral makes them likely key players in effecting chemical changes that can impact dissolution.

To this end, we assessed the microbial diversity on HgS surfaces in the Hg-contaminated sediments of the East Fork Poplar Creek (EFPC) in Oak Ridge, TN and examined the effect of these communities on HgS solubility. Mineral sections of metacinnabar, the dominant Hg species in EFPC sediments, were incubated 4 cm below the sediment surface in the creek channel and bank. Cinnabar and other metal sulfides were also incubated to distinguish mineral structure and host metal effects on the colonizing community.

Bacterial community composition and diversity were determined after 6 weeks of incubation via pyrosequencing targeting the 16S rRNA. Metacinnabar colonization was dominated by sulfur-oxidizing bacteria. Specifically, members of the genus *Thiobacillus*, *Sulfuricurvum* and *Sulfuricella* were among the most abundant community members. Members of these genera are known to use reduced sulfur compounds as electron donors during growth.

Following field incubation, oxidation rinds were observed on metacinnabar. Synchrotron-based X-ray microprobe mapping and X-ray absorption spectroscopy reveal the incubated metacinnabar interior contained pyrite inclusions, and the rind was enriched in Fe(III). Oxidation was not observed on cinnabar where, interestingly, sulfur-oxidizing bacteria were not dominant community members.

Microbial enrichments obtained from field-incubated sulfides were incubated in the presence of HgS in the lab. Both metacinnabar and cinnabar solubility were significantly enhanced in the presence of these consortia. The extent, rate, and mechanisms of HgS dissolution by the consortia and, in particular, sulfur-oxidizing bacteria are currently under investigation. The results from this study may have important implications on the role of microbial communities in the dissolution of HgS phases and hence Hg mobility in the environment.

[1] Jew et al. (2007) AGU Fall Meeting.