Modeling the impact of variable pH and dissolved salt concentrations on metal ion transport observed in field experiments

DOUGLAS B. KENT[1*], MATTHIAS KOHLER[2], GARY P. CURTIS[3], GILLIAN M. FAIRCHILD[4], AND DENIS R. LEBLANC[5]

[1]U. S. Geological Survey, Menlo Park CA, USA, dkbent@usgs.gov (*presenting author)
[2] U. S. Geological Survey, Menlo Park CA, mkohler@usgs.gov
[3] U. S. Geological Survey, Menlo Park CA, gpcurtis@usgs.gov
[4] U. S. Geological Survey, Northborough MA, gfairchi@usgs.gov
[5] U. S. Geological Survey, Northborough MA, dleblanc@usgs.gov

Field experiments show that the mobility of the divalent metal ions Ni, Zn, and Pb in a mildly acidic aquifer varies with both pH and dissolved salt concentrations. Field experiments were conducted by injecting groundwater with added Ni, Zn, and Pb at 2 or 20 μM into a shallow aquifer on Cape Cod, Massachusetts, USA. The mineralogy of the sediments is dominated by quartz but the sorption properties are controlled by well-ordered, nanometer-size Al-substituted goethite and micrometer-size clay minerals like chlorite and illite in mineral-grain coatings [1]. Uncontaminated groundwater had approximately 90 μM Na, 8 μM K, 20 μM Mg, and 9 μM Ca. Concentrations in a wastewater-contaminated zone of the aquifer were 10-20 times higher. Much more extensive retardation of Ni and Zn were observed in the uncontaminated zone at pH 6 over a one-meter transport distance than in the wastewater-contaminated zone. Much less extensive retardation of Zn and minimal retardation of Ni was observed in the uncontaminated zone at pH 5 than at pH 6. Concentrations of Pb remained above background in the injection ports for several months under all sets of conditions. Lead still had not been detected one meter downgradient one year after the injection but was readily mobilized by EDTA.

Models for metal ion sorption were calibrated by using laboratory experiments conducted with site-specific aquifer sediments over the relevant range of chemical conditions. Sorption of all three metal ions increased with increasing pH (4.8-6.3). Sorption decreased with increasing dissolved salt concentrations, but the impact on Pb sorption was much less extensive than for Ni and Zn. Sorption of Na, K, Mg, and Ca also increased with increasing pH. Sorption could be described quantitatively by using a set of cation exchange and surface complexation reactions: $M^{n+} + nHY = MY_n + nH^+$ and $Me^{2+} + {>}SOH = {>}SOMe^+ + H^+$, where M = Na, K, Mg, Ca, Ni, Zn, or Pb; Me = Ni, Zn, or Pb; and HY and >SOH represent generic surface sites.

Reactive transport simulations incorporating the laboratory-calibrated sorption models capture the principal trends in the field experimental data. Mobility of Ni is controlled by ion-exchange-type reactions, mobility of Pb by surface-complexation-type reactions, and mobility of Zn by both types of reactions. Results show that simple model structures like this can account for the impact of pH and dissolved salt concentrations on metal ion mobility.

[1] Zhang et al. (2011) *J. Contam. Hydrol.* **124**, 57-67.

Changes in North Atlantic deepwater circulation during the past 4 Myr

NABIL KHÉLIFI[1*], MARTIN FRANK[1], AND DIRK NÜRNBERG[1]

[1]Helmholtz Centre for Ocean Research (GEOMAR), Kiel, Germany, nkhelifi@geomar.de (* presenting author)

Abstract

Changes in northern North Atlantic deep water circulation during the past 4 million years (Ma) were studied at a suite of five IODP/ODP sites at water depths from 2400 to about 5000 m. Benthic $\delta^{13}C$ records at these sites oscillate in parallel around values lower than today by ~0.2 ‰ during interglacials and by ~0.7 ‰ during pronounced glacials of the late Pliocene warm period. However, Pliocene Mg/Ca-based deep-water temperatures were 2 to 3 °C higher than today during interglacials and near modern levels during glacial periods. The coeval changes in ventilation at a lower level than today may indicate a weaker difference between these warm water masses than today, which is probably caused by water mixing in the northern North Atlantic. This is corroborated by ε_{Nd} bottom seawater values near -9 to -10 at all sites, which differs markedly from the modern situation characterized by clear differences in ε_{Nd} signatures between the water masses at these sites. Accordingly, the lesser ventilated, warm, and mixed water masses are most likely the result of the weaker overturning in the northern North Atlantic during that time of global warmth [1].

After 1.6 Ma, benthic $\delta^{13}C$ records show a gradually improving ventilation, with pronounced glacial/interglacial oscillations, which came close to the modern-to-late-Pleistocene levels. This ventilation change in deep water masses was coeval with a clear divergence in ε_{Nd} of bottom water masses between the different sites towards modern signatures. This is apparently linked to a significant change in the sources of circulating deep waters in northern North Atlantic. Accordingly, the first reorganization of the deep circulation in northern North Atlantic towards the modern situation appears to have started only after ~1.6 Ma, most likely as a response to increases in the amplitude of the Earth's obliquity cycle during that time [2].

[1] Haywood & Valdes (2004) *Earth and Planetary Science Letters* **218**, 363-377. [2] Laskar *et al.* (1993) *Astronomy and Astrophysics* **270**, 522-533.