Arsenic dynamics in lake sediments

R.-M. Couture[1,2]*, C. Gobeil[1], A. Tessier[1],
B. Shafei[3] AND P. Van Cappellen[3]

[1]Université du Québec, INRS-ETE, Québec, Canada
(*correspondence: raoul-marie.couture@ete.inrs.ca)
[2]CEREGE CNRS UMR 6635, Aix-en-Provence, France
[3]School of Earth and Atmospheric Sciences, Georgia Institute
of Technology, Atlanta, USA

To quantify arsenic (As) dynamics during early diagenesis, we applied a reactive transport and thermodynamic model to an extensive dataset comprising porewater profiles of pH, As, Fe, Mn, total sulfide, zero-valent sulfur, organic C and major ion, as well as solid-phase profiles of As, S, Fe, Mn, Al, organic C, ^{210}Pb and ^{137}Cs from two adjacent basins of the same lake, one being perennially oxygenated and the other seasonally anoxic. Both thermodynamic modeling and comparisons between the various profiles point to As adsorption onto Fe oxyhydroxides and Fe sulfides as the main processes controlling As mobility.

Assuming steady-state, an inverse kinetic model based on a one-dimensional transport-reaction equation was applied to the porewater As profiles to constrain As net adsorption rates (R_{net}) and rate constants (k). The measured As sedimentary records differed markedly among the two adjacent basins but converged once they were mutually corrected for the amount of As added to or removed from the solid phase during burial and for differences in sedimentation rate and sediment focusing. Constrained As reaction rate constants and reconstructed As historical fluxes were then implemented as parameters and boundary conditions, respectively, in a non-steady state coupled reactive-transport model designed to simulate the biogeochemical cycling of organic C, O_2, Fe, S and As. Results illustrate that depth profiles of sediment-bound As reflect both past changes in As deposition and the diagenetic redistribution of As among Fe (III) oxyhydroxide and Fe (II) sulfide pools.

Biogeochemical evolution of groundwater chemistry impacted by leachate from a closed landfill

I.M. Cozzarelli

U.S. Geological Survey, MS 431, 12201 Sunrise Valley Dr.
Reston, VA 20192 (icozzare@usgs.gov)

Leachate from the decomposition of landfill wastes can generate ground-water contaminant plumes that may last for centuries. Understanding the evolution of redox zones in a leachate-impacted aquifer has important implications for the natural attenuation of contaminants, including the transport and fate of trace organic compounds and metals. An interdisciplinary team of USGS and University researchers has been studying the temporal evolution of redox zones downgradient from the Norman Landfill, Norman, Oklahoma, at different temporal and spatial scales, for more than a decade. The leachate plume contains elevated concentrations of non-volatile dissolved organic carbon (NVDOC, ≥ 300mg/L), methane (≥ 16 mg/L), ammonium (≥ 650 mg/L), ferrous iron (≥ 23 mg/L), chloride ($\geq 1, 032$ mg/L), and bicarbonate (≥ 4269 mg/L). Investigation of the distribution of plume constituents in two dimensions reveals that NVDOC and methane biodegradation consume electron acceptors in the sulfate-rich aquifer, depleting the natural attenuation capacity over time. The sulfate-depleted zone, in the core of the plume containing NVDOC concentrations greater than 75 mg/L, expanded in size by a factor of two over a ten-year period. High concentrations of NVDOC persist in the groundwater more than 200 m from the edge of the landfill. Laboratory bioassay experiments conducted at the weeks-to-months time scale confirmed the field observations that the NVDOC in the leachate is resistant to biodegradation, indicating this system is carbon limited. The conceptual model of biogeochemical processes developed for the Norman Landfill study has provided a framework for detailed *in situ* experiments on the rates of processes and the fate and transport of leachate compounds in the aquifer.