4.3.14

Sulfur gas dynamics in an aquatic cave ecosystem

P.C. BENNETT, A.S. ENGEL, K. MABIN AND L.A. STERN

Dept. of Geological Sciences, University of Texas Austin (pbennett@mail.utexas.edu)

At Kane Cave, Wyoming, USA, sulfidic springs discharge into a 350m cave forming in Madison Limestone. This cave is undergoing active sulfuric acid speleogenesis (SAS), and reduced sulfur compounds are oxidized to sulfuric acid in both subaqueous and subaerial settings. The cave floor and walls are covered with replacement gypsum, and thick microbial mats have developed along the discharge stream. The microbial community is dominated by sulfur oxidizing "*Epsilonproteobacteria*" and *Gammaproteo-bacteria*, with an associated population of dissimilatory sulfate reducers (DSRB) in the anaerobic interior of the mat. To characterize the consumption of inflow H_2S and the production of H_2S and volatile organic sulfur compounds (VOSC), water and gas compositions were characterized seasonally for 3 years. Gas flux from the cave water to the atmosphere was determined in the field using a modified portable GC with FPD detector, combined with measure-ments of gas production in laboratory microcosms. More than 20 real-time flux measurements were made at ~2 m intervals along the cave stream with 400 gas samples collected from the boundary layer above the cave stream. Anaerobic sulfidic water discharges at a rate of ~21.6 m^{-3} hr^{-1}; a representative composition is 1.58 mmol L^{-1} Ca^{2+}, 1.13 mmol L^{-1} SO_4^{2-}, 0.12 mmol L^{-1} Cl^-, 3.39 mmol L^{-1} HCO_3^-, and 34 μmol L^{-1} total dissolved sulfide ($C_TS^=$) at a pH 7.3 and 21.5 °C. $H_2S_{(g)}$ concentration at the air-water interface averages 30 ppmv, with an average flux of 44 μmol m^{-2} min^{-1}. Methanethiol is present at 1ppmv. The $H_2S_{(g)}$ flux increases downstream even as $C_TS^=$ decreases, with distinct maxima over the microbial mats. Laboratory microcosms were constructed with bulk mat, filter-sterilized cave water, and calcite to buffer pH, with water blanks and killed controls. An initial period of 12-36 hr of dissolved H_2S and O_2 consumption was followed by a rapid increase in headspace H_2S as production by the DSRB population exceeds consumption by the oxidizers. This is followed several days later with the production of methane-thiol and dimethylsulfide, and carbonyl sulfide later. Spike experiments show that these compounds are consumed by sulfur-oxidizers, and there is no correlation between the production of VOSC and methane or methanogenic activity.

The occurrence of VOSC in a subsurface environment is unusual, and our data suggest that local production of both H_2S and VOSC are fundamental to the sulfur cycle in this system. In contrast to the classic models of SAS, we find that both microbial consumption *and* production of sulfur gases are part of the cave forming process in SAS.

4.3.15

# Evolution of nitrate and sulfate in a fractured aquifer related to pumping

V. AYRAUD[1], L. AQUILINA[1], H. PAUWELS[3], C. TARITS[2], A-C. PIERSON-WICKMANN[1] AND O. BOUR[1]

[1] Geosciences Rennes, France (virginie.ayraud@univ-rennes1.fr; luc.aquilina@univ-rennes1.fr; anne-catherine.pierson-wickmann@univ-rennes1.fr; olivier.bour@univ-rennes1.fr)
[2] Université de Bretagne Occidentale, France (ctarits@univ-brest.fr)
[3] BRGM, France (h.pauwels@brgm.fr)

Many aquifers of French Brittany show nitrate concentration exceeding 50mg/L. The Ploemeur fractured aquifer is located in a granite/schist shear zone, at a depth of 40-100 m. It is the water source for 10,000 inhab., and has been monitored for more than ten years. After the beginning of pumping, water from the pumping well never exceeds 10mg/L while in the area other wells show NO_3^- concentration ranging from 30 to 120mg/L.
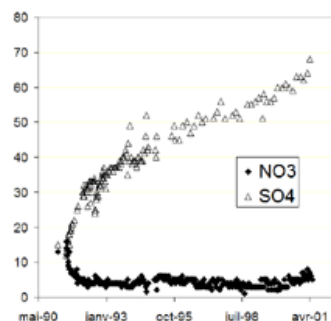
The SO_4 and NO_3 concentration evolved rapidly during the 2 first two years after pumping initiation, and show a anticorrelated evolution which is attributed to autotrophic denitrification related to microbial activity.

$$5FeS_2 + 15NO_3^- + 10H^+ --> {}^{15}/_2 N_2 + 5Fe^{2+} + 10 SO_4^{2-} + 5H_2O$$
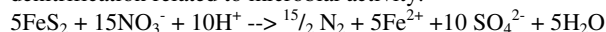
In the upper part of the aquifer, SO_4 and Fe concentrations became extremely high during the last years, This is attributed to more reducing conditions, related to the continuous high flow in the system, initiating sulfide oxidation coupled to Fe^{3+}/Fe^{2+} reduction :

$$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4 + 16 H^+$$
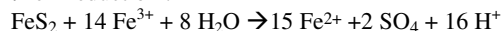
$\delta^{15}N_{-NO3}$, $\delta^{18}O_{-SO4}$, $\delta^{34}S_{-SO4}$ allow to characterize the source and the processes in the groundwater. All high SO_4-contents waters shows low $\delta^{34}S_{-SO4.}$ and $\delta^{18}O_{-SO4}$ The evolution of the SO_4, NO_3 and Fe concentrations in the pumping well can not be related to a unique stochiometry. In this well high nitrite concentrations also show that the reaction is not complete. It is interpreted as a result of the influence of the water flow on the bio-chemical process.