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Sources of dissolved sulfate in the upper Moselle river (France): S and O isotopes

A. BRENOT, J. CARIGNAN AND C. FRANCE-LANORD

CRPG-CNRS, 15 rue Notre Dame des Pauvres, 54501 Vandoeuvre les Nancy, France (brenot@crpg.cnrs-nancy.fr)

The upper part of the Moselle river basin, France, shows contrasted lithology and topography: mountains with granitic formations upstream in the Vosges and carbonated platform downstream in the Lorraine plateau. We use concentration and isotopic composition of dissolved SO_4 in the Moselle river and its main tributaries to identify the sources of sulfate. Isotopic signatures of dissolved SO_4 , combined with other geochemical data, allow to determine the contribution of evaporite sulfate dissolution and sulfur oxidation and thus to give further information about the relative contribution of silicate, carbonate and evaporite weathering.

$\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ were measured on precipitated barium sulfate by EA-IR-MS. Both S and O compositions increase downstream systematically from 6-7‰ and 7-10‰ respectively in the granitic watershed up to 7-14‰ and 10-14‰ in the carbonated basin. The isotopic signatures of the Moselle in the upper part reflect the alteration of silicates rocks (oxidation of pyrite) and/or the rain water contribution. Downstream the Moselle river water is mixed with tributaries draining limestone and some evaporitic layers. A sulfate source corresponding to the dissolution of evaporates is clearly represented by the isotopic composition of two tributaries (Euron and Durbion) and gypsum layers. The Madon is the main Moselle tributary on the carbonated basin. It integrates various lithologies and flows in an area dominated by agricultural land use. In details, during the winter period (2002-2004), the Madon has an isotopic composition of $\delta^{34}\text{S}=10\text{-}11\text{‰}$ and $\delta^{18}\text{O}=11\text{‰}$, which deviates from the general mixing trend. It suggests that the Madon integrate other sources of sulfate like fertilizers in addition to the evaporite sulfate. This hypothesis is based on the isotopic analysis of S-fertilizers used in this area that give an average value of $\delta^{34}\text{S}=5\text{‰}$. The isotopic compositions of SO_4 associated with $^{87}\text{Sr}/^{88}\text{Sr}$ over the period 2002-2004 shows that the Moselle river sources are distinct in S and Sr isotopic compositions for different seasonal river flows. These seasonal variations can be interpreted as changes in weathering conditions and water sources.

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High chemical weathering induced by agricultural pressure

A.-C. PIERSON-WICKMANN¹, L. AQUILINA¹,
C. MARTIN², C. GASCUEL² AND A. JAFFREZIC²

¹ CAREN-Géosciences Rennes, France (anne-catherine.pierson-wickmann@univ-rennes1.fr; luc.aquilina@univ-rennes1.fr)

² CAREN-INRA-ENSA, Rennes, France (chantal.Gascuel@roazhon.inra.fr; Anne.Jaffrezic@roazhon.inra.fr)

Chemical weathering on first-order catchments

The Kerrien (0.095 km²) and Kerbernez (0.120 km²) watersheds, two first-order adjacent catchments, located in south western Brittany (France) are experimental sites for the quantification of chemical weathering in a catchment dominated by agricultural activities. These watersheds are located on a granitic basement under oceanic temperate climatic conditions.

In order to quantify the chemical weathering, the runoff, the precipitations and chemical composition of stream waters were measured and calculated. The chemical fluxes are corrected from the atmospheric and the agricultural inputs, as well as from the water balance, using P-PET for the runoff.

The estimate of the atmospheric inputs is based on the chemical composition of local precipitations, sampled and analyzed monthly from January 2001 to November 2002. This period corresponds to two hydrologically contrasted years.

The agricultural inputs consist mostly of organic (cattle manure and pig slurry, ~4 m³.yr⁻¹) and mineral (KCl, NPK and ammonium nitrate, ~160 kg.ha⁻¹.yr⁻¹) fertilizers. A database of the various fertilizers used by local farmers on a 10-year period, coupled with chemical composition of local fertilizers and data from the literature, has been established.

High chemical weathering

Major agricultural cation input is potassium, which is almost consumed by local biosphere. The other cation (Ca^{2+} , Mg^{2+} and Na^+) fluxes range from 100 to 7000 mol.ha⁻¹.yr⁻¹, which is higher, by a factor 2 to 10, than those of small catchments on granitic basement [1]. Agricultural inputs seem to control and increase the chemical weathering by either (1) a preferential mineral dissolution, or (2) release by leaching of cations from old agricultural inputs adsorbed on soil particles.

The first major impact of such chemical fluxes is the chemistry of soil solution and soil composition and thus eventually on soil productivity.

References

[1] White, A. F. and Blum A. E. (1995) *GCA* **59**, 1729-1747.