Rare Earth Elements origin and dynamic in contaminated river basins: Nd isotopic evidence

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Uncertainties in identifying the origin of pollutants in river systems and in quantifying their impact particularly exist for ecosystems in strongly contaminated river basins. The difficulty of such estimations is based on the relative significance of both anthropogenic and natural sources of trace metals in the environment. The natural geochemical background is characterized by important variations at global, regional or local scales. Moreover, elements currently considered to be undisturbed by human activities and used as tracers of continental crust derived material have become more and more involved in industrial or agricultural processes. The global production of lanthanides (REE), used in industry, medicine and agriculture, for instance, has increased exponentially from a few tons in 1950 to about 150 kt in 2012. Consequently, these contributions interfere in the estimation of natural REE sources.

The application of Nd isotope ratios has very recently been successfully used for the first time for tracing the anthropogenic contribution of atmospheric deposition in urban and industrial areas (Lahd Geagea *et al.*, 2008; Hissler *et al.*, 2008; Guéguen *et al.*, 2012). However, at our knowledge, no study focused on the fractionation of the Nd isotopic ratio due to anthropogenic activity in river systems. For this reason, this work is dedicated to the understanding of processes that control the Nd isotopic fractionation in river waters heavily contaminated by anthropogenic activities.

The upper Alzette River basin, in Luxembourg, suffers from substantial historical and current contamination principally due to the presence of the steel industry, which has been active from 1875 until now. The particulate and dissolved fractions of river waters were monitored using a multitracer approach (including REE and Nd isotopes) during two hydrological cycles (bi-weekly and flood event based sampling). This extensive sampling design allowed to understand the seasonal dynamics of the waters Nd isotopic compositions according to the REE composition of the particulate fraction of the water. Combining REE concentrations and the Nd isotopic information allowed us to quantify the annual anthropogenic fluxes of REE.

A review of CO_2 and O_2 gas dynamics within the sub-surface Critical Zone and implications for early-atmosphere studies using paleosols

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The pCO_2 concentrations of early Earth's atmosphere are a key component for resolving the faint young Sun paradox and have been intensely debated for some time. Regolith models that use mass-balance geochemical arguments, based on the consumption of CO_2 through the neutralization of soil, saprolite and rock, prove to be one of the more reliable methods for estimating atmospheric pCO_2 [1, 2, 3]. Yet, many of the assumptions used to estimate the early atmosphere are difficult to test in the modern biotic Earth. This study serves as a review of modern regolith gas research and explores the potential use of deep weathering profiles for refining paleoatmosphere reconstructions. We compiled 248 soil CO_2 and O_2 assays from 29 regolith studies spanning a range of environments that includes deep (>3 m) profiles. Soil CO_2 values (n=174) range from 0.01 to 15.5% by vol., whereas soil O_2 values (n=74) range from 0.2 to 22.85% by vol. The compilation of regolith gas data shows that only 30% of the assays were collected from a depth >3 m; and few of these studies include both gas and bulk geochemical data. The data that do extend to depths >3 m show O_2:CO_2 ratios that exponentially decline with increasing depth. This deep portion of the modern sub-surface Critical Zone has lower O_2:CO_2 ratios and presumed lower biomass concentrations than the modern surface. These observations suggest that the highly acidic, low-oxidizing soil atmosphere *deep* in modern regolith may be a suitable analogue for Precambrian abiotic *near-surface* weathering. Contemporary deep (> 3 m) regolith studies that include both bulk geochemical and gaseous phase data are not only lacking but could provide a much-needed empirical dataset for refining Precambrian atmosphere estimates using paleosols. [1] Sheldon, 2006, *Precambrian Res* 147, 148-155. [2] Driese *et al.*, 2011, *Precambrian Res* 189, 1-17. [3] Brantley *et al.*, *in press*, *In Treatise of Geochemistry, The Atmosphere – History*.

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