

Heavy metals mobility in the Loures alluvial aquifer (N-Lisbon, Portugal)

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The Loures alluvial aquifer is exploited for irrigation of an important agricultural area. It is an unconfined aquifer, formed by sediments mainly originated from the volcanic basaltic complex of Lisbon, and seasonally invaded by the estuarine brackish water of Tagus River

The groundwaters are characterised by a very large range of conductivity (660 to 4640 $\mu\text{S}/\text{cm}$) and pH (6.8 to 8.7), being divided in two main hydrochemical groups: 1) calcomagnesian bicarbonate waters associated to the basaltic sediments dissolution; and 2) slightly basic, strongly mineralised sodium chloride waters resulting from estuarine brackish water contribution. The medium concentrations (ppb) of heavy metals in the groundwaters are: 0.6 for Co, 5.7 for Cr, 12.8 for Cu, 3.0 for Ni, 1.3 for Pb, and 7.5 for Zn [1]. The bicarbonate waters are enriched in Cu, Zn, Pb, Ni and Co, while the chloride waters have the higher Cr concentrations.

The Factor Analysis applied to the heavy metals concentrations show that Pb, Zn, Cu, Co and Ni, behave coherently, and present a close correlation with calcium and bicarbonate. Conversely, Cr concentrations strongly correlate with the groundwater conductivity, pH, and dissolved cations such as sodium, potassium and magnesium.

The acid pH favours elemental solubility and the metals retention/mobility, which is controlled by its affinity to form soluble species. The groundwater speciation shows that the Co, Cu, Ni, Pb and Zn are transported as simple bivalent ions (Co^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}) or as complex ions involving carbonate or bicarbonate anions. The Cr mobility is controlled by Cr-hydroxides formation, namely the CrOH_2^+ , explaining why this metal is concentrated in the more basic waters.

The water-rock concentration ratios, estimated in order to evaluate the extent of the chemical fractionation of the heavy metals, show that Ni, Co and Cu in the groundwaters result from basaltic sediments leaching, while Pb and Zn was introduced by anthropogenic contamination.

[1] Silva, M.C.R. (2003) PhD thesis, Univ. Lisboa, pp. 338.

Biogeochemical cycling in the critical zone: From process to pattern and back again

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Biogeochemistry can both define and be defined by the critical zone in terrestrial ecosystems. I draw on examples from biogeochemical cycling research in humid tropical forest watersheds in the Luquillo Experiment Forest, Puerto Rico. These watersheds are characterized by rapid weathering rates and deep, clay- and iron-rich soils depleted in most primary minerals. The soils experience variable redox conditions on the scale of days and weeks in surface and near surface depths. The frequency and magnitude of redox fluctuations leads to a suite of biogeochemical reactions that define the nutrient environment for plants and microbes and contribute to C storage and loss at a watershed scale [1]. Nitrogen dynamics are driven by rapid nitrification during oxic periods followed by dissimilatory nitrate reduction to ammonium (DNRA) during anoxic periods. DNRA competes with N loss mechanisms, and increases N availability for plant and microbial growth [2]. The availability of P is also intimately linked with redox dynamics. High redox microsites and periods lead to the formation of insoluble iron-phosphates. Low redox periods and locales produce more labile P when Fe is reduced, fuelling plant and microbial activity [3]. Low redox reactions result in considerable CO_2 production via Fe reduction. The magnitude of this C release accounts for up to 40% of soil respiration in this forest. Autotrophic and heterotrophic Fe oxidation regenerates the FeIII providing a continuous cycle driven by redox dynamics [3, 4]. These examples show how plants, microbes, and minerals interact to drive key biogeochemical cycles in the critical zone of this tropical forest.

[1] Silver, W.L., Lugo A.E, and Keller M. (1999) *BGC* **44**, 01-328 [2] Silver, W.L., Herman D.J, and Firestone M.K. (2001) *Ecology* **82**, 2410-2416. [3] Chacon, N. Silver W.L, Dubinsky E.A, and Cusack D.F. (2006) *BGC* **78**, 67-84 [4] Buss, H. L., Bruns M.A, Schultz M.J, Moore J, Mathur C.F, and Brantley S.L. (2005) *Geobio* **3**, 247-260.