## Isotope study of S-cycle of Lago di Cadagno

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Lago di Cadagno is a permanently stratified (meromictic) ~19 meter deep lake in the southeastern Swiss Alps. The monolimnion, located below ~12-13m depth, is sulfidic (~300µM sulfide), and has relatively low sulfate concentrations of ~2mM, where sulfate is supplied by deep spring sources. The mixolimnion is flushed by surface runoff, and as a result, has lower sulfate concentrations of about 400µM. With its low sulfate concentration, and stratified water column, we view Lago Cadagno as a relevant analogue to past gradient-type sulfidic systems. Here, we report the results of a study of the sulfur cycle of Lago Cadagno undertaken as part of a larger effort to characterize the geochemistry and biology of this lake. We report sulfur isotope results ( $\delta^{34}$ S and  $\Delta^{33}$ S) from water column sampling campaigns undertaken in June 2006, August 2007, and October 2008, as well as results of incubations and flux experiments undertaken with Cadagno water and sediments collected during these campaigns. Incubations with water from Lago di Cadagno yield large <sup>34</sup>S/<sup>32</sup>S fractionations (50-60‰) between sulfate and product sulfide that are the result of sulfate reduction. Similar large <sup>34</sup>S/<sup>32</sup>S fractionations were observed between sulfate and sulfide in the water column in June 2006 (~50‰), and smaller fractionations were observed in the subsequent two campaigns (~33-36‰). The depth profiles of sulfate and sulfide both show an increase in  ${}^{34}S/{}^{32}S$  (~2-5‰) with increasing depth across the chemocline. Modelling of the depth-resolved, combination of  $\delta^{34}$ S and  $\Delta^{33}$ S data in the context of concentration data suggest that the controls on isotopic compositions in the chemocline and in the lake are principally sulfate reduction in the monolimnion combined with phototrophic oxidation of sulfide across the chemocline.

## Heavy metals and arsenic contamination in mining areas: A biogeochemical approach

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In order to offer a general panoramic of the most representative types of Sn and W mines in Portugal, areas were selected according to mineralization and environmental factors: Ervedosa Mine with cassiterite and diverse sulphides; Rio de Frades Mine and Regoufe Mine with wolframite, scheelite, cassiterite and sulphides; Adoria Mine with volframite, cassiterite and sulphides; and Tarouca Mine with scheelite, cassiterite and sulphides.

The geochemical soils data show the anomalies in the dependency of the mineralization or the relation to mining influence. Beyond the mining soils, it is shown that the highest registered levels, for the elements in general, are the soils involving the mineralized areas or the ones situated under tailings influence. The representative samples of the local geochemical background and the contaminated samples were discriminated by application of the Principal Components Analysis (PCA). The sequential selective chemical extraction verified that pH is the most important factor in the control of the geochemical distribution of the elements. Consequently a majority of the metallic cations (Mn, Cd, Cu, Zn, Pb, Co, Cr, Ni) show an identical behaviour, presenting important enrichments in the most bioavailable fractions (water soluble and changeable), contrasting with the oxi- anions, as the As and the Mo, which evidence a lower mobility, due to adsorption to the Fe oxi- hydroxides, revealing important increase of reducible fractions.

Plants growing on the abandoned mines have been studied for their biogeochemical indication/prospecting and mine restoration potential. The results of analysis show that the species best suited for biogeochemical indicating are by order of importance: aerial tissues of *Halimium umbellatum* (L.) Spach, for As and W; leaves of *Erica arborea* L. for Bi, Sn, W and mostly Pb; stems of *Erica arborea* L. for Pb; needles of *Pinus pinaster* Aiton and aerial tissues of *Pteridium aquilinum* (L.) Kuhn for W; and leaves of *Quercus faginea* Lam. for Sn. These are the key stone species allowing biogeochemical delineation of areas of similar anomalous soil composition.