Metal ion speciation in smelter impacted soils and soil solution

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Bio-availability and toxicity of the metals in polluted soils are influenced by the total metal content and the metal speciation in the soil. These two parameters are largely determined by the free metal ion concentration in the soil pore water. We need to predict the evolution of the behavior of the metals due to change of soil pH or organic matter content to estimate the mobility, then the bioavailability of the metal ions at long term.

The objectives of this work, are to determine the differents chemical forms of heavy metals (Cd, Pb, Zn) present in a contaminated soil and its solution. With the help of speciation models (NICA-Donnan and CD-MUSIC) using as input values the total metal content in the soil and the main soil properties, we determine the speciation of the metal ions in the soil solution as well as in the soil. Then, we compare calculated results with experimental values to validate the model.

The studied area is located in North of France. The presence of a Pb and Zn smelter lead to the contamination of the surrounding soil throughout a 40 km2 area. Dust emissions consist mainly of sulfide and oxide metal (PbS, ZnS, PbO…). The site under investigation, located 500 m NE from the smelter, is a wooded plot and has not been disrupted for the last 50 years.

To take into account the temporal and spatial variations, sampling has been done regularly since 1998 at different places in the parcel. After each sampling, the soil solution is extracted by centrifugation and analysed for comparison with model results. Parallel selective chemical extractions (exchangeable, bound to organic matter and bound to Fe or Mn oxyhydroxides) have been applied to soil samples to validate model speciation. Zn and Pb EXAFS data obtained on the same soil samples are used to validate the calculated speciation.

Our results show that in the soil solution, dissolved organic matter controls Pb speciation. Zn and Cd organic complexes represent approximately 50% of the total metal concentration in solution. In the soil, Pb and Cd speciation is dominated by organic matter. Zn speciation is controlled by organic matter and Fe and/or Mn oxyhydroxydes.

These results are in agreement with the speciation obtained by in situ spectroscopic data as well as selective chemical extractions.

Xe isotope evolution of the mantle

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Xe isotope systematics provide strong constraints on the volatile evolution of the mantle. 1) Mantle Xe has a lower $^{136*Pu}Xe/^{129*}Xe$ ratio than that of air Xe, and cannot be the residue that remains after degassing of the atmosphere (Ozima et al. 1985). This is true unless all of $^{136*}Xe$ in MORB is Pu-derived, but data for CO_2 well gases and MORB indicate that a large fraction of the $^{136*}Xe$ is in fact from U. 2) In a closed system reservoir, Pu-derived $^{136*}Xe$ will dominate over U-derived $^{136*}Xe$ and will accompany $^{129*}Xe$ excesses. MORB and CO_2 well gas data requires that, after decay of ^{244}Pu, there was a large decrease in Xe/U in the source region, or transfer of Xe to a low Xe/U reservoir. 3) Approximately 40% of the Pu-derived $^{136*}Xe$ produced in the Earth (after a closure age of ~80Ma) is now in the atmosphere. 4) If isotopic fractionation of nonradiogenic Xe occurred during losses from the atmosphere to space, then degassing occurred early while this was still possible. In contrast, atmospheric fissiogenic Xe is not fractionated. 5) Nonradiogenic Xe isotopes in the mantle appear fractionated with respect to atmospheric Xe and requires retention in the mantle of Xe that was either less fractionated relative to solar Xe, or that is unfractionated solar Xe mixed with subducted Xe.

These factors suggest: 1) Nonradiogenic noble gases were degassed to the atmosphere early from an unknown volume and fractionated by losses to space. 2) Radiogenic Xe was then degassed quantitatively (either directly from the mantle, or after transport of parent Pu and I to the crust) from at least 40% of the mantle. 3) Xe contained in another, deep mantle reservoir was subsequently added to the upper mantle where $^{136*}Xe$ became dominated by U-derived Xe.

The size of the deep mantle reservoir cannot be easily constrained from Xe isotopes. Since the fraction of Pu-derived $^{136*}Xe$ in the atmosphere is similar to that of ^{40}Ar, it might be concluded that 60% of both are retained there. However, it is possible that a significant fraction of degassed fissiogenic Xe in the atmosphere was lost during late bombardment of the Earth. Then the similarity between the apparent ^{40}Ar and $^{136*Pu}Xe$ budgets is coincidental.