

## Isotopic fractionation of Cd and Zn onto humic acid at low and high ionic strength

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The behaviour and fate of Cd and Zn in the soil environment has attracted much attention, particularly due to the historical release of large amounts of metals-contaminated waste. Knowledge about the behaviour of these cationic metals in the environment is important for predicting the potential toxicological risks associated with their elevated concentration in soils. Cd and Zn isotopes have been used as tracers of pollution in the environment, but in order to successfully interpret such data, one needs to identify and quantify isotopic fractionation during separate biogeochemical processes.

In this study, the main goal is to provide robust and quantifiable data on Cd and Zn isotope fractionation resulting from their adsorption onto humic acid (leonardite from IHSS). Adsorption experiments were thus performed under N<sub>2</sub> atmosphere at three different initial metal concentrations (10<sup>-6</sup>, 10<sup>-5</sup>, 10<sup>-4</sup> M), three ionic strengths (10<sup>-1</sup>, 10<sup>-2</sup>, 10<sup>-3</sup> M NaNO<sub>3</sub> as background electrolyte) and pH ranging from 2 to 10. Solution and solid samples were separated using a centrifugal 3 kDa filter device.

The %Cd and %Zn associated with humic acids were strongly controlled by the ionic strength between pH 4 and 6. Therefore, adsorption experiments with Cd and Zn isotope standard (NIST 3108 Cd and AA-ETH Zn, respectively) were performed under N<sub>2</sub> atmosphere at three fixed pH values (4, 5 and 6), three different initial metal concentrations (10<sup>-6</sup>, 10<sup>-5</sup>, 10<sup>-4</sup> M) and five ionic strengths (10<sup>-1</sup>, 5.10<sup>-2</sup>, 10<sup>-2</sup>, 5.10<sup>-3</sup>, 10<sup>-3</sup> M NaNO<sub>3</sub> as background electrolyte). Following, Cd and Zn isotopic compositions were determined using a multi collector TIMS at the Czech University of Life Sciences Prague. Prior to analysis, anion chromatography was performed for Cd and Zn. A double spike technique based on two Cd and Zn isotope spikes was applied.

The relation between ionic strength and Cd/Zn isotope composition ( $\delta^{114}\text{Cd}$  and  $\delta^{66}\text{Zn}$  values) shows that inner/outer sphere complexes as well as electrostatic effects are responsible for the observed isotopic fractionation.