

## Ni isotopic fractionation due to interaction with small organic acids and purified humic acids

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The biogeochemical cycle of metals in the environment can be considerably influenced by the role of vegetation. Several Ni accumulating plants are able to enrich Ni composition up to 5% in dry leaf matter [1]. Some recent studies have reported a significant Ni isotopic fractionation in hyperaccumulating plants between roots and storage organs, until the maximum absorption is reached (-0.18‰) [2], therefore, the use of stable isotopes can allow to understand the dynamics of trace elements and tracing Ni fate in the soil-plant system and in the environment.

Several organic acids are present in plant roots, such as citric or malic, that are involved in soil-plant processes, including metal mobilization and uptake, and plant detoxification [3]. However, up to now, no specific investigations were performed about the potential Ni isotopic fractionation due to complexation with organic acids present in plant roots, or due to adsorption to organic matter in soils.

To investigate the potential mechanisms responsible for Ni isotopic fractionation in the soil-plant system, the complexation by two different organic acids, citric and oxalic, with increasing complexation constants, was studied at pH=5 and pH=7. In addition, Ni adsorption onto purified humic acid (PHA) [4] from peats collected in São Paulo State, Brazil, an analog of organic matter, was investigated at pH=7 with PHA concentration of 40mg L<sup>-1</sup> and 80mg L<sup>-1</sup>. According to Visual-Minteq modeling, in these conditions, free Ni<sup>2+</sup> in solution represents 63% and 40% of the total Ni, respectively, which is coherent with the measurements. The Donnan Membrane device (DMT) was used to separate complexed Ni from free Ni<sup>2+</sup> after reaching equilibrium. The obtained results revealed that Ni complexation with citric and oxalic acids did not induce any significant isotopic fractionation, whatever the pH considered. On the contrary, in both PHA experiments, Ni complexed with PHA is slightly enriched in heavier isotopes compared to free Ni<sup>2+</sup>, inducing a  $\Delta^{60}\text{Ni}_{\text{complexed-free}}$  ranging from 0.1 to 0.2 ‰.

[1] Baker A.J.M. (2000), *Phytoremediation of contaminated soil and water*, Lewis Publishers, 85-107. [2] Estrade et al. (2015), *EPSL*, 423, 24-35. [3] Jones D.L. (1998), *Plant and Soil*, 205, 25-44. [4] Swift, R.S. (1996) *Methods of soil analysis*. D.L. Sparks et al. (eds), 35, 1018-1020.