Fractionation of Zn upon complexation with physiologically relevant organic ligands in plants

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The contribution of ligand-facilitated uptake of Zn in graminaceous plants, such as rice, is studied with the purpose to better understand the mechanism of Zn efficiency. Previous work suggested that the formation of Zn complexes with naturally available organic ligands introduces an enrichment in heavy ^{66}Zn isotope, analogous to the mechanisms shown for Fe uptake [1]. Organic compounds that have been associated with a Zn transport role in plants include low molecular weight organic acids such as citrate and malate, small amino acids e.g. cysteine, as well as strong chelators from the group of phytosiderophores (PS) and peptide based metallothioneins.

This study quantifies isotopic fraction upon Zn^{2+} complexation with three synthetic ligands (i.e. EDTA, TMDTA and CyDTA) similar in reactivity and structure to 2'-deoxymugineic acid (DMA), a phytosiderophore from the group of mugineic acids utilised by rice to facilitate Zn translocation. Under the experimental conditions used, we observe heavy isotope enrichment within the complex (expressed as Δ^{66}Zn) of 0.52±0.06‰, 0.48±0.04‰ and 0.63±0.08‰ for EDTA, TMDTA and CyDTA respectively.

Heavy ^{66}Zn enrichment (0.18 to 0.22‰), previously reported by our group in field-grown rice [2], was explained by involvement of DMA in Zn uptake mechanisms under Zn deficient conditions. To estimate Zn partitioning when complexed by DMA, we calculate $\delta^{66/64}$Zn using computational methods (i.e. DFT) as well as extrapolate the anticipated value from the experimental results shown above. Both methods agree in the direction of bias and the extent of isotopic fractionation, where $\delta^{66/64}Zn_{free\text{-}Zn\ -\ [ZnDMA]2-} \sim 0.32‰$.

Our results demonstrate advances in the application of DFT as a fast and powerful tool in future environmental and stable isotope studies. Nevertheless, further efforts in optimising analytical techniques are necessary to overcome the challenges of measuring Zn fractionation *in situ*.

[1] Römheld V. and Marchner H. (1986) *Plant Physiol*. **80**, 175-180. [2] Arnold T. et al. (2010) *Plant Cell Environ*. **33**, 370-381.