Fractionation of Zn isotopes during uptake of ZnO nanomaterials by plants.

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Growing interest on the properties of nano zinc oxide (nano-ZnO) has lead to increasing release of these materials to the environment. However, relatively little is known about their toxicity and accumulation in aquatic plants. Here we investigated the uptake, accumulation, and toxicity of nano-ZnO on common reed (*Phragmites australis*) and the associated isotopic effects. Plants were grown in nutrient solution containing four ZnO materials: micron-size (bulk), nanoparticles (NP) less than 100 nm (NP100), NP less than 50 nm (NP50), and nanowires of 50 nm diameter (NW50). Each material was tested at a range of concentrations (0, 0.1, 10, 100, and 1000 mg l^{-1}). Plants were measured for growth, leaf chlorophyll content, transpiration, and photosynthetic rates. The Zn concentration [Zn] of solutions, roots, shoots, and ZnO materials was quantified. Three plants each of controls, 10 mg l^{-1} (NW), and 100 mg l^{-1} (bulk, NP100, NP50) treatments were analysed for Zn isotope content together with the initial ZnO materials.

[Zn] in solutions, roots, and shoots increased with increasing ZnO supply. Those were significantly higher for NP50 relative to other ZnO materials (100 and 1000 mg l^{-1} treatments only). ZnO decreased plant growth from 1 mg l^{-1}. Chlorophyll content, photosynthetic performance, and transpiration were reduced at higher concentrations (10- 100 mg l^{-1}). Plants treated with NP50 showed stronger inhibition of root growth and photosynthesis performance. Zinc isotopic fractionation between roots and ZnO materials ($\Delta_{root-ZnO}$) was smaller in NP50 (-0.18‰) and NW (0.07‰) compared to NP100 and bulk (-0.3‰). By contrast, fractionation of Zn isotopes between shoots and roots ($\Delta_{shoot-root}$) was not statistically different between ZnO treatments.

Our results clearly show that ZnO is toxic to key aquatic plants at current environmental concentrations (1 mg l^{-1}). NP <50 nm released more Zn^{2+} and were more damaging to plants than particles of bigger size. The $\Delta_{root-ZnO}$ suggests that nanomaterials with one dimension < 50 nm could be partly taken up by the root. By contrast, $\Delta_{shoot-root}$ was the same for all treatments, which points to Zn transport to the shoot mainly as Zn^{2+}.