

## A stable isotope methodology to trace nanoparticles fates in biota

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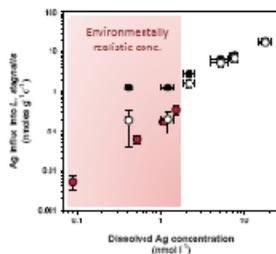
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### Introduction

One challenge in understanding the environmental implications of nanotechnology lies in tracing nanoparticles in organisms during controlled experimental studies as well as in the environment. Stable isotope methodologies offer great potential to address this challenge. Metallo-nanoparticles can be synthesized from a metal enriched with a rare stable isotope [1,2]. Here we quantify the bioavailability of metal nanoparticles (NPs) from food and water under conditions that might be typical of nature, and develop links to toxicity. Metal oxides NPs (CuO, ZnO) as well as Ag NPs were synthesized with an enriched stable isotope. We use a tracing technique that allows us to determine uptake and loss rates in freshwater snails exposed to NPs dispersed in water or mixed with food. The rate constants developed in these experiments were used to model bioaccumulation from both routes under environmentally realistic conditions. The isotope tracer was also used to quantitatively evaluate physiological processes like feeding rates and assimilation efficiency that might be adversely affected by exposure to metal NPs in diet.

### Results and Conclusion

We demonstrate that isotopically modified <sup>67</sup>ZnO and <sup>65</sup>CuO NPs are required in uptake experiments because the high natural background metal concentrations limit the ability to detect bioaccumulation at environmentally relevant exposures. A tracer is also required when studying uptake of Ag NPs at environmentally relevant concentrations. For example, we demonstrate that Ag concentrations as low as 0.005 nmol g<sup>-1</sup> can be detected in freshwater snails exposed to 0.1 nM of dissolved Ag enriched with <sup>109</sup>Ag (Fig.1). Exposures more than 20-times higher would be required to detect Ag uptake if no tracer were used. Without a tracer, uptake rates can only be determined at concentrations typical of extreme contamination.



**Figure 1.** Silver uptake rates in snails after exposure to AgNO<sub>3</sub> (solid circles) or enriched <sup>109</sup>Ag (red circles). Open circles show uptake rates when Ag background is removed with a mathematical correction.

[1] Dybowska et al. (2011) *Environ. Pollut.* **159**, 266-273.

[2] Misra et al. (2012) *Environ. Sci. Technol.* **46**, 1216-1222.

## Cr isotopes in a ferruginous lake

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Cr isotope signatures have recently been introduced as a robust paleo-redox proxy and Cr isotopes in banded iron formations (BIFs) broadly track Earth's oxygenation history as revealed by other proxies [1]. Cr isotopes, however, appear to reveal additional structure in the evolution of atmospheric oxygen not exposed by other proxies. Notably, Cr isotopes indicate an oxygen pulse nearly 400 Ma prior to the widespread oxygenation of the atmosphere at the 2.3 Ga Great Oxidation Event (GOE). To better constrain the behaviour of Cr isotopes and their record of paleo-redox conditions, we examined the Cr cycle and its accompanying isotope fractionation in Lake Matano—a modern analogue for the iron-rich oceans from which BIFs were deposited [2]. Cr speciation in Lake Matano's oxic surface waters and inflowing streams is dominated by Cr(VI). This Cr(VI) is quantitatively reduced in the lake's ~100m deep chemocline. With  $\delta^{53}\text{Cr}$  values between +2.2 and +3.3 ‰ ( $\delta^{53}\text{Cr} \text{ ‰} = [({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{sample}} - ({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{NIST SRM 979}}] / ({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{NIST SRM 979}} \cdot 1000$ ), this Cr(VI) is isotopically heavy relative to mantle inventories, and the catchment bedrock and soils. Cr(III) in the lake's anoxic bottom waters is also isotopically heavy ( $\delta^{53}\text{Cr} = +2.22$  to +2.61 ‰), suggesting that Cr(III) records the heavy composition of Cr(VI) from the lake's surface waters and inflowing streams. Our observations are thus consistent with the mechanisms proposed to explain the  $\delta^{53}\text{Cr}$  record in BIFs.

[1] Frei et al. (2009), *Nature*, **461**, 250-254, [2] Crowe et al. (2008), *PNAS*, **105**, 5938-15943