

Low Concentration Soil Exposure to ZnO Nanoparticles by Stable Isotope Labelling

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The tracing of engineered nanoparticles (NPs) in the environment is hampered by analytical limitations. In particular, difficulties lie in the detection of these materials against the natural background of elements and NPs found in complex systems. To overcome these problems excessive dosing is often employed in exposures, calling into question the relevance of findings. The novel application of stable isotope labelling in conjunction with high precision isotope ratio measurements can overcome these shortcomings.

Presented here are results obtained for the exposure of the earthworm *Lumbricus rubellus* to isotopically labelled ZnO NPs in soil. To this end, ZnO NPs were synthesised using Zn enriched to 99.5% in the Zn-68 isotope relative to the natural abundance of 18.8%. The introduction of this enriched isotope into the experimental system creates distinct non-natural deviations in the diagnostic isotope ratio ⁶⁸Zn/⁶⁶Zn. Precise determination of isotope ratio changes then enables accurate detection and quantification of the isotope label in the components of the exposure system.

The study compares dietary vs. dermal uptake of ⁶⁸ZnO NPs and soluble ⁶⁸Zn from soil by *Lumbricus rubellus*. Exposures were performed simultaneously in triplicate with earthworms being sampled at 4, 8, 24, 36, 48 and 72 hours. The labelling method allows use of an environmentally relevant exposure concentration of 4 µg/g ⁶⁸Zn against a natural Zn background content of up to 1.7 mg/g. After 4 hours of dermal exposure, the enriched ⁶⁸Zn contributes about 0.02% to the total Zn concentration of an exposed earthworm but this already produces a sufficient deviation in the diagnostic ⁶⁸Zn/⁶⁶Zn ratio to be detectable when measured by high precision multiple-collector ICP-MS.

For the exposures with ⁶⁸ZnO NPs and soluble ⁶⁸Zn, our data reveal that dermal ⁶⁸Zn uptake accounted for less than 10% of the worms total uptake, with dietary ⁶⁸Zn uptake being by far the most important route. In both cases, the uptake rates determined for ⁶⁸ZnO NPs and soluble ⁶⁸Zn are identical, within error. This indicates that Zn from both nano and ionic based exposures display similar bioavailability.

Substantial changes in the salinity and paleo-hydrology of the late Quaternary Dead Sea revealed in the ICDP deep drill

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Vertical profiles of chloride (Cl) and oxygen isotopes ($\delta^{18}\text{O}$) of Lake Lisan the late Quaternary precursor of the Dead Sea were established from analyses of pore-fluids that were extracted from cores drilled during the ICDP campaign in the deep basin of the Dead Sea at water depth of 300 m. The pore fluids data provide the first direct measurements of the composition of the Dead Sea deep brine that was evolved over the past several glacial interglacial intervals. Specifically, pore fluid profiles suggest that during the last glacial (70-14 ka BP) Cl concentrations at the bottom of the lake were not more than 2/3 of their present values and $\delta^{18}\text{O}$ reached values higher than 6.7 ‰. The low chloride values of porewaters indicate that during MIS2 the deepest part of Lake Lisan was significantly less salty than the present Dead Sea. This is compatible with the heaviest $\delta^{18}\text{O}$ values that could be produced by evaporation of the waters at the shallow southern lake margins. Continuous turbulent mixing of such an evaporated solution with the lower brine across the epi/hypolimniom interface, led the dilution of the latter and the buffering of the Sr/Ca ratios and radiocarbon reservoir ages in the epilimniom[1]. However, upon the abrupt decline of the lake to minimum levels (below 450 m bmsl)[2] e.g. at ~14-13 ka (the Bolling-Allerod period), the bottommost brine retained its highest salinity, lowest $\delta^{18}\text{O}$ and highest Sr/Ca ratios.

[1] Stein M., Lazar B., Goldstein S.L. (2013), *Radiocarbon*. Accepted. [2] Stein M., Torfstein A., Gavrieli I. Yechieli Y. (2010), *Quarter. Sci. Rev.* **29**, 567-575.