Impact of Natural Sulfidation of Silver Nanoparticles on Bioavailability and Biouptake

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Engineered silver nanoparticles (Ag NPs), often partially or fully sulfidized, enter the environment. There, sulfidation of Ag NPs greatly decreases the rate of oxidation of Ag^0 and the release of Ag^+. We hypothesized that sulfidation of Ag^0 NPs added to an emergent freshwater wetland mesocosm would greatly decrease silver bioavailability. We dosed a 1.2x1x3m freshwater wetland mesocosm with 30nm PVP-coated Ag NPs (25 mg/L Ag) and then determined the distribution and speciation of Ag NPs after 18 months. A sediment diagenetic model was developed and used to predict the distribution and speciation of Ag in the mesocosms.

Ag^0 NPs in sediments sulfidized over 18 months. Ag speciation was approximately 50% Ag_2S, 30% Ag-S-R (likely organic matter complexed) and 20% Ag^0 as determined by X-ray absorption spectroscopy. Sulfidation decreased dissolved Ag concentration in the water column to below method detection (2 μg/L). The sediment diagenetic model could predict Ag distribution and speciation well using parameter values (e.g. bioturbation) and partition coefficients (e.g. Ag-organic matter) in the range expected for freshwater sediment and demonstrated seasonal fluctuations. There was measurable uptake of Ag into several sediment dwelling organisms, suggesting that Ag_2S or Ag-S-R species remained bioavailable. The uptake of Ag2S in duckweed roots was confirmed with synchrotron based micro-X-ray fluorescence (μ-XRF) and μ-XANES indicates that the silver within the root cortex was predominantly Ag^0.

Cavity ring-down spectroscopy for the high-precision analysis of the triple oxygen isotope composition of water and water vapor

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High precision analysis of the $^{17}O/^{16}O$ isotope ratio is an important new tool in water isotope analysis. The ^{17}O-excess (= $\ln(\delta^{17}O+1)-0.528\ \ln(\delta^{18}O\ +1)$) is sensitive to kinetic fractionation processes and nearly invariant with temperature [1]. For most applications, measurements of ^{17}O-excess must have a precision of ~5 per meg. This precision is normally obtained by flourination of H_2O to O_2 and analyzed by dual-inlet isotope ratio mass spectrometry (IRMS).

Cavity ring-down spectroscopy (CRDS), commonly used for measurements of $\delta^{18}O$ or δD in water [2, 3], provides several advantages over IRMS, including streamlined sample handling and the ability to measure ambient water vapor in the field. Use of CRDS for ^{17}O-excess poses unique challenges not addressed by existing commercial instruments. While a $H_2{}^{17}O$ absorption region is present in some instruments, the absorbance is influenced by the tail of the $H_2{}^{16}O$ spectrum; resulting precision is inadequate for distinguishing samples from the meteoric water line.

We describe a new CRDS system for high precision ^{17}O-excess measurements. Innovations include i) use of two lasers that measure absorption in different IR regions; ii) sample introduction system for continuous introduction of water vapor over long time periods (similar to [3]); iii) novel improvements to the spectroscopy. Samples can be analyzed with ~5 per meg precision in 60 min. Calibration with respect to VSMOW is achieved using working laboratory standards previously calibrated with IRMS [4]. The results show that both the precision and the accuracy of the new CDRS are competitive with IRMS methods. An additional benefit is improved precision of $\delta^{18}O$ and δD (0.02 ‰, 0.08 ‰).

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