Fate of Metallic Silver Nanoparticles in a Sewer System

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The biocidal properties of Ag^+ ions have led to the incorporation of metallic Ag nanoparticles (Ag-NP) in a wide range of industrial and commercial products. Therefore, the emission of Ag-NP to the aquatic environment seems inevitable, most likely occuring via urban water systems. However, the understanding of the transport behavior of Ag-NP in urban water systems is still incomplete. It has been shown that Ag-NP are readily transformed to Ag_2S during wastewater treatment [1] and based on laboartory studies, Liu et al. [2] speculated that the transformation might already occur in the sewer system. To assess whether Ag-NP sorb to and are retained by the sewer biofilm and to investigate the physical-chemical changes during the transport in a sewer line, we conducted experiments in a 5-km sewer stretch (no exfiltration, no confluents).

The wastewater flow rate for our experiment was adjusted to 30 l/sec. Over 30 seconds, we spiked 1g of Ag-NP (15 nm diamter) to the wastewater. Subsequntly, wastewater samples were collected at three locations 500 m, 2.4 km, and 5 km downstream. The transit times for unretarded Ag-NP at the respective locations were derived from tracer experiments and equalled 10 min, 60 min, and 120 min, respectively. Around these times, forty wastewater samples were collected at each location and immediately acidified for analysis of total Ag contents. Additional samples were prepared for transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS) to assess changes in Ag-NP aggregation state and speciation along the sewer stretch.

Between 95 and 105% of the spiked Ag were recovered at all sampling stations, indicating that Ag retention by the sewer biofilm was negligible, which was also confirmed by Ag contents in the biofilm before and after the experiment. TEM revealed that the Ag-NP did not aggregate amongst themselves but were dominately attached to other colloids. Energy dispersive X-ray analysis indicated that the Ag-NP were partially transformed into Ag_2S already after 500 m (10 min), consistent with high acid-volatile sulfide levels of 0.15mM in the raw wastewater. The quantitative Ag speciation will be determined in XAS measurements scheduled for March 2012.

[1] Kaegi, R. *et al.* (2011) *Environ. Sci. & Tech.,* **45(9)**, 3902–3908.
[2] Liu, J. *et al.* (2011) *Environ. Sci. & Tech.,* **45(17)**, 7345–7353.

Zinc isotope fractionation during metabolic uptake by bacteria

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Zinc is a trace metal responsible for the normal operation of living organisms but can be toxic at elevated concentrations. The biogeochemical processing of Zn in microorganisms may be reflected in changes in the ratios of stable Zn isotopes. If so, the isotopic signatures of Zn might be used as a tool to learn more about cellular metal processing and toxicity. Despite pioneering work on how Zn isotopes are fractionated during interaction with diatoms and plants, Zn isotopes in bacterial systems remain largely unexplored.

In this study, we conducted a series of metabolic uptake experiments with bacteria using different concentrations of Zn-citrate. Experiments were conducted using the Gram-negative bacteria, *Pseudomonas mendocina* and *Escherichia Coli*, as well as with a natural consortium of desert soil bacteria. Each experimental system was sampled as a function of time/cell growth and the elemental and isotopic compositions of Zn were determined for both the bacterial cells and the solution.

When exposed to 2 ppm of Zn, the growth curves for both *E. coli* and the natural consortium were similar in that the stationary phase occurred 8 days after inoculation. The stationary phase for *P. mendocina* occurred at 6 days after inoculation. However, when *P. mendocina* cells were exposed to 20 ppm of Zn, there was a time lag and the populations reached stationary phase 9 days after inoculation. Cell counts also suggested that fewer bacteria grew under the elevated Zn concentrations. In the 2 ppm experiments, *E. coli*, *P. mendocina* and the natural consortium incorporated a maximum of 17, 16 and 29 ppm of Zn, respectively. In contrast, when exposed to 20 ppm of Zn in the growth solution, *P. mendocina* incorporated 509 ppm of Zn. Zn isotopes, reported as $\Delta^{66}Zn_{bacteria\text{-}solution}$, for the 2 ppm Zn experiments varied as a function of the growth phase. A separation factor of +0.22‰ was measured for the log phase of *E. coli*, but this decreased to slightly negative values during the death phase. In contrast, *P. mendocina* showed the most negative $\Delta^{66}Zn_{bacteria\text{-}solution}$ during the log phase of its growth (-0.4‰). When *P. mendocina* cells were exposed to 20 ppm of Zn, the $\Delta^{66}Zn_{bacteria\text{-}solution}$ was positive, ranging from +1.02 to +1.5‰. The largest values were again found in the log phase of growth. The natural bacterial consortium did not substantially fractionate Zn isotopes ($\Delta^{66}Zn_{bacteria\text{-}solution}$ = -0.04 to +0.05‰) when exposed to 2 ppm of Zn.

Despite some broad similarities, our experiments demonstrate that the bacterial species, growth phase, and the dosage of Zn all impact the Zn isotopic composition of bacteria. This may suggest that Zn isotopes could be used as a chemical tool for understanding Zn homeostasis within cells. The observation of a dose-dependent fractionation further suggests that Zn isotopes might serve as a tool for understanding toxicological impacts on these microorganisms. However, because of these same complexities, the use of Zn isotopes as a possible biological marker in natural systems deserves further scrutiny.