# Using µ-XRF and XAS to characterize the fate and bioavailability of manufactured nanoparticles in soil

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Manufactured metal nanoparticles are likely to enter wastwater streams and partition to sewage sludge, which may be applied as biosolids to agricultral lands [1]. We have investigated the fate of a variety of Ag, Cu and Au nanoparticles in soils, as well as bioavailability and toxicity in nematodes (*Caenorhabditis elegans*) and earthworms (*Eisenia fetida*) using synchrotron based x-ray fluoresence microspectroscopy (µ-XRF) microfocused x-ray absorption near edge spectroscopy (µXANES) and bulk extended x-ray absorption fine structure spectroscopy (EXAFS) as described previously for trace-element studies [2] along with gene expression studies.

We have obtained strong evidence for the uptake and biodistribution of nanoparticles in earthworms and nematodes and have differentiated metal and metal oxide particle uptake from uptake of metal ions for Cu and Au (e.g. fig 1). We have also shown that reproductive effects of Ag nanoparticles are likely due to $Ag^+$ exposure while behavioral effects are likely caused by the Ag nanoparticles.

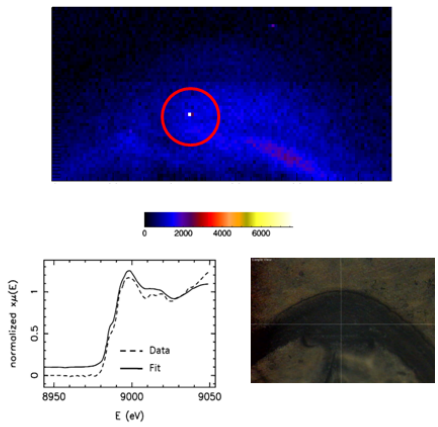


**Figure 1:** X-ray fluorescence micrograph (top) showing a pixel of high Cu intensity in the main dorsal blood vessel of an earthworm (light micrograph bottom right). Interrogation of this pixel with XANES (bottom left) demonstrated that it was a mixture of Cu (0), CuO and $Cu_2O$.

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# Dissimilatory iron reduction in subzero brines

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Ferric iron ($Fe^{3+}$) minerals are potential electron acceptors in cold and icy environments, such as those in the ice-hosted sediments in icebergs and glaciers [1]. Microbial dissimilatory iron reducers have been found in many icy environments, such as subglacial sediments [2], Arctic marine sediments [3], permafrost [4] and Antarctic sea ice [5]. Theoretical and laboratory studies have reported that supercooled, solute-rich veins within ice samples are viable habitats for microorganisms [6, 7]. Further, it has been suggested that dissimilatory iron reducers may reduce iron at temperatures as low as -9°C in the solute-rich vein network within basal ice [8], however, no direct evidence of microbial iron reduction at subzero temperatures has been reported to date.

The gammaproteobacteria *Shewanella frigidimarina* was originally isolated from sea ice in eastern Antarctica [5]. This organism can respire on ferric iron, and has been demonstrated to grow at temperatures from 0 to 28°C, and salinities up to 8% NaCl [5]. We quantified the effect of temperature and salinity on the growth and iron reduction rates of *S. frigidimarina* at subzero temperatures. Cultures were incubated at 15°C, 4°C and -5°C, over a range of salinites from 0-8% NaCl. Our results indicate that *S. frigidimarina* is capable of growth at temperatures as low as -5°C at 2% and 4% NaCl in the presence of ferric citrate as sole electron acceptor and lactate as sole electron donor. No growth was observed at 8% NaCl over the temperature range tested. To the authors' knowledge, these results represent the first direct evidence of an organism respiring and growing on ferric iron at subzero temperature and increased salinity.

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