	Experiment title: In situ study of the sulfidation of silver nanoparticles	**Experiment number**: ev-158
Beamline: ID16b	**Date of experiment**: from: nov 02, 2015 to: nov 09, 2015	**Date of report**: Fev 2016
Shifts: 18	**Local contact(s)**: **Remi Tucoulou**	*Received at ESRF:*

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Background

Silver nanoparticles (Ag-NPs) are widely used in consumer products due to their antimicrobial activity. However, they are easily leached from them, for example during laundry, ending in wastewaters and then in the sewage sludge produced in Waste Water Treatments Plants (WWTP). 40 to 50% of sewage sludges are applied on agricultural soils as fertilisers in France. There is a lack of information regarding the impacts that the input of these Ag nanomaterials could have on soil quality and fertility, phytotoxic effects for the crops, and health effects for the consumers if they are transferred in the edible parts of the plants. Recently, we have published the first work to study the fate of Ag in soils amended with a sewage sludge polluted with Ag-NPs and produced in a real WWTP (Pradas del Real et al., 2016). The sludge containing 400 mgAg·Kg^{-1} was mixed with an agricultural soil and rape and wheat were grown for 4 weeks. By bulk EXAFS and µXANES (see exp report 30-02-1070 and EV32), we found that Ag_2S was the main species in sludge and soil samples. The second most abundant species was an organic and/or amorphous Ag-S. µXRF observations on ID21 (ESRF) showed that Ag was well dispersed in the sludge and soil and mainly associated with the organic fraction of soils. However, the resolution (0.3 x 0.7 µm), although very good, did not allow the determination of the actual size of the particles. A feasibility test was performed at ID16b on one of the soil samples showing the presence of nanosized particles, and of zones of diffuse Ag concentration, suggesting some dissolution and possibly complexation and/or sorption of Ag+ ions. Another important finding derived from this analysis was the presence of mixed metallic sulfides. The objective of our experiment on ID16b was to study Ag distribution and possible association with other metallic sulfides on all soil conditions at the nanoscale, and also to perform nanoXANES in regions of interest to determine Ag speciation in these samples. This second part was challenging because nanoXANES was not tested yet on ID16B.

Experiment

We studied 4 samples: sludge, soil withouth plant, soil planted with rape and soil planted with wheat. Soil and sludge samples were prepared as thin sections (embedded in an epoxy resin) that were previously analysed on ID21. They were mounted on ID16b sample holder and studied at room temperature. NanoXRF maps were recorded in pink mode at 29.6KeV. Nano-EXAFS was performed at 25.650 keV after localization of areas of interest in coarse maps collected at this energy. Spectra were collected in mapping mode (one nanoXRF map was recorded at each energy across the Ag K-edge) to avoid problems related with beam drift during acquisition. Then, the stack of the obtained nano XANES maps was processed with MATLAB and PyMCA softwares to extract the nano XANES spectra.

Results

As seen in figure 1, very high quality nano XRF maps were obtained, and provided information about the distribution of Ag nanoaggreagates and the elemental associations with other metals such as Cu or Ti.The high flux enabled us to detect diffuse zones. We collected high quality maps for all our samples.

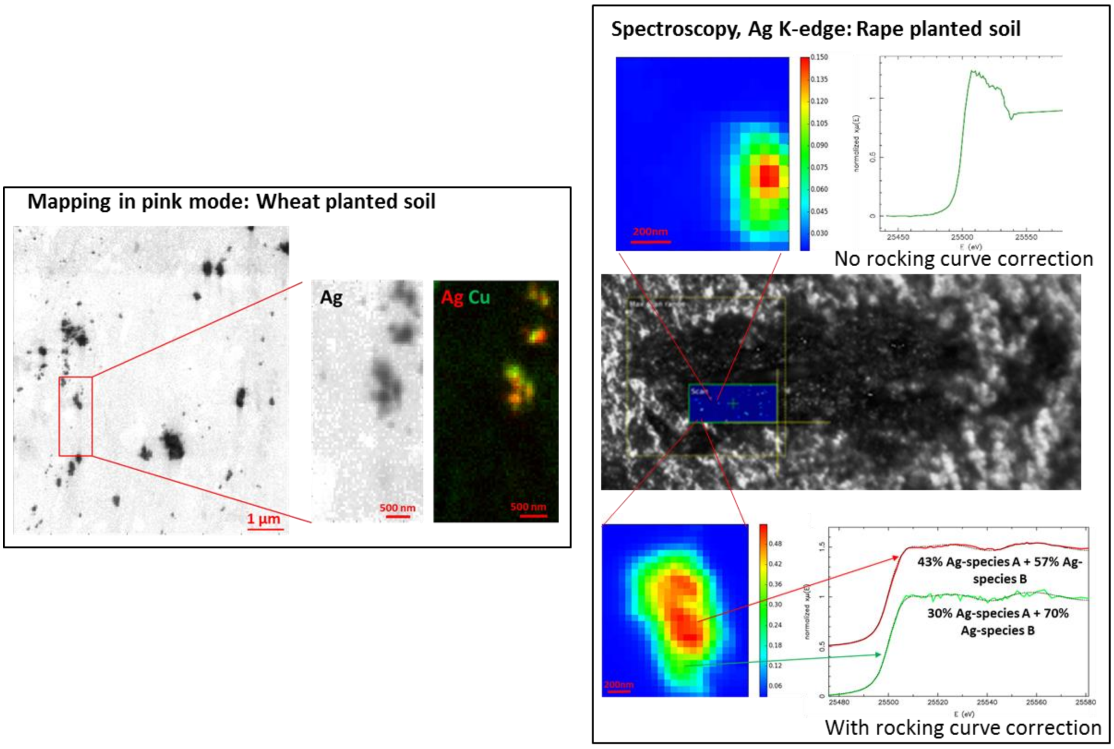

Figure 1. Wheat planted soil: nanoXRF map showing Ag distribution and the colocalization of Ag with Cu. Rape planted soil: nanoEXAFS mapping

The acquisition of good quality EXAFS spectra of such a small Ag particles was challenging so we adjusted the adquisition mode during the experiment. One of the main improvements was the incorporation of a rocking curve before each map acquisition (see figure 1). This acquisition mode (130 maps/area) was very time consuming (~6h/area), but it allowed extracting very nice nanoXANES spectra from different areas of the particles, showing a change in Ag speciation from the center (most concentrated) to the more external regions. Because it was one of the first nanoXANES experiment on id16b, we were only able to get nanoXANES data from three Ag aggregates in the rape planted soil. Significant improvements are being implemented at the beamline to speed up the XANES acquisition and make it more user friendly.

To conclude, results are promising and provide an unprecedented characterization of the final form of Ag in soils amended with polluted sludge. We hope to get new beamtime on ID16b to complete the speciation study on the sludge and soil samples.

Reference

Pradas del Real, A. E., et al., 2016. Fate of Ag-NPs in sewage sludge after application on agricultural soils. Environmental Science & Technology. DOI: 10.1021/acs.est.5b04550