



	Experiment title: Temporal and spatial evolution of zinc speciation in the Seine river	Experiment number: 30-02- 984
Beamline:	Date of experiment: from: 16/04/2010 at 08:00 to 20/04/2010 at 08:00	Date of report: Feb 27, 2011
Shifts:	Local contact(s): Dr. Denis TESTEMALE	<i>Received at ESRF:</i>

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Report:

The objective of this proposal, following experiment 30-02-942 (from: June 24 to: June 30 2009), was to further characterize zinc species in complex natural suspended matter from the Seine River collected from various sites and time period in relation to water chemistry and zinc bioavailability.

This additional beamtime was used to complete the set of data in order to characterize the seasonal evolution of Zn speciation in relation with the increased Zn inputs for sewage water overflows. In addition the complexity of Zn speciation in the samples studied required to record an additional set of model compounds including redox sensitive mineral phases containing Zn at dilute levels. During the 12 shifts beamtime EXAFS and XANES data were recorded at the Zn K-edge in fluorescence detection mode using 30 Ge-elements detectors, at a temperature of 5-15 K, using a liquid He cryostat. The monochromator was equipped with Si(220) crystals with sagittal focusing of the 2nd crystal.

15 samples were analyzed with Zn concentrations varying within the 100 – 600 ppm range, including specific model compounds synthesized at IMPMC and LSCE (Zn:calcite, Zn sorbed calcite, amorphous Zn sulfides, amorphous Zn-Fe hydrous phosphates). Special care was taken for preserving samples under anoxic conditions from the sampling to the analysis. Samples were dried and prepared as pellets under anoxic conditions at IMPMC laboratory. Samples were then brought to ESRF under controlled anoxic conditions and mounted in an anoxic glove box on the cryostat sample holder. After mounting on the cryostat rod within the glove box. The sample rod was then put under low pressure He atmosphere for data analysis in the liquid He cryostat at a temperature of 10-15K. The data were of very good quality, with a usable signal to noise ratio after 8 to 10 scans depending on the Zn concentration. Comparison of spectra taken on well preserved samples

and on air-dried samples revealed dramatic changes in Zn speciation after air-drying, indicating the presence of redox sensitive Zn-bearing phases (Figure 1).

Combined with that from the previous experiment, the present set of data yields new constraints on the nature of the solid phases hosting Zn in the particulate matter transported by the Seine river and thus controlling Zn solubility and bioavailability in the water column. We have especially demonstrated, using classical shell-by-shell analysis of the data, that reduced Zn species as amorphous Zn sulfides that may form in the sediments are mobilized and persist as a dominant Zn species in the particulate matter within the oxic water column (Figure 1). These first results have been submitted for publication (Priadi et al. submitted)

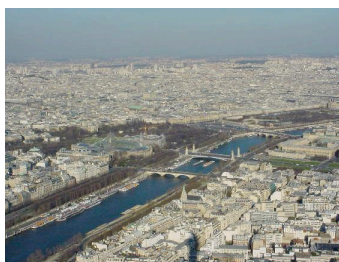
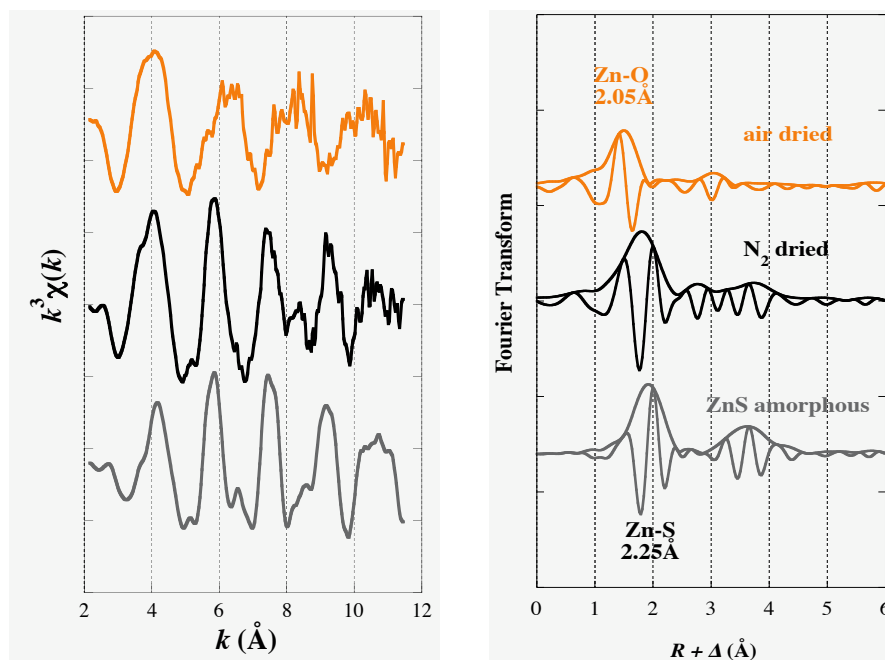


Figure 1. Zn-K edge EXAFS data of some samples studied showing the effect of sample drying procedure and the importance of amorphous ZnS as a dominant Zn species in suspended matter from the Seine river. For comparison, experimental data for amorphous ZnS as references for Zn-S first shell coordination is reported.



Further data analysis is under progress and is based on Principal component analysis (PCA) of the large set of EXAFS spectra recorded during the previous 30-02-942 experiment and during the present experiment. This PCA analysis will be followed by a linear least-squares fitting using a set of more than 50 model compounds, including Zn-bearing crystalline and amorphous phases as well as inorganic and organic sorption samples, already collected from previous synchrotron experiments from the group.

Analyzing Zn speciation in particulate matter from the Seine river will give strong constraints on the biogeochemical cycling of this metal within the Seine river basin, and is required for modeling the spatial and seasonal evolution of dissolved Zn in the Seine water.

Priadi C., Morin G., Ayrault S., Maillot F., Juillot F., Llorens I., Testemale D., proux O., Brown Jr. GE. EXAFS and SEM evidence for zinc sulphide in suspended matter from the Seine River, France. Submitted to *Environ. Sci. Technol.* (Jan 2011).