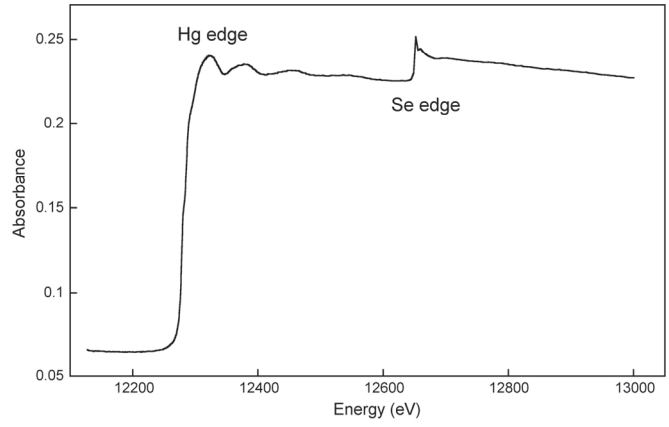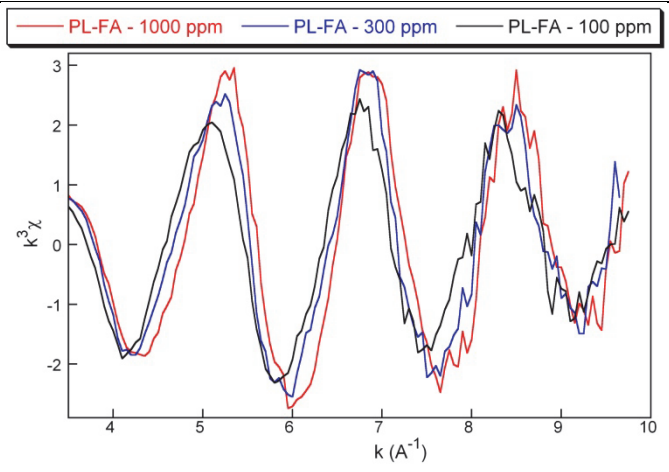# Standard Project

Experimental Report template

Proposal title: Binding mechanism of mercury to microbial organic matter		Proposal number: 30-02- 1014
Beamline:	**Date(s) of experiment:** from: 8/06 to: 11/06 (9 shifts)	**Date of report:** 10/09/2011
Shifts:	**Local contact(s):** Olivier Proux	*Date of submission:*

Objective & expected results (less than 10 lines):

The objective was to characterize the bonding environment of Hg in a natural organic matter (PL-FA) from purely microbial origin that is exceptionally rich in sulphur. Increasing the amounts of binding sites is a way to access natural molecular processes at very low Hg concentration, and to identify new complexation mechanisms on strong affinity sites. The targeted Hg concentrations were ~50 or lower, 100, 300 and 1200 ppm and the measured temperatures at ambient conditions and 10-20K.

Results and the conclusions of the study (main part):

The filling mode was 7/8+1, therefore it was not possible to setup the pre-amplifiers of the 30-Ge Canberra to 125 ns, but to 500 ns. With this shaping time the maximum count rate is 30 kHz, compared to 80 KHz at 125 ns. The lowest dilution limit which could be reached in these conditions without exceeding one shift per sample was 100 ppm. We tried to record a 40 ppm sample, but the total Hg-Lα fluorescence counts was insufficient (due to detector saturation) to obtain good data in reasonable time. Another difficulty has been the unexpected presence of high amounts of Se in this natural organic matter, as shown in Figure 1. We tested if the data could be recorded at the Hg-L$_2$ edge instead of the Hg-L$_3$. At the L$_2$ edge the spectra could be recorded up to 12 Å^{-1}, that is 2Å^{-1} higher than at the L$_3$ edge, but the number of counts was 30% lower. So, it was decided to return to the L$_3$ edge and to record the data until the Se K-edge, that is to k_{max}=9.8 Å^{-1}.

Three samples (100, 200, 1000 ppm) and three references were measured at 10K, we did not have time to go to RT. Figure 2 shows that the EXAFS oscillations are shifted progressively leftward when the concentration in Hg decreases. This evolution shows that, with decreasing Hg/S$_{red}$ mol ratio, Hg binding transitions from dominant shorter bonds (long wave frequency) with S atoms to longer bonds (short wave frequency), also with S atoms. The average Hg-S bond length is 2.32 Å at 1000 ppm, which is the typical distance for the linear Hg-(Cys)$_2$ complex, and 2.38 Å at 100 ppm, which is between the range of two- and three-coordinated Hg. The proportion of each type of Hg complex at 100 ppm can be evaluated from the average value (2.38 Å) and the 2.32 Å and 2.44 Å bond distances for the two end-members, that is for the pure Hg-(SR)$_2$ and Hg-(SR)$_3$ complexes. This amount is 50%. We hope to be able to run a 20 ppm sample of this materials at a later time to have >80% of the Hg in three-coordination. Then it will be possible to know if this high-affinity binding environment is "Y-shaped" (Nagy et al., 2011) or "T-shaped" (Skyllberg et al., 2006).

Figure 1

Figure 2