



	Experiment title: Mercury speciation in Hg-contaminated sediments from a drill core recovered from a hydroelectric reservoir (central Italy)	Experiment number: EV-372
Beamline: BM-16	Date of experiment: from: 7 October 2020 to: 13 October 2020	Date of report:
Shifts:	Local contact(s): Mauro Rovezzi	<i>Received at ESRF:</i>
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Report: The study was directed to mercury (Hg)-contaminated sediments collected from a hydroelectric reservoir located along the Tiber River (Alviano, central Italy). The reservoir acts as a hydraulic barrier to Hg dispersion downstream from the Mt. Amiata dismissed Hg mine district [1]. An accurate characterization of the chemical speciation of Hg in sediments recovered from a 5 m core drilled in the Alviano reservoir was attempted by means of high-resolution X-ray Absorption Near-Edge Structure spectroscopy (XANES). XAS measurements were conducted at BM16-FAME-UHD at the Hg L_{III}-edge (12284 eV) on six sediment samples from the drill core taken at different depths. By comparison, we also analyzed four stream sediment samples from the Siele creek (Mt. Amiata district), supposed to be the source of the Hg-contaminated material. Portions of the same samples used for chemical characterization were newly ground for synchrotron analysis in an agate mortar, then mixed and homogenized with cellulose, and finally pressed into a pellet. This procedure should ensure a homogenous distribution of Hg in the analyzed samples. All sample spectra were measured in fluorescence yield detection mode with crystal analyzers. The Hg L α 1 ($3d_{5/2} \rightarrow 2p_{3/2}$) fluorescence line was selected using the 555 reflection of spherically bent (radius 1 m) Si crystal analyzers (diameter 100 mm), aligned at an 81.8° Bragg angle in a vertical Rowland geometry. Spectra were collected in vacuum, and at low temperature (~10°K) to avoid possible photon-induced redox reactions. Al-filters of suitable thickness were used to attenuate the strong fluorescence signal from the matrix, especially from Fe. Depending on the concentration of Hg, 5 to 52 consecutive scans (roughly half an hour each) were acquired to improve statistics. The spectra were acquired on different sample ROIs to prevent possible beam damage redox effects. Mercury references included: i) Hg sulphides (α -HgS, the primary mineral in the Mt. Amiata ores; β -HgS, which occurs

as a transformation product in metallurgical wastes); ii) Hg species which may derive from the binding of Hg with organic matter, such as Hg(II)cysteine, Hg(II)phenol, Hg(SR)₂, and Hg(SR)₃. Some of them were kindly provided by Dr. Marie Pierre Isaure (also acquired at BM16-FAME-UHD). Least Combination Fitting (LCF) was applied to the XANES spectra to obtain quantitative information on the sample speciation. LCF consists of a weighted linear combination of the reference standards, and was performed using the IFEFFIT packages [2]. The averages of the acquired sample spectra are displayed in Figure 1a. Figure 1b reports an example of the LCF procedure on sample MSIE14 (8.1 mg/kg Hg).

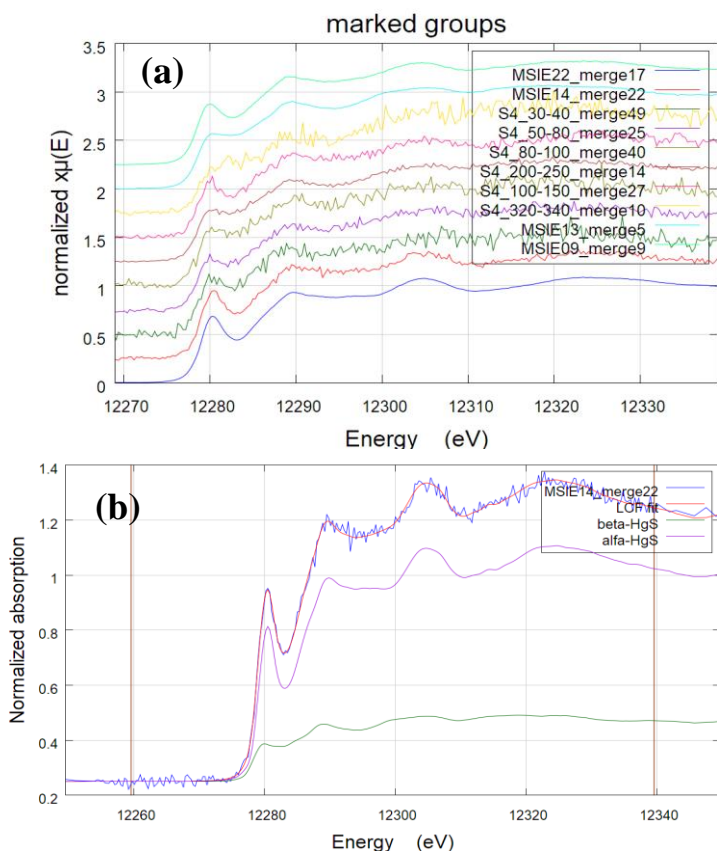


Fig. 1. a) sample spectra; b) calculated fit (red line) for the MSIE 14 spectrum, obtained by LCF of two reference spectra.

These results will be of fundamental importance to understand the level of Hg mobility in the environment, and to assess the actual health risk in the Tiber basin, which includes the city of Rome, and in the Mediterranean Sea, where the Tiber flows to.

References [1] Rimondi V., et al., 2019. Environmental pollution 255, 113191
 [2] Ravel, B., Newville, M., 2005. J. Synchrotron Radiation 12, 537–541

Table 1 reports the results of the fitting procedure; unfortunately, for one sample (shown in red) the quality of the acquired spectrum was inadequate to allow a meaningful fit. Only the species necessary to achieve good fits are reported. The four samples from the Siele mining area (labeled as MSIE_{xx}) show the presence of Hg sulphides only, i.e. the original species of mining and smelting activities. By contrast, all samples from the drill core at Alviano (S4 xx-yy, where the numbers represent the depth intervals from the surface) show also the presence of Hg bound to thiol groups such as those occurring in Hg-cysteine. This result is interpreted as an evidence of a transformation occurring in the reservoir sediments, presumably by interaction with organic matter. Such a transformation will increase the mobility of Hg with respect to the highly insoluble sulphide species, and may eventually lead to the formation of highly toxic species such as methyl-Hg.

Sample	Hg mg/kg	β -HgS %	α -HgS %	Hg-cysteine %	Σ	χ^2
MSIE22	5400	13	87	-	100	0.044
MSIE14	8.1	21	80	-	101	0.045
MSIE09	1200	89	10	-	98	0.008
MSIE13	690	46	53	-	99	0.009
S4 30-50	2.5	-	33	66	99	0.42
S4 50-80	1.5	54	-	43	98	0.13
S4 80-100	1.7	-	73	23	96	0.38
S4_100-150	1.8	-	81	16	97	0.19
S4_200-250	9.3	93		8	101	0.09
S4_320-340	8.7	-	-	-	-	-

Table 1. LCF data on of the analyzed samples.