

Characterization of biomineralized selenium solid phases by XAFS spectroscopy

M. LENZ^{1,2}, E.D. VAN HULLEBUSCH³, F. FARGES⁴
AND P.F.X. CORVINI^{1,5}

¹University of Applied Sciences Northwestern Switzerland (FHNW), School of Life Sciences, Institute for Ecopreneurship, Gründenstrasse 40, 4132 Muttenz, Switzerland

²Sub-Department of Environmental Technology, Wageningen University, 6700 EV Wageningen, The Netherlands

³Laboratoire Geomatériaux et Environnement (LGE), Université Paris-Est, EA 4508, 5 bd Descartes, 77454 Marne la Vallée Cedex 2, France

⁴Laboratoire de Minéralogie et de Cosmochimie du Muséum (LMCM), UMR CNRS 7202, Museum National Histoire Naturelle, 61 rue Buffon, 75005 Paris, France

⁵School of the Environment, Nanjing University, 22# Hankou Rd., Nanjing, 210093, P.R.China

The ability to reduce water soluble toxic selenium oxyanions is widespread in the microbial environment [1]. Firstly, specialized dissimilatory reducers can 'respire' selenium oxyanions to elemental selenium, producing energy for growth. Secondly, different microbial groups can catalyze selenium oxyanion reduction without gaining energy for growth (e.g. sulfate reducing bacteria) [2]. Since elemental selenium and most metal selenides are insoluble, microbially catalyzed reduction is thus thought to impact selenium environmental fate to large extents. However, little definitive information is available regarding the speciation of such (suppositional insoluble) phases, in particular in natural environments. We studied such phases formed by both mixed and pure cultures in metal poor and rich environments *in situ* by X-ray Absorption Fine Structure spectroscopy (XAFS). We demonstrated that in laboratory (i.e. metal depleted) incubations, amorphous elemental selenium is formed by most species, yet that natural (i.e. metal rich) environments are often rather dominated by complex mixtures of metal selenides.

[1]Lenz, M. & P. N. L. Lens (2009) *Science of the total Environment* **407**(12). [2] Stolz, J. E., P. Basu, J. M. Santini and R. S. Oremland (2006) *Annual Review of Microbiology* **60**.

Coupling $\delta^{34}\text{S}$ [SO_4^{2-}] and [^{206}Pb / ^{207}Pb]: Origin of trace metals in the urban Orge River, France

P. LE PAPE^{1,2} *, S. AYRAULT², J-L. MICHELOT¹
AND C. QUANTIN¹

¹UMR 8148 IDES, UPS11 - CNRS, Orsay, 91405, France
(*correspondence: pierre.le-pape@u-psud.fr)

²UMR 8212 LSCE, IPSL/CEA-CNRS-UVSQ, Gif-sur-Yvette, 91198, France

Several studies reported the close relationship existing between trace metal contamination in rivers and urbanization [1]. To reduce and constrain the emissions of urban trace metals and their transport due to runoff on urban surfaces, it is necessary to quantify the contribution of the different sources. It implies to study both the origins of water as a vector of transport (urban runoff, sewer network, groundwater...), the sources of metals and those of their bearing-phases. In that context, isotopic analyses are powerful tools to discriminate water and metal sources.

The study concerns the Orge-River urban catchment, part of the Seine-River watershed (Paris, France). Four sampling campaigns have been performed at a seasonal time scale from upstream (forestry and agricultural lands) to downstream (residential and urban areas). Sampled materials were water (filtered at 0.45 μm), suspended particulate matter (SPM) and bed sediments.

Both dissolved (<0.45 μm) SO_4^{2-} and $\delta^{34}\text{S}$ [SO_4^{2-}] ratios increased from upstream to downstream, indicating sulfate inputs. Analysis of samples representing potential sources revealed that part of this additional sulfate was related to the leakages of sewer networks. In the particulate compartment, an anthropogenic Pb enrichment was clearly detected. Indeed, as Pb contents increased along the river, the [$^{206}\text{Pb}/^{207}\text{Pb}$] ratio evolved from a natural to an anthropogenic signature. Otherwise, anthropogenic contribution was especially noticed during low waterflow periods, when SPM load was low. [$^{206}\text{Pb}/^{207}\text{Pb}$] ratio also gave information about long term dynamics of particulate Pb in the watershed, indicating that the contribution of Pb from a Pb-gasoline endmember to SPM ended during the last decade.

Coupling of both $\delta^{34}\text{S}$ [SO_4^{2-}] and [$^{206}\text{Pb}/^{207}\text{Pb}$] ratios finally provided a good indicator of anthropogenic impact.

Furthermore, the isotopic approach described above was completed with studies at the particle scale (SEM or TEM-EDX), which revealed the presence of specific urban metal-bearing particles, such as barite or phosphate phases.

[1] Thévenot *et al.* (2007) *Sci.Tot Env.* **375**, 180–203.