Imaging and structural characterization of HgS nanoparticles in organic matrice: results and challenges

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Mercury, from natural or industrial origin, is one of the most toxic inorganic contaminant for living organisms, despite its relatively low concentration in soils and aquatic environments. Its methylated form is extremely neurotoxic as a result of its bioaccumulation in the food chain. However, the high thiophilicity of divalent mercury (Hg(II)) reduces methylation rates via the formation of strong complexes with thiol groups in organic matter and precipitation of mercury sulfide minerals (HgS) in anoxic conditions. Recent XANES spectroscopy measurements [1] and quantum chemical calculations [2] demonstrated that HgS also can form directly from organically bound Hg-thiolate complexes in oxygenated conditions. Nanosized HgS particles were observed by high-resolution transmission electron microscopy (HRTEM) in dissolved organic matter with 200 ppm added Hg(II) and aged for six months in the dark and aerated solution [1]. However, the scarcity and nanometer dimension of the HgS crystals render their identification and fine characterisation extremely challenging. Detecting rare HgS nanoparticles burried in an organic matrice by EDX spectroscopy on conventional TEM is difficult because the signal is low, the analytical resolution rather poor and the organic matrice rather unstable under the electron beam. New TEM techniques, such as STEM-HAADF on spherical-aberration-corrected microscopes that amplify the electron contrast of heavy elements at the nano and subnanometer scale, allow these experimental difficulties to be partly overcome. Coupled with image Fourier transform analysis and STEM-EDX mapping, it is possible to image the distribution of mercury in the organic matrice and charaterise more precisely its chemical and structural state.

[1] Manceau *et al*. (2015) *ES&T* 49, 9787-9796
[2] Enescu *et al.* (2016) *Sci. Rep.*, 6, 39359.