



Mercury in polluted soils: speciation using micro-XRF, micro-XRD, and micro- and bulk XAFS.

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In this research, mercury speciation was assessed for soil samples collected inside and outside an industrial polluted area of National environmental interest located in “Val Basento” (Basilicata, Italy). Hg concentration in these soil samples ranged from 12 up to 240 mg/kg.

Mercury chemical forms in these samples were identified by a combination of sequential extraction procedures, thermal desorption analyses, and different bulk- and micro-analytical techniques exploiting high intensity synchrotron generated X-rays.

Bulk XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) spectra were collected for direct Hg-speciation in soil samples sieved at 2mm as well as in the clay fraction (<2um), where the highest amount of mercury was concentrated.

The interpretation of the complex mixture of Hg-chemical forms in the soil samples was made simpler by performing, beside bulk XAS investigations, microanalyses on soil thin sections by combined u-XRF/u-XRD (micro X-ray Fluorescence/micro X-ray Diffraction) and u-XANES, with a resolution of 20 um. The information deriving from the micro-scale was then used to understand the bulk data.

m-XRF maps were collected to localize microscopic Hg-containing particles in areas of several hundreds of mm². Simultaneous to u-XRF spectra, microdiffraction patterns were collected in each point of the map, to identify possible crystalline Hg-mineral forms or mineral associations. Once points of interest were localized, u-XANES spectra were also collected. In general, two main representative XANES spectra (S1 and S2) were observed from Hg-rich spots at the microscopic level. Interestingly, all the bulk XANES spectra from all soil samples could be fitted by a linear combination of the microscopic S1 and S2 spectra. Therefore, by fitting the S1 and S2 spectra by means of known standard spectra it was then possible to decipher Hg-speciation for all the soil samples. In conclusion, the main constituents in the soil samples were cinnabar (HgS), metacinnabar, corderoite (Hg₃S₂Cl₂), and amorphous Hg-S-Cl phases, in different proportions. The presence of these amorphous forms was suggested by EXAFS and XRD structural analyses. The speciation obtained is also in agreement with the chemical behaviour of the soil samples as assessed by sequential extractions and thermal desorption analyses.

The chemical species identified are typical of soils contaminated with wastes produced by chlor-alkali plants. Actually, a chlor-alkali plant was active in the area during the 1960-80's, and now is no more existing.

In conclusion, notwithstanding the diffuse Hg-pollution in the investigated area, it seems that Hg is speciated in scarcely soluble and hardly mobilisable forms.

The determination of the chemical forms of toxic elements in polluted soils is an indispensable step to identify the source of pollution, to formulate a correct risk assessment and to develop effective remediation strategies.