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Mercury distribution and speciation in agricultural soils around a polluted site in the South of Italy

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Mercury is known as one of the most toxic elements for living organisms and, for this reason, its concentration in soil is one of the lowest allowed for inorganic pollutants by environmental regulations all over the world. Chlor-alkali plants are one of the main sources of diffuse Hg environmental pollution, concerning atmosphere, water and soil. Also former industrial sites, now dismissed since several years, may still present high Hg levels. Another dramatic aspect to be considered is that Hg pollution by chlor-alkali plants has reached soils located far away from the industrial site and often intended for agricultural use.

In this research, an industrial area located in the South of Italy polluted by chlor-alkali Hg emissions was investigated in order to determine the distribution and speciation of this toxic element. Particular attention was paid to this site owing to its location in a river basin, a quite shallow groundwater and widespread agricultural activities all around. Soil samples were collected at two depths (0-10 and 40-50 cm) in different points located within few tenths of meters all around the industrial site. All the analysed samples (at both depths) turned out to be polluted by Hg with concentrations ranging from 1.5 to 15 μg/g. Further analyses on soil columns of 2 m depth showed that Hg-pollution is limited to the first 0.5 m without evidence of migration to deeper soil levels.

Mercury speciation was assessed by a sequential extraction procedure specifically developed for Hg-polluted soils as well as by Hg thermal-desorption analysis. From these investigations Hg was found speciated in scarcely soluble forms, most probably as Hg(0) (90%) and HgS (10%). Organic matter did not seem to contribute to Hg

speciation. SEM-EDX analyses excluded either Hg to be related to Fe-oxides and its presence in particles bigger than 2 μm. In addition, sub-microscopic HgS phases were directly identified. These data were also confirmed by analysing the soil fraction lower than 2 μm, where Hg concentration was found 2-3 times higher than in the overall 2 mm fraction.

XRD analyses, with a particular attention to the <2 μm fraction, were also carried out in order to identify soil minerals likely to interact with Hg species. Detailed Hg distribution in the soil colloidal fraction (<2 μm) is being studied by using Sd-FFF-ETAAS (Sedimentation Flow Field Fractionation coupled to Electro-Thermal Atomic Absorption Spectroscopy) to identify the most relevant Hg-bearing fractions. Finally, those fractions containing the highest Hg levels will allow for a more direct Hg speciation by means of analytical techniques employing synchrotron generated X-rays.

All the obtained information can be used to formulate a more correct risk analysis and to develop more responsible and effective remediation strategies.