

## **Deciphering As and Hg immobilization mechanisms by nanoscale zero-valent iron in polluted soils via synchrotron analysis**

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The utilization of nanoscale zero-valent iron (nZVI) stands as a promising and recognized technology for soil remediation, garnering increasing attention in recent years. While the mechanisms of metal sorption in solution are well-documented, their application in the soil compartment remains unclear. Consequently, this study aims to elucidate, at molecular scale (synchrotron radiation, X-ray absorption spectroscopy), the mechanisms of As and Hg immobilization associated with the new Fe speciation in soils following nZVI application.

Asturias (northern Spain) has a rich history of mining and metallurgical activities. The Hg-mining district of El Terronal, a significant producer in Spain from 60s to 70s, particularly impacted nearby environmental compartments. Therefore, in this investigation, a 1% dosage of nZVI was applied in soil at El Terronal site [1]. Subsequently, soil samples were collected from the treated and untreated plots after six years to monitor the As and Hg mobility through their specific sequential extractions. Additionally, analyses were conducted as follows: (i) As and Hg speciation in bulk soil samples using Hg L<sub>III</sub>-edge XANES at the CLAES beamline (ALBA synchrotron) and Fe speciation using Fe K-edge XANES at the LUCIA beamline (SOLEIL synchrotron); and (ii) nano-XRF analysis for As and Fe mapping, followed by nano-XANES spectra collection at the Fe K-edge and As K-edge at the Nanoscopium beamline (SOLEIL synchrotron).

The results indicated that nZVI application effectively reduced As and Hg mobility in soil. There were no discernible alterations in Fe bulk speciation compared to untreated soil, indicating minimal negative impact while maintaining the geogenic soil phases. Regarding As, bulk soil analysis revealed unchanged As speciation (predominantly 98%), yet iron oxides with As(III) enrichment on their surface were identified, originating from the

agglomeration and oxidation of nZVI, facilitating the reduction of As(V) to As(III). Conversely, Hg speciation remained consistent between treated and untreated soils, predominantly comprising HgS such as cinnabar/metacinnabar, and Hg adsorbed to goethite. These stable Hg phases ensure low mobility, mitigating long-term environmental risks. In summary, nanoremediation proves to be a nature-based and eco-friendly solution for soil remediation.

[1] Gil-Díaz, Rodríguez-Valdés, Alonso, Baragaño, Gallego & Lobo (2019), *Science of the Total Environment* 675, 165-175.