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Biogeochemistry of As in a mining-affected river floodplain

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Many rivers worldwide are enriched with toxic trace elements originating from past or present mining. Even after closure of the mines and remediation of the tailing impoundments, contaminated river floodplains can remain a potential threat to surface and ground water quality. In a current project, we are investigating the spatial distribution, chemical speciation, and biogeochemical cycling of As in the highly-contaminated floodplains of the river Ogosta, NW-Bulgaria. Soil samples collected along transects ranging from the river bed through the lower and upper floodplains were collected and analysed using standard methods. Soil arsenic speciation was investigated by As K-edge X-ray absorption spectroscopy (XAS). Additionally, selected samples were investigated by micro-X-ray fluorescence (μ-XRF) spectrometry and As and Fe K-edge μ-XAS. The floodplain soils contained between 40 and 37,400 mg kg^{-1} As. Highly As-contaminated soils were also enriched in Fe, Mn, S, Pb, Sb, and other trace elements. Bulk and micro-XAS, combined with ascorbate-extractions, revealed that most As was present as As(V) sorbed to poorly-crystalline Fe(III)-oxyhydroxides, with smaller amounts of As bound in arsenopyrite. The fine particle size fractions $<$5 and 5-20 μm were strongly enriched in As (up to 93,000 mg kg^{-1}) as compared to the corresponding bulk soils ($<$2 mm). XAS spectra and the extremely high molar As/Fe ratio of the ascorbate-extractable fraction indicated that also short-range ordered ferric arsenates were likely present in the most highly contaminated soils, which may have important implications for As solubility and bioavailability. Overall, our results suggest that As and Fe in these soils may be readily bioavailable for microbial reduction and plant uptake, especially upon soil flooding, which is currently investigated in soil microcosm and column leaching experiments.