Microbial sulfidogenesis of As in naturally contaminented wetland soil

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Microbial sulfidogenesis plays a potentially important role in As biogeochemistry within wetland soils, sediments and aquifers. This investigation was situated in the natural geochemical arsenic anomaly at Smolotely-Líšnice Au district (Czech Republic). Two wetland soil profiles have been characterised using geochemical (bulk soil and pore water analyses, selective chemical extractions, S isotopes), mineralogical (XRD, Raman spectrometry, SEM/EDX) and DNA extraction analyses to determine the distribution and speciation of As in the soil. Solid-phase analyses showed that As forms mostly nanocrystalline realgar and bonazziite (both As_4S_4), strongly associated with particles of natural organic matter (NOM) at a depth >70 cm. Minor As-bearing sulfide phases were represented by mackinawite (Fe_9S_8), greigite (Fe_3S_4) and framboidal pyrite (FeS_2). Small amount of As was also accumulated in Fe (hydr)oxides. Results of S isotope, microbial community and pore water analyses indicated that sulfide phases were generated by in-situ microbial reduction of aqueous sulfate in strongly reducing microenvironments. The newly-formed sulfide phases are associated with particles of NOM, probably acting as a C source for sulfate-reducing microbes. We propose that microbes in NOM create strongly-reducing microenvironments in suboxic bulk soil where secondary sulfides and Fe (hydr)oxides coexist next to each other in micrometer to millimetre scales. The formation of secondary sulfides has been identified as one of the prominent As sequestration pathway in the naturally As-enriched wetland at this site.