Abstract

A natural arsenic anomaly at Mokrsko is a site of biogenic precipitation of realgar (As_4S_4) in stream sediment. The extent of the phenomenon in Mokrsko is globally unique. A previous study showed the ability of microorganisms to solubilize arsenic from its secondary minerals and to produce realgar precursors, i.e. sulfides and arsenites, by anaerobic respiration. The study also raised questions about the mechanism of realgar precipitation since physicochemical conditions favoring this reaction were never detected despite significant sampling efforts.

We chemically and microbiologically analyzed sedimentary profiles to the depth of ca. 120 cm in order to understand the functioning of the biogeochemical system. The profiles comprised both the unsaturated and the saturated zone. We distinguished six different domains representing environments from the surface soil to anoxic sedimnent containing realgar-encrusted wood. An analysis of phylogenetic dissimilarity revealed that microbial communities from the various domains form distinct clusters. This suggests that different conditions prevail in the various domains, and that different biogeochemical processes take place there.

Incubation (microcosm) experiments showed that bioprecipitation of realgar can be conducted in vitro. It requires a suppression of the microbial activity in the solution and a strict localization of the biogenic processes to the wood material. To our best knowledge, this is the first successful bioprecipitation of realgar in laboratory conditions.

Our results form a chain of indirect proofs, showing that realgar precipitation does not depend on the presence of specific microorganisms, but instead requires a combination of contrasting microhabitats. The presence of decomposing wood that was burried here during the early 1980s is of special importance. The wood remnants form organic carbon-rich domains in the extremely oligotrophic and sulfate-containing bulk sediment. The solution is locally oversatureted towards realgar due to an intensive sulfate and arsenate respiration on the wood surface. The anoxic domain is depleted in iron content thanks to the long-lasting gley process. This is important since ferrous ions can outcompete arsenic during sulfide precipitation. An exact characterizaton of the conditions in the sediment domains will require further research using advanced instruments for *in situ* measuring of the parameters of pore solution in extremely small volumes.