TITLE: BIOGEOCHEMISTRY OF MERCURY IN CONTAMINATED ENVIRONMENT IN THE WIDER IDRIJA REGION AND THE GULF OF TRIESTE

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SCIENTIFIC BACKGROUND OF THE PROJECT

Activities at mercury (Hg) mines can lead to the mobilization of large quantities of Hg that enter the environment and are transported downstream. Although much of this Hg is deposited near the source, over time much of this Hg can be carried hundreds of kilometers where it can potentially enter and bioaccumulate in distant food webs. Mining activities in the Idrija, Slovenia mining district occurred for 500 years and the legacy of that mining can be seen in high concentrations of Hg throughout the watershed and into the Gulf of Trieste. Mercury concentrations are high in the sediments near the mouth of the Soca/Isonzo River in the Gulf, and the Soca River continues to deliver ~1.5 tons of Hg to the marine environment ~100 km from the mine. Much of the Hg carried to the sea is probably as fine cinnabar particles, and the potential remobilization and further transformation of this Hg is of concern with regard to local environmental and the accumulation of methylmercury (MeHg) in seafood. Mercury sulfide minerals are subject to dissolution and increased bioavailability when they contact sulfidic environments such as what occurs in coastal marine sediments. This "newly" available Hg can potentially undergo methylation to supply the environment with newly formed MeHg. Indeed, Gulf sediments contain significant concentrations of MeHg and effluxes of MeHg from Gulf sediments have been observed in recent studies. However, sediments can also support active demethylation by aerobic and anaerobic bacteria. This demethylation can be due to either oxidative or reductive pathways. The present study was conducted to determine the potential of sediments from the Gulf of Trieste to methylate and demethylate Hg including an assessment of which demethylation pathway is most prevalent.

PROJECT OBJECTIVES

- Location of primary sources and sinks of total and MeHg
- Determine the relationship between the sulphur cycle and Hg methylation and demethylation and reduction
- Perform tracer experiments on Hg methylation and demethylation using radiotracer experiments and stable isotopes, if possible
- To quantify Hg fluxes and the fate of Hg in the river system, accumulation in the flood plain and final input to the marine environment

ACHIEVEMENTS

The scientific achievements of the project conducted so far can be summarized as follows:

- The Hg transport legacy of the mining in Idrija is seen at the mouth of the Isonzo River where Hg levels are quite high but the concentrations of Hg decrease quickly offshore.
- Hg transformations are active throughout the Gulf of Trieste suggesting that Hg is remobilized into bioactive forms near the mouth of the river due to the effects of increased sulfide production as salinity increases.
- Although total Hg and MeHg were highest near the river mouth, concentrations of dissolved Hg species were similar, suggesting equilibrium between production and flux, or relatively similar rates of production and/or dissolution of Hg species.
- Concentrations of MeHg decreased greatly with sediment depth suggesting that MeHg demethylation was much more rapid in surficial layers than below ~3.0 cm.
- Rates of both methylation/demethylation processes were most rapid in summer by up to 10 fold. Carbon of MeHg was mainly converted primarily to CO_2 suggesting oxidative demethylation, however, significant proportions of CH_4 were detected in surface sediments in winter (March) at sites with lowest total Hg.
- The formation of CH_4 from MeHg must have occurred by the reductive pathway of the mer operon genetic system in bacteria. The fact that this pathway was only important in surface sediments and during colder periods suggests that the reductive pathway is restricted to oxidizing sediments while the oxidative path is primarily anaerobic.
- Preparation of the intercompariosn soil sample SOIL-1.
- Development and validation of methodology to study methaltion, demethylation and reduction in soils, experimental animals and lichens.