

Abstract

A natural geothermal source of arsenic (As) causes elevated concentrations in the Los Angeles Aqueduct, a major drinking water source for the City of Los Angeles. The As is removed by precipitating an amorphous iron (Fe) oxyhydroxide floc in the aqueduct waters. The floc is removed via sedimentation at Haiwee Reservoir, where the Fe- and As-rich sediments provide a unique field site for studying the mechanisms of As mobilization to sediment porewater.

In this study, a gel probe equilibrium sampler was developed to measure the porewater concentrations as well as the As sorption behavior in Haiwee Reservoir sediments. The gels consisted of a polyacrylamide polymer matrix and were 92% water. Undoped gels (clear gels) were used to determine porewater composition, and gels doped with hydrous ferric oxide (HFO) were used to measure *in situ* As adsorption chemistry. Gels were placed in a plastic holder, covered with a membrane filter, and allowed to equilibrate for 24 hours with the sediment porewaters. This study combined data from the gel probe samplers, gravity cores, and laboratory studies, to elucidate the biogeochemical processes governing As partitioning between the solid and aqueous phases. The gel probe device allowed for *in situ* observation of the effect of porewater chemistry on As adsorption, a unique contribution to the techniques available for field measurements.

Arsenic was reduced from As(V) to As(III) in the upper layers of the sediment, but the change in redox state did not cause As to be mobilized into the porewaters. Arsenic mobilization occurred as the Fe(III) oxides were reductively dissolved. Both As(V) and Fe(III) reduction were most likely microbially mediated. Arsenic sorption onto the HFO-

doped gels was inhibited at intermediate depths (10-20 cm), most likely due to competitive sorption by dissolved carbonate produced from the mineralization of organic carbon. The partitioning of As onto the solid phase in this region may be primarily controlled by porewater chemistry, rather than sorption site availability. Deeper in the sediment column, the Fe was partially transformed from amorphous Fe(III) oxyhydroxide to green rust, possibly sequestering dissolved carbonate. In this region, As adsorption onto HFO-doped gels was controlled by the presence of dissolved phosphate in the porewater. The accumulation of As in the porewater in this region may be due to lack of available surface adsorption sites on the sediment. Arsenic partitioning between solid and aqueous phases depends on microbially driven diagenetic processes, as well as porewater composition.