Chapter 7

Concluding Remarks

7.1 Summary

The biogeochemical mechanisms controlling arsenic (As) mobilization in Haiwee Reservoir sediments were investigated. A hydrous ferric oxide (HFO)-doped gel probe equilibrium sampler was developed to simultaneously measure porewater composition and As adsorption behavior. Gel probe deployment was combined with laboratory studies, bacterial incubations, and solid phase measurements. The purpose of this chapter is to summarize the findings of this study and answer the questions posed in section 1.3.

7.1.1. What circumstances cause mobilization of As, Fe, and other elements into Haiwee sediment porewater?

Early diagenetic changes in the sediment cause redox transformations of both As and iron (Fe). In the surficial sediment, oxygen is rapidly consumed, and the sediment becomes reducing. Arsenic adsorbed onto the floc in the LAA is in the oxidized form (As(V)), as expected in the flowing, oxygenated water of the aqueduct. Upon deposition, As(V) is reduced to As(III) in the upper layer of the sediment. Arsenate reduction may be microbially mediated, as laboratory microcosms showed that the ambient microbial population was capable of reducing As(V). In addition, laboratory microcosms with a pure culture of bacteria, *Shewanella* sp. strain ANA-3, incubated with As(V) adsorbed onto HFO, provide evidence that dissimilatory As(V) reduction is more favorable than

Fe(III) reduction when coupled to lactate oxidation. This observation supports the As(V) reduction observed in the upper layers of Haiwee Reservoir sediments. In both the laboratory microcosms and in the field, As(V) reduction occurs even when most of the As is adsorbed to the Fe(III) oxide phase. Since As oxidation state affects the extent of sorption onto Fe oxides, the reduction of As(V) to As(III) may affect the partitioning between solid and aqueous phases.

Reductive dissolution of Fe(III) oxides in the sediment, which is most likely microbially mediated, drives the mobilization of As and other elements into the porewaters. The strong correlation between dissolved Fe, As, P, and W indicates that reductive dissolution is the primary process responsible for mobilization to the porewater. However, the accumulation of dissolved As is partly due to the effects of porewater chemistry.

7.1.2. What are the mechanisms controlling the partitioning of As and Fe between the sediments and porewaters?

A wide variety of compounds can inhibit As adsorption on Fe(III) oxides, including phosphate, carbonate, silicate, and organic carbon. Using an HFO-doped gel probe, the role of competing ions in inhibiting As sorption was measured *in situ*. The HFO-doped gels introduced fresh adsorption sites into the subsurface to measure the extent of As sorption as a function of depth and porewater composition. The HFO-doped gel probes were used to observe whether the presence of dissolved As in the porewater was due to lack of available surface adsorption sites on the sediment or to sorption inhibition by competitive ions.

At intermediate depths (10-20 cm), dissolved carbonate from the mineralization of organic matter may inhibit adsorption onto the HFO-doped gels. In this region, the presence of dissolved As is at least partially controlled by the porewater composition rather than sorption site availability.

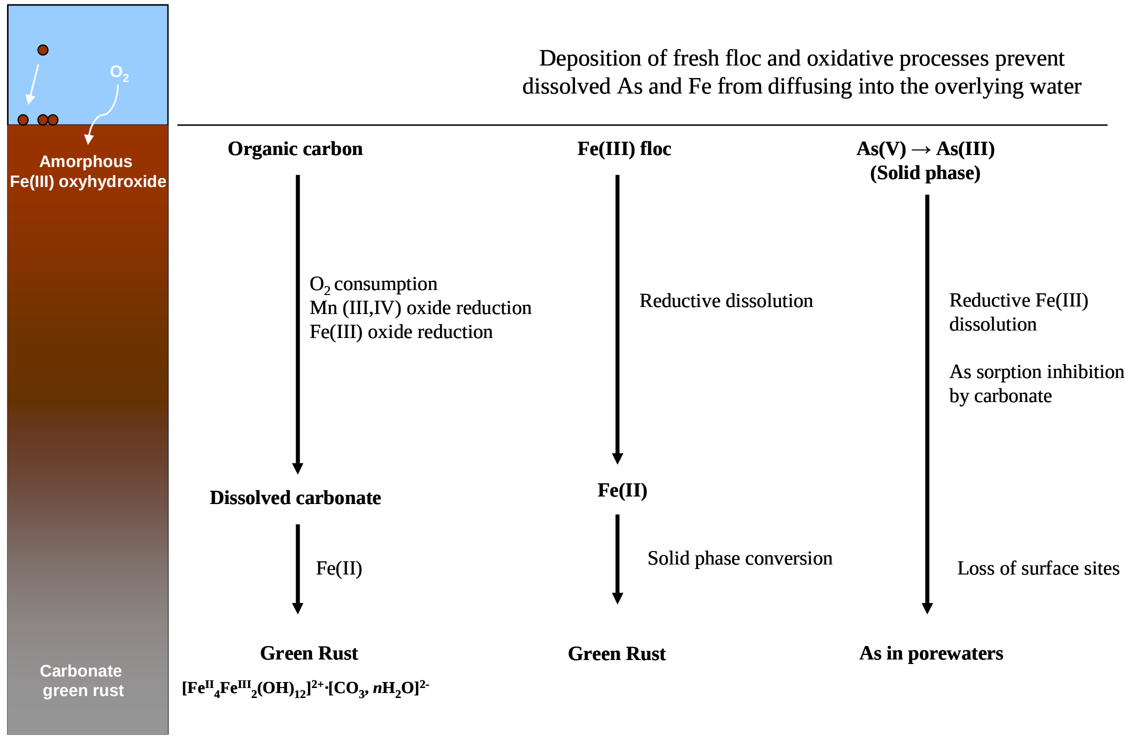
Deeper in the sediment column (15-30cm), carbonate green rust formed. In this region, As adsorbed to a greater extent on the HFO-doped gels, and As adsorption behavior was consistent with the presence of dissolved phosphate. The persistence of dissolved As in the porewater suggests that As partitioning is controlled primarily by lack of available sorption sites as the amorphous Fe(III) oxide converts to green rust.

The sediment diagenetic processes affecting carbon, Fe, and As cycling in Haiwee Reservoir sediments is summarized in Figure 7.1.

7.1.3. What processes determine the fraction of total As and Fe in the solid phase that is mobilized into the porewater?

The amount of Fe(III) available for bacterial reduction is often less than the total pool of Fe(III). In addition, the conversion of amorphous Fe(III) oxyhydroxide to green rust may also decrease the susceptibility of the solid phase to microbial Fe reduction. As a result, the extent of Fe(III) reduction is probably the main reason why only a few percent of the total As and Fe in the solid phase accumulates in the porewater.

Figure 7.1. Schematic diagram of sediment diagenetic processes in Haiwee Reservoir sediment.



7.2. Wider Implications

The detailed mechanisms presented in this study may be somewhat unique to Haiwee Reservoir, since the sediments contain an artificially high amount of As and Fe from the water treatment process. However, the effects of porewater chemistry on As adsorption were directly measured using a gel probe equilibrium sampler. The ability to observe whether sorption site availability and/or porewater composition controls As partitioning using a gel probe is a valuable addition to the wide array of field-based techniques.

The gel probe equilibrium sampler is applicable to other sedimentary environments where Fe(III) oxides are prevalent. Amorphous Fe(III) oxyhydroxide was chosen for this study because it is mineralogically similar to the floc precipitated in the LAA, but the gels could be doped with any other Fe(III) oxide depending on the field application. In addition, the gel probe could be modified to measure *in situ* rates of Fe(III) reduction by extending the deployment time. The rates of Fe(III) reduction is a very important parameter for modeling the fate of contaminants such as As.

This study also highlights the importance of microbially-driven processes, especially Fe and As reduction. The observation that As(V) reduction may be more favorable than Fe(III) reduction under certain circumstances challenges the commonly held notion that Fe(III) reduction occurs before As(V) reduction. Adsorption chemistry can affect the thermodynamic driving force of these reactions.

An interesting outcome of the field observations at Haiwee Reservoir is that there appears to be very little diffusion of As from the sediment porewaters into the overlying water, either due to oxidation processes occurring at the surface of the sediment, or the deposition of fresh floc. This observation is important for the efficacy of the water treatment operation, but also raises some questions about the stability of the sediments. If the ferric chloride injection at Cottonwood ceased for any significant length of time, the effect it would have on the “capping” of the sediments with respect to As diffusion into the surface water is uncertain. It is important to study in more detail the precise mechanism that prevents As from diffusing from the porewaters into the surface water, determine under what circumstances these processes would be insufficient to prevent As contamination in the surface water, and assess whether dilution into the main body of the reservoir would be adequate to maintain As concentrations below the drinking water standard.