BIOGEOCHEMICAL PROCESSES IN A TREATMENT WETLAND MITIGATION METAL DISCHARGE INOT A SAVANNAH RIVER STREAM TRIBUTARY

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Abstract. The H-02 wetland system was designed to treat building process water and storm water runoff from multiple sources associated with the Tritium Facility at the DOE-Savannah River Site, Aiken, SC. Modeled after the A-01 system, which has been operating successfully at the Savannah River Site for approximately a decade, the H-02 system was constructed in 2007. Both wetland systems were designed for the removal of trace metals from treatment water, in particular Cu and Zn. The wetland construction included the addition of gypsum (calcium sulfate) to foster a sulfate-reducing bacterial population, and thus a source of sulfides for the sequestration of Cu and Zn into sulfide mineral phases within the sediments. Conceptually, the wetland functions as follows:

- Cu and Zn initially bind to both dissolved and particulate organic detritus within the wetland.
- A portion of this organic matter is subsequently deposited into the surface sediments within the wetland.
- The fraction of Cu and Zn that is discharged in the wetland effluent is organically complexed, less bioavailable, and consequently, less toxic.
- The Cu and Zn deposited in the surface sediments are eventually sequestered into insoluble sulfide minerals in the sediments.

Development of the H-02 system has been closely monitored; sampling began in August 2007, shortly after its construction. This monitoring has included the measurement of water quality parameters, Cu and Zn concentrations in surface water and sediments, as well as, characterization of the prokaryotic (e.g., bacterial) component of wetland biogeochemical processes. The objective of this study was to determine changes in biogeochemical parameters as the H-02 wetlands progressed to a mature, steady-state system and monitor how seasonal variations in these parameters affect wetland function over time.

Data from water samples taken biweekly at several sites within the wetland system and upstream and downstream reference locations in Upper Three Runs Creek (UTR) include total and dissolved metals, and standard water quality constituents including dissolved organic carbon, pH, temperature and redox potential. These data indicate that significant quantities of Cu and Zn discharged from the Tritium Facility are removed from the water in the wetland. Since the beginning of the study, the mean influent Cu concentration was 31.5±12.0 ppb and the mean effluent concentration was 11.84±7.29 ppb, corresponding to an average Cu removal of 64%. Zn concentrations were more variable, averaging 39.24±13.8 ppb in the influent and 25.68±21.3 ppb in the effluent. Average Zn removal was 52%. In addition, the wetland ameliorated high pH values associated with the influent water, occasionally greater than 10, to values similar to those measured at reference sites in Upper Three Runs Creek.

Seasonal variations in DOC concentration corresponded to seasonal variations in Cu and Zn removal efficiency. Water samples were also collected seasonally for standard EPA toxicity assays using *Ceriodaphnia dubia*. The results of these assays demonstrated that toxicity of Cu was reduced in wetland effluent waters as compared to standard laboratory water, and that constituents in both particulate and dissolved phases played a role in reduction of toxicity.

The water chemistry data were used in parameterizing the biotic ligand model (BLM) to predict the bioavailable forms of Cu and Zn and assess the toxicity to receptor organisms. The model predictions were compared with the EPA water effects ratio calculated using results from the *C. dubia* assays. It was concluded that the water effects ratio is a better predictor of toxicity in the H-02 wetland system, because the BLM results overestimated the toxicity of the water as compared to results from the *C. dubia* assays. This is likely due to the acidic pH and low harness values of the blackwater streams of the SRS.

Sediment core samples have been collected approximately biannually since wetland construction to monitor changes in trace metals, sulfides, and organic C and N. The concentration of Cu and Zn in the surface layer of the sediments has increased over the lifetime of the wetland and, like removal efficiency, demonstrated seasonal variation. By design, sulfate-reduction in the wetland should contribute to mineralization of Cu as copper sulfides within the sediments over time. We measured sulfide in vertical profiles in sediment cores to

determine potential for this process and the depth at which it occurs. Black layers within sediment cores, indicating sulfide formation, were observed with increasing frequency since wetland construction. Reduced sulfur concentrations in the sediments ranged from below detection limits (<200 ppm) to 1480 ppm; however, the highest concentrations did not necessarily correspond to sediment depth or color. Determination of organic C and N provides an estimate of the nutrient quality of the sediment organic matter. C and N did not vary considerably in the H-02 samples analyzed thus far, but comparison with A-01 suggested some additional changes to be expected in the wetland over time which are being examined more closely with recently collected sediment samples.

Our results demonstrate that the H-02 wetlands are functioning successfully to remove Cu and Zn from influent waters. The continued success and long-term sustainability of the functioning H-02 system is predicated on maintaining *in situ* biogeochemistry; however, the relative importance of various biogeochemical cycles remains unclear. For example, the Cu and Zn deposited in the sediments are associated with organic detritus at the sediment surface. The extent and rate at which the metals will redistribute to more recalcitrant sulfide mineral phases remain to be determined. In a larger context, these aspects of constructed wetlands are important considerations that should influence selection, design and operation of future constructed wetlands for treatment of metals in processing facility discharge waters. Thus, the H-02 wetland system is a valuable resource not only for metal removal at SRS, but also for elucidation of the conditions that can further enhance the understanding of wetland function within the scientific and regulatory communities.