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METAL REMOVAL FROM PROCESS AND STORMWATER DISCHARGES BY CONSTRUCTED TREATMENT WETLANDS

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ABSTRACT: The A-01 NPDES outfall at the Savannah River Site receives process wastewater and stormwater which passes through a wetland treatment system (WTS) prior to discharge. The overall objective of our research is to better understand the mechanisms of operation of the A-01 WTS in order to provide better input to the design of future systems. The system is a vegetated surface flow wetland and has a retention time of approximately 48 hours. Sampling conducted during the fourth year of operation validated continued wetland performance, and assessed the fate of a larger suite of metals present in the water. Copper and mercury removal efficiencies were still very high, both in excess of 80% removal from the water after passage through the wetland system. Lead removal from the water by the system was 83%, zinc removal was 60%, and nickel was generally unaffected. Nitrates entering into the wetland cells are almost immediately removed from the water column and generally no nitrates are discharged from the A cells. The wetland cells are very anaerobic and the sediments have negative redox potentials. As a result, manganese and iron mineral phases in the sediments have been reduced to soluble forms and increase in the water during passage through the wetland system. Dissolved organic carbon in the water column is also increased by the system and reduces toxicity of the effluent. Operation and maintenance of the system is minimal, and consists of checking for growth of the vegetation and free flow of the water through the system

INTRODUCTION

The ability of natural wetlands to improve many aspects of water quality has been recognized for many years. This natural process has been utilized in many different forms and applications to use constructed treatment wetlands for the purpose of water quality improvement (Moshiri, 1993; Kadlec and Knight, 1996). One aspect of the natural wetland functions that has been capitalized on is the biogeochemical cycling and storage processes that occur in the systems. Heavy metal retention by constructed and natural wetlands has been effectively used in mining regions of the U.S. and Europe to reduce levels of Cu, Zn, Ni, Pb, and other metals in runoff and drainage (Mays and Edwards. 2001). They are equally effective at treating stormwater runoff with high metal concentrations (Walker and Hurl, 2002).

The A-01 NPDES outfall at the Savannah River Site receives process wastewater discharges and receives stormwater runoff. Routine monitoring indicated that copper concentrations were regularly higher than the regulatory permit limit and the water routinely failed biomonitoring tests. Other chemicals (e.g. lead, chlorine, mercury, etc) were occasionally higher than the permit limit. A series of studies revealed that the copper was coming from a wide variety of sources and was also elevated in stormwater runoff. The end result of these analyses was that nearly one million gallons of water needed to be treated routinely each day, and during storms up to 20 million gallons would need to be treated. Conventional treatment systems for metal removal (e.g. ion exchange, chemical precipitation, etc.) proved to be very expensive for the volume of water that needed to be treated and the extremely low concentrations that must be achieved in the water before it was released to the stream. The search for more cost-effective alternatives resulted in constructed wetlands being considered as an alternative. Constructed wetlands are widely used to treat both domestic and industrial wastewater and have been effective in treating metal containing waters from acid mine drainage. Preliminary evaluations showed that a wetland system might achieve the required level of treatment at the lowest cost for construction and operation. A pilot study was conducted using mesocosms to confirm that the design concept would provide the required treatment. After treatment in the mesocosms, effluent copper concentrations were routinely below permit limits, even though the influent concentrations varied widely. During the research phase the wetland system was also effective at reducing total dissolved mercury.

MATERIALS AND METHODS

The Treatment Facility. The design provided for a stormwater retention basin that would be used to manage the amount of water going to the wetland treatment cells, moderating the effects of stormwater surges and providing additional water to keep the wetland flooded during dry periods. The treatment cells consisted of four pairs of one acre (0.4 hectare) wetland cells with water flowing from one cell to a second cell, then to the discharge point (Figure 1). The cells have been previously described in detail (Nelson et al., 2003a, 2003b). Normal water depth in the cells is maintained at 30.5 centimeters (12 inches). The soils in the wetland cells were amended with organic matter, fertilizer and gypsum at the time of construction and are vegetated with giant bulrush (*Schoenoplectus californicus*). Water retention time in the wetland system is approximately 48 hours, depending on the flow rate, and the wetland cells operate at circumneutral pH. Vegetation development within the cells was excellent, surpassing 2.5 kg/sq. meter of dry aboveground biomass and a density of over 140 shoots per square meter. The bulrush plants provide a continuing source of organic material to the sediments where bacteria and fungi decompose the plants and maintain anoxic (no oxygen) conditions in the hydric soil. The combined effects of the organic matter and anoxic soil conditions work to capture and immobilize the metals in the soils, with yearly growth, dieback, and decomposition of the plants keeping the soil ecosystem functioning year after year to remove metals and toxicity from the water. Construction of the system began in January 2000, and construction of the entire system was completed in the early fall of 2000. The establishment of vegetation in the system and the removal of copper and mercury during the initial two years of operation have been previously published (Nelson et al., 2003b).

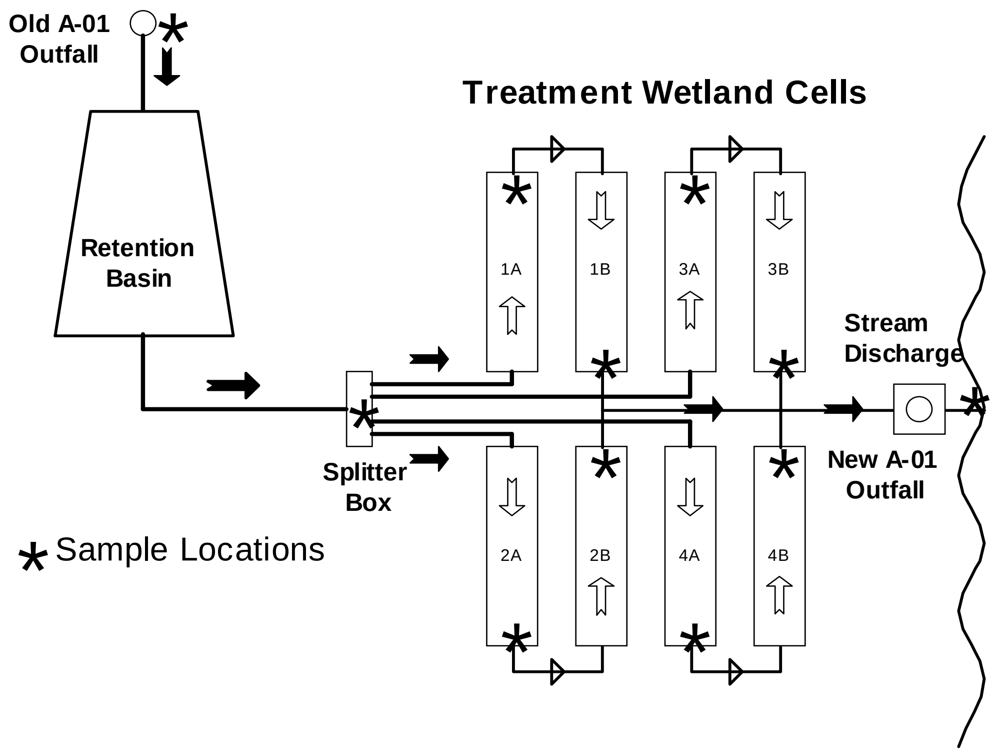

FIGURE 1. Schematic diagram of wetland treatment system and sample locations

Sampling and Analysis. Routine monitoring samples are collected at a compositing sampler at the compliance point for monthly reporting. As part of the separate research effort, monthly grab water samples were collected from numerous other locations from the inflow to the system through the discharge to the receiving stream from April through September 2004. Water samples were collected from the old compliance point, at the entrance into the wetland cells (after the retention basin), after passage through each of the first wetland cells (A cells), after passage through each of the second wetland cells (B cells), and at the discharge to the stream. A total of eleven water samples were collected on each monthly sampling date in 2004. Samples are analyzed by ICP-MS for cations, by ion chromatography for anions, by the new EPA methods 1630 and 1631 for low level detection of total mercury and methylmercury, and for carbon by an O.I. Analytical 1020A Total Organic Carbon Analyzer. All samples were analyzed as unfiltered samples.

RESULTS AND DISCUSSION

Copper removal efficiency was excellent from the start-up of the system, while mercury efficiency improved with maturation of the treatment cells during the first two years of operation. Methylmercury was only a small component of the total mercury discharged from the system. Water samples collected at irregular intervals during the third year of operation were analyzed for a wider suite of metals and anions. Copper and mercury removal continued to be excellent (82% and 86% respectively), and the expanded analysis showed lead was reduced by 89% and zinc by 47% from the influent concentration.

Sampling of the water course through the wetlands was conducted during the fourth year of operation validated continued performance during systematic monthly sampling, and assessed the fate of the larger suite of metals present in the water. Copper and mercury removal efficiencies were still very high, both in excess of 80% removal from the water after passage through the wetland system. Copper reduction continued to occur primarily during passage of water through the first wetland cell. After passage through the second wetland cell, copper concentration is generally near the detection limit of analysis (Figure 2).

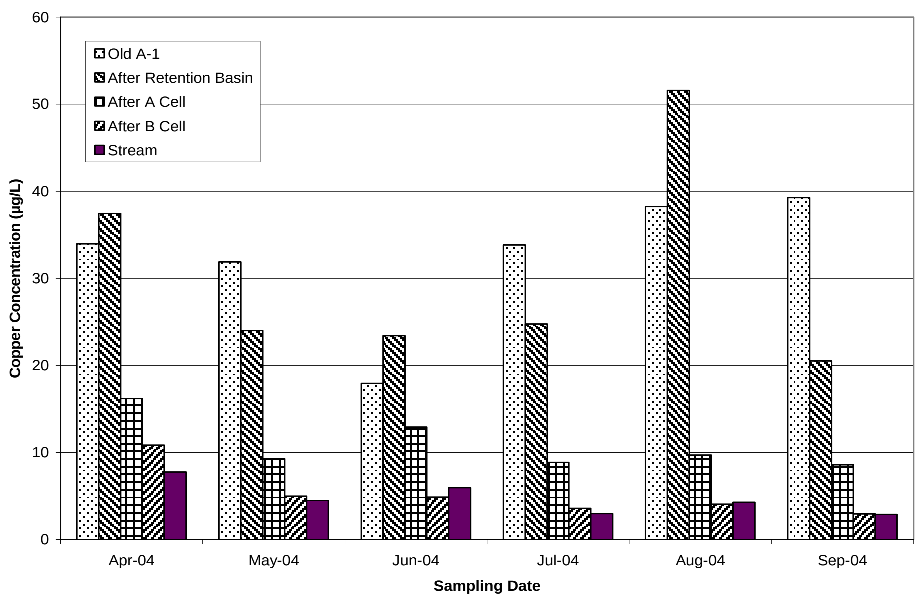

FIGURE 2. Copper removal from water column during passage through the wetland treatment system.

Mercury continued to be removed during water movement through both the first and second of the wetland cells. Methylmercury concentration in the effluent from the wetland system continued to be very low, averaging less than 0.26 ng/L. This was equivalent to methylation of only 0.5% of the influent mercury or 3.5% of the total discharge mercury. Average lead removal from the water by the system was 83% in 2004, average zinc removal was 60%, and nickel was generally unaffected. Most other metals analyzed during the six monthly samplings either showed no trend during passage through the wetland cells or were present in such low levels that no pattern was discernable. Influent metal concentrations into the wetland cells were highly variable during the six sampling events of 2004, and affected the removal efficiency of the cells. When influent concentrations were higher, removal percentage of each metal was also higher. Average overall removals for each metal during the four years of operation are summarized in Figure 3. Copper and mercury removal have been very similar over the four years of analysis. Lead concentration in the influent is generally very low, but still removed very efficiently. Zinc removal was more variable, based primarily on influent concentration, and therefore, overall removal was less.

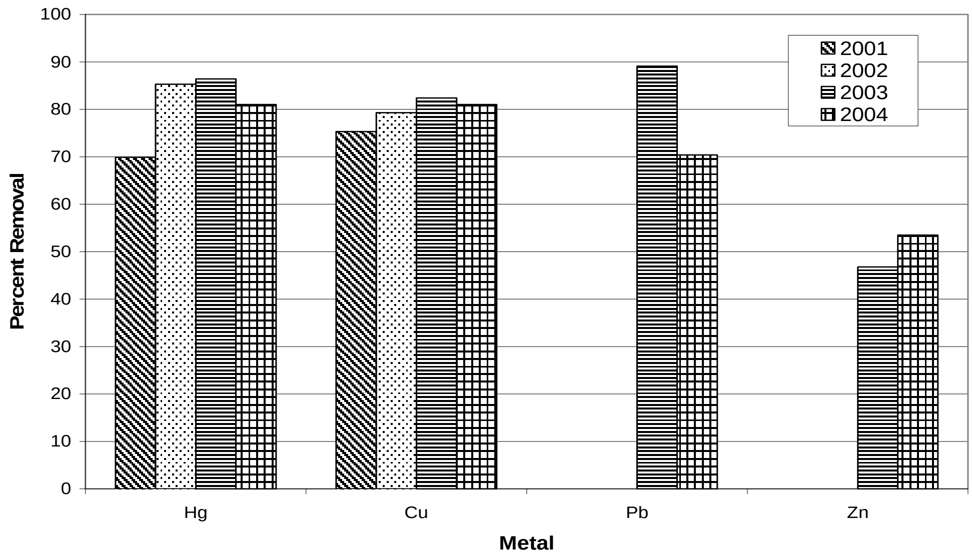

FIGURE 3. Average removal of metals from influent during passage through the wetland cells during four years of operation.

Nitrates entering into the wetland cells are almost immediately removed from the water column and generally no nitrates are discharged from the A cells. Potassium and phosphate levels in the water column after passage through the wetlands were generally slightly reduced to unaffected. Based on the high vegetative productivity of the wetland cells, nitrogen retention in the sediments and organic components of the wetland system are very efficient.

The wetland cells are very anaerobic and the sediments have negative redox potentials. As a result, manganese and iron mineral phases in the sediments have been reduced to soluble forms and increase in the water during passage through the wetland system. Average effluent concentration of iron was 476 µg/L and of manganese was 123 µg/L. These metals are rapidly oxidized and deposited on the rock discharge from the wetland, as indicated by analysis of the periphyton at the discharge to the receiving stream. Dissolved organic carbon in the water is also increased by the system due to the high additions of organic matter to the system and the normal decompositional processes. Levels generally doubled during passage through the wetlands. High organic ligand levels in the water reduce the toxicity of some metals resulting in a three-fold increase in the regulatory copper limit through application of a Water Effects Ratio (WER). This high organic material concentration is also responsible for the ability of the effluent to pass toxicity testing.

CONCLUSIONS

Sampling of the water course through the wetlands conducted during the fourth year of operation validated continued performance, and assessed the fate of a larger suite of metals present in the water. Copper and mercury removal efficiencies were still very high. Mercury removal continues along the entire water course through the system, while copper is removed almost immediately upon entering the wetland cells. Lead removal from the water by the system was 83%, zinc removal was 60%, and nickel was generally unaffected. Nitrates entering into the wetland cells are almost immediately removed from the water column, while potassium and phosphate are only slightly reduced. The high negative redox potentials in the cells results in release of manganese and iron from the soil mineral. Dissolved organic carbon in the water is also increased by the system, and reduces toxicity of the effluent.

The wetland treatment system has very low operation and maintenance costs associated with it, and these mainly consists of checking for growth of the vegetation and free flow of the water through the system. The system is entirely passive, relying on gravity as the power source of water flow. No reportable permit exceedances of metals, toxicity, or other regulated parameters have been experienced since the wetland began treating the outfall discharge.

ACKNOWLEDGEMENTS

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