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Full-Scale Treatment Wetlands for Metal Removal from Industrial Wastewater

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Abstract

The A-01 NPDES outfall at the Savannah River Site receives process wastewater discharges and stormwater runoff from the Savannah River National Laboratory. Routine monitoring indicated that copper concentrations were regularly higher than discharge permit limit, and water routinely failed toxicity tests. These conditions necessitated treatment of nearly one million gallons of water per day plus storm runoff. Washington Savannah River Company personnel explored options to bring process and runoff waters into compliance with the permit conditions, including source reduction, engineering solutions, and biological solutions. A conceptual design for a constructed wetland treatment system (WTS) was developed and the full-scale system was constructed and began operation in 2000. 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 design of future systems. The system is a vegetated surface flow wetland with a hydraulic retention time of approximately 48 hours. Copper, mercury, and lead removal efficiencies are very high, all in excess of 80% removal from water passing through the wetland system. Zinc removal is 60%, and nickel is generally unaffected. Dissolved organic carbon in the water column is increased by the system and reduces toxicity of the effluent. Concentrations of metals in the A-01 WTS sediments generally decrease with depth and along the flow path through the wetland. Sequential extraction results indicate that most metals are tightly bound to wetland sediments.

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; Hammer, 1989; Shutes, 2001). One aspect of 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 used effectively in mining regions of the USA and Europe to reduce levels of Cu, Zn, Ni, Pb, and other metals in runoff and drainage (Mays and Edwards, 2001; Sobolewski, 1999). They are equally effective at treating stormwater runoff with high metal concentrations (Walker and Hurl, 2002; Carleton et al., 2001; Scholes et al., 1998).

Removal of metals from the water occurs by two primary mechanisms: sorption and precipitation. Sorption of metal ions to organic matter and/or clay particles begins immediately.

In surface flow wetlands, vegetation in the wetland cell continuously adds new organic matter to the sediment and provides new sorption sites. This removal is especially effective for divalent metals, such as copper, lead, and zinc (Mitsch and Gosselink, 1993). Maintenance of an anaerobic soil matrix can increase removal by precipitation of metals as sulfides. This is an outgrowth of the reduction of sulfate by sulfate-reducing bacteria present in this environment. Metal removal from the water depends on several factors, including loading rate, hydrological character of the wetland (hydraulic retention time, water depth, flow rate, etc.), and ecological characteristics (vegetation, soil matrix, nutrients, etc.). Some of these variables can be adjusted after construction to fine tune performance of the wetland.

A regulated outfall (A-01) by the Federal National Pollutant Discharge Elimination System (NPDES) at the Savannah River Site (SRS) receives process wastewater discharges and stormwater runoff. Routine monitoring indicated that copper concentrations were regularly higher than the regulatory permit limit and the water routinely failed biomonitoring tests. Concentrations of other chemicals (e.g., lead, chlorine, mercury, etc.) were occasionally higher than the permit limit. A series of studies revealed that copper was coming from a wide variety of sources and was elevated in stormwater runoff. The end result of these analyses was that nearly 3,785 cubic meters of water needed to be treated each day, and during storms up to 75,000 cubic meters required treatment. Evaluation criteria for selection of a solution included technical feasibility of the methods, economic factors, regulatory issues, and implementation time. Conventional treatment systems for metal removal (e.g., ion exchange, chemical precipitation, source removal, 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 release to a nearby stream. The search for more cost-effective alternatives resulted in constructed wetlands being considered. 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 (Harmon, 2003). During the pilot study, the wetland system was effective at reducing total mercury from the influent water (King et al., 2002). Wetland mesocosm systems must take into account flow and retention time approximations of scaling when compared to full-scale constructions (Ahn and Mitsch, 2002).

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. Removal of divalent metals in wetlands is reported in the range of 50% to over 95 % (Kadlec and Knight, 1996). The results of the pilot mesocosm study at SRS indicated that the system achieved the upper end of the removal range for copper (Mitsch and Gosslink, 1993). The focus of the current research was to determine the metal removal process and performance of the full-scale wetland system and how this performance varied with age of the system. This information will enable us to provide input for the design of future wetland treatment systems.

Methods and Materials

Location:

The SRS was established as a federal facility in the early 1950’s, and is administered by the United States Department of Energy. The 80,000 hectare facility is located near Aiken, South Carolina, USA. The full-scale wetland treatment system discussed in this paper was built to treat a permitted outfall near the main administration area and the Savannah River National Laboratory (SRNL).

Wetland Facility:

The design provided for a stormwater retention basin to manage the volume of inflow to the wetland treatment cells. The basin moderates the effects of stormwater surges and providing additional water to keep the wetland flooded during dry periods. The treatment cells consist of four pairs of 0.4 hectare wetland cells with water flowing from one cell (A cell) to a second cell (B cell), and then to the discharge point (Figure 1). Design parameters are for base flow of approximately 800,000 gallons per day (3,050 cubic meters) of water through the system, with a maximum daily flow of approximately 2.5 million gallons (9,500 cubic meters). Normal water depth in the cells is maintained at 30.5 cm. The cells have been previously described in detail (Nelson et al., 2003 a,b).

A geosynthetic liner and compacted clay layer was installed under each wetland cell to prevent water infiltration into the underlying aquifer. A 60 cm layer of sandy soil was placed on top of the liner complex to support growth of vegetation. Soils in the wetland cells were amended with organic matter, fertilizer and gypsum at the time of construction and were planted with giant bulrush (*Schoenoplectus californicus*). 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 sq meter. The bulrush plants provide a continuing source of organic material to the sediments where bacteria and fungi decompose the plants and maintain anoxic conditions. The combined effects of organic matter and anoxic soil conditions work to capture and immobilize the metals. Yearly growth, dieback, and decomposition of the plants keeps the soil ecosystem functioning year after year to remove metals and toxicity from the water. Water retention time in the wetland system is approximately 48 hours, depending on flow rate, and the wetland cells operate at circumneutral pH.

Construction of the system began in January 2000, and construction of the entire system was completed in the early fall of 2000. Vegetation was planted late during the 2000 growing season during construction and spread of new shoots was therefore limited. Vegetation establishment and spread data were collected from permanent one square meter plots during the second growing season (spring 2001). Two plots were established in each wetland cell and measured on an alternate week basis for growth and stem density. Above ground biomass was collected at the end of the growing season and expressed as dry weight per square meter. The spread of the vegetation, *S. californicus*, was very impressive during the second growing season (2001), and continued to perform well during the subsequent year. During the second season most plots increased their number of total shoots as much as five-fold (Figure 2). Densities of the plots are now near optimal maximums that have been reported in the literature for other species of bulrush (Tanner, 1996). Growth rates for newly emerging shoots above the water have been most impressive. Rates of growth of these new shoots have averaged up to 8 centimeters per day during the most rapid expansion phase, and shoots often surpass 2 meters in length. Aboveground live biomass was harvested after the second growing season, and averaged 2.5 kg/sq. meter of dry material in the wetland cells. This value is above any reported values for *Scirpus* (current taxonomy changed to *Schoenoplectus*) dominated wetlands (Tanner, 1996). Belowground biomass was not measured.

Sampling:

Routine monitoring samples are collected at a compositing sampler at the compliance point for monthly reporting and the data are not reported here. As part of a separate research effort over the life of the treatment system, monthly grab water samples are collected from numerous additional locations from the inflow to the system through discharge to the receiving stream. For the current investigation water samples were collected upstream of the retention basis, 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 (Figure 1). A total of eleven water samples were collected on each sampling date. Samples were acidified after collection for preservation. Samples were analyzed for total copper by method #220.1 and for mercury by EPA methods 1630 and 1631 for low level detection of total mercury and methylmercury. All samples were analyzed as unfiltered samples.

Results and Discussion

Flow:

The treatment system was designed for discharge of 24 million gallons (90,850 cu meters) per month of treated process water, not including stormwater, from the wetlands. The monthly outflow has been slightly less than that based on process water only, but stormwater additions have produced as much as 38 million gallons (143,850 cu meters) of discharge during a single month (Figure 3). Estimated water loss from the system due to evapotranspiration has not been calculated, but may be responsible for much of the lower than anticipated discharge from the system. The design for the cells was for approximately a 48 hour hydraulic retention time prior to discharge. During base flow operation, that retention time is nearer to 60 hours and during larger storm events it is reduced to approximately 24 hours.

Metal Removal:

Since the wetland treatment system has been operational, no NPDES permit exceedences, violations of metals limits, or toxicity have been recorded at the compliance point for the outfall. Metal removal efficiency of the treatment system improved as the plants became established. Geochemistry of the system and highly reducing conditions in the wetland sediments reached equilibrium as hydrological conditions and rate of organic input stabilized.

Copper levels at the old A-01 outfall were above permit limits during 18 of the 22 sampling events after the system was put online (Figure 4). Total copper inflow to the system ranged up to 180 µg/L, and copper concentrations at the effluent discharge were commonly below detection limits (10 µg/L). After passage through the treatment cells, the concentrations during all sample dates were well below permit limits (22 µg/L), often falling below detection limits of the analytical procedure. This removal process from the water is occurring very rapidly in the wetland system, with most removal already completed prior to exiting the first cell of the series (A cells in Figure 1, data not reported here).

Sediment sampling at 8 locations along the water course of a pair of wetland cells was conducted in September 2001 (Specht and Nelson, 2002). Samples were analyzed for metals in the surface layer (0-1 cm) of sediment and in deeper sediments (1-10 cm) by EPA method 2007. Copper concentrations in the surface sediments of the first section of the A cell averaged 20 mg/kg, fell to 10 mg/kg in the mid-sections of the A cell, and fell to background levels by the last section of the A cell. Copper levels in the deeper sediments did not vary significantly among the sample locations. No differences were seen among the B cell samples. This rapid removal of copper from the water column into the sediment was confirmed by water chemistry at the exit from the first cell.

Mercury levels in the water as the wetland system matured in terms of vegetation and geochemistry (Figure 5). By June 2001 the total mercury level was below the permit limit (13 ng/L), and was considerably better than mercury reductions anticipated during the design phase and initial mesocosm testing. The level has remained below the limit, which confirms stability of vegetation and geochemistry of the system. Mercury removal is occurring through the entire water course of the system. Levels after passage through the first cell are typically reduced to 40 percent of the influent value, and are reduced by an additional 30 to 40 percent after passage through the second cell. Methylmercury production in the system has shown a seasonal trend and has been a small component of the total mercury in the effluent. Methylmercury has increased during the warm summer months, but has never exceeded 10 percent of the total mercury at the discharge point. Methylmercury discharge concentrations are routinely less than 0.5 ng/L during the summer when concentrations are highest.

Water samples were collected during the fourth year of operation of the full-scale wetland treatment system to evaluate continued metal removal performance. Copper and mercury removal efficiencies were still very high, both in excess of 80% removal from the water after passage through the wetland system (Figure 6). Copper removal continued to occur primarily in the first wetland cell. After passage through the second wetland cell, copper concentration was generally near the analytical detection limit. The sediments were sampled and analyzed to identify the copper distribution. Most of the copper was found in the upper 5 cm of the sediments and organic layer in the first half of the A cell (Specht and Nelson, 2002). Most of the divalent metals are rapidly removed from the water and held shortly after making contact with treatment wetlands. More recent sediment sampling results have been reported and support the original conclusions (Knox et al., 2006).

During 2004 mercury continued to be removed during water movement through both the first and second wetland cells (Figure 7). 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. This is an extremely low rate of methylation, and is likely attributable to a large sulfate content of the sediment (Benoit et al., 1999). Mercury removal from the water continued along the entire path of water movement through the wetland cells. Average lead removal from the water by the system was 83% in 2004, average zinc removal was 60 %, and nickel was generally unaffected. Other metals, including lithium, boron, magnesium, aluminum, potassium, chromium, cobalt, molybdenum, cadmium, tin, and barium, in the 2004 water samples 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 high, removal percentage of each metal was also high. Average overall removals for each metal during the first four years of operation are summarized in Figure 8. Copper and mercury removal have been very similar over the four years of analysis. Lead concentration in the influent was generally very low, but still removed very efficiently. Zinc removal was more variable, depending primarily on influent concentration.

<u>Water Effects Ratio</u>:

Water discharged at SRS is typically very soft, with low hardness and low buffering capacity. Total organic carbon in the water is increased by passage through the wetland system due to additions of organic matter to the system by normal decompositional processes. Levels of total organic carbon generally doubled during passage through the wetlands to 7.01 mg/L. This natural wetland process and the reduction of metal bioavailability have been documented for surface water discharges at SRS (Specht, 2005). High organic ligand levels in the water reduce the toxicity of some metals because of the formation of non-bioavailable complexes. This results in a greatly reduced toxicity of the effluent. Through negotiations with the regulatory agency responsible for the outfall, a greatly increased concentration in the regulatory copper limit was determined to be appropriate by the Water Effects Ratio (WER). The high organic content is also responsible for the ability of the effluent to pass acute toxicity testing using the U.S. Environmental Protections Agency methodology on all sample dates.

Regulatory Sampling Requirements:

The A-01 Outfall is a permitted NPDES outfall through the Department of Health and Environmental Control of South Carolina. Testing and monitoring are required for properties that may be of concern relating to the water quality of the discharge. Because of the performance of the wetland treatment system at removing metals and toxicity from the effluent, the SRS is no longer required to report heavy metal concentration or to perform toxicity testing of the A-01 discharge. Monitoring of the treatment system has provided data that have demonstrated that there is no longer a reasonable expectation that these parameters would be exceeded, and therefore the monitoring and reporting on a monthly basis is no longer required by the state.

Conclusions

Sampling of the water course through the wetlands during the initial two years of operation showed excellent copper and mercury removal. Additional sampling 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 remained very high. Mercury removal continues along the entire water course of the system, while copper is removed almost immediately upon entering the first wetland cell. Lead removal by the constructed wetland system was 83 %, zinc removal was 60 %, and nickel was generally unaffected. Total organic carbon in the water is increased by the system, which reduces toxicity of the effluent. Because of the system performance, permit limits for copper were raised and monitoring for metals and toxicity were greatly reduced by the regulatory authority.

The wetland treatment system has very low operation and maintenance costs (less than $50,000 US per year). These costs consist mainly of checking for growth of the vegetation and free flow of 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 occurred since the wetland began treating the outfall discharge. The wetland treatment system has met or surpassed all expectation, and confirms the selection of a biologically based solution to the industrial problem of wastewater discharge quality.

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Figure Captions

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

Figure 2. Average *Schoenoplectus* shoot density in the treatment wetland cells during the second growing season.

Figure 3. Average monthly water flow through the wetland treatment system.

Figure 4. Copper concentration in the influent and effluent water of the wetland treatment system.

Figure 5. Total mercury concentration in the influent and effluent water of the wetland treatment system.

Figure 6. Copper removal from water during passage through the wetland treatment system (sample locations indicated in Figure 1).

Figure 7. Mercury removal from water during passage through the wetland treatment system.

Figure 8. Average removal of metals from influent after passage through the wetland cells.

Fig 1

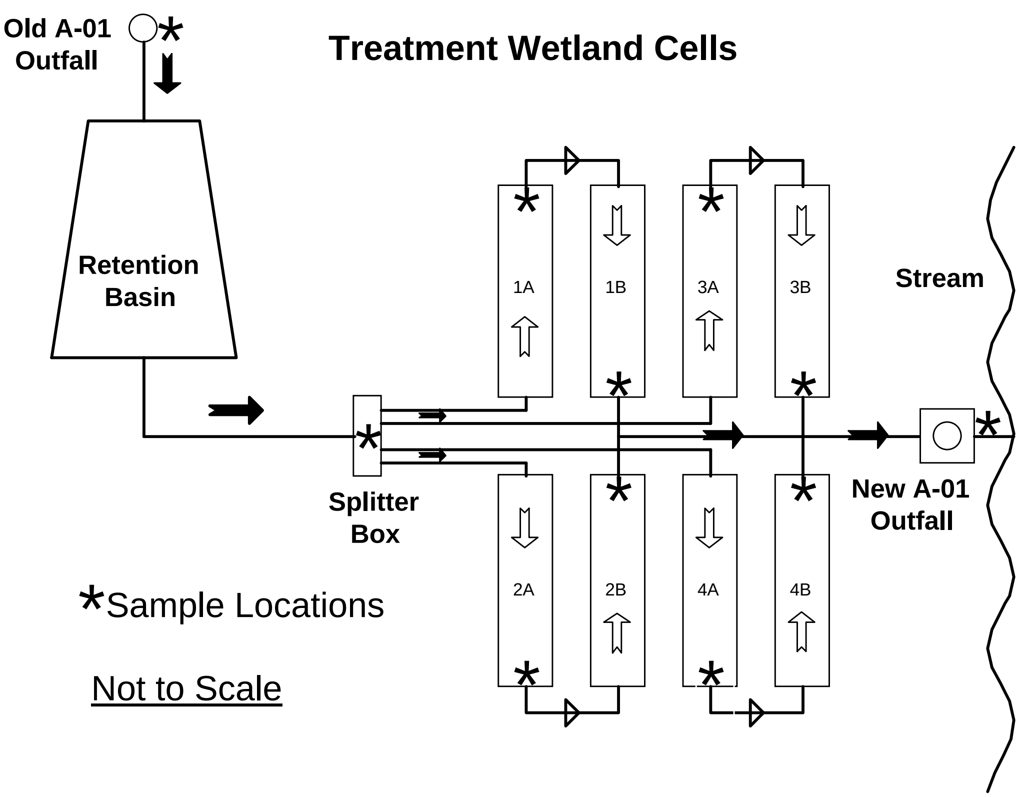

Old A-01
Outfall
Treatment Wetland Cells
Retention
Basin
1A
1B
3A
3B
Stream
Splitter
Box
New A-01
Outfall
2A
2B
4A
4B
*Sample Locations
Not to Scale

Fig 2

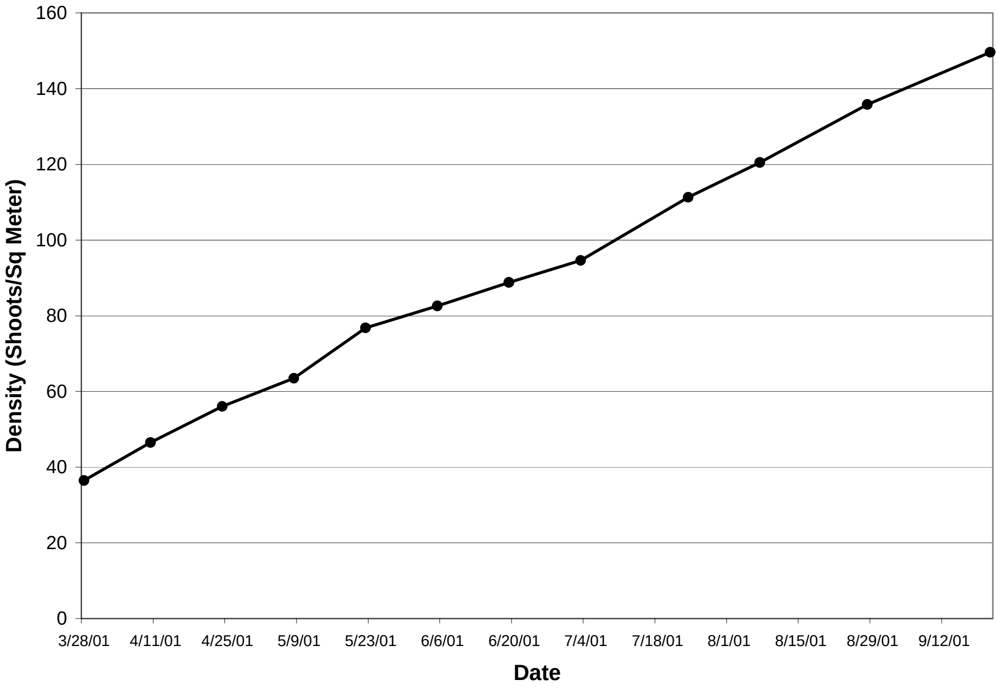

Density (Shoots/Sq Meter)
160
140
120
100
80
60
40
20
0
3/28/01
4/11/01
4/25/01
5/9/01
5/23/01
6/6/01
6/20/01
7/4/01
7/18/01
8/1/01
8/15/01
8/29/01
9/12/01
Date

Fig 3

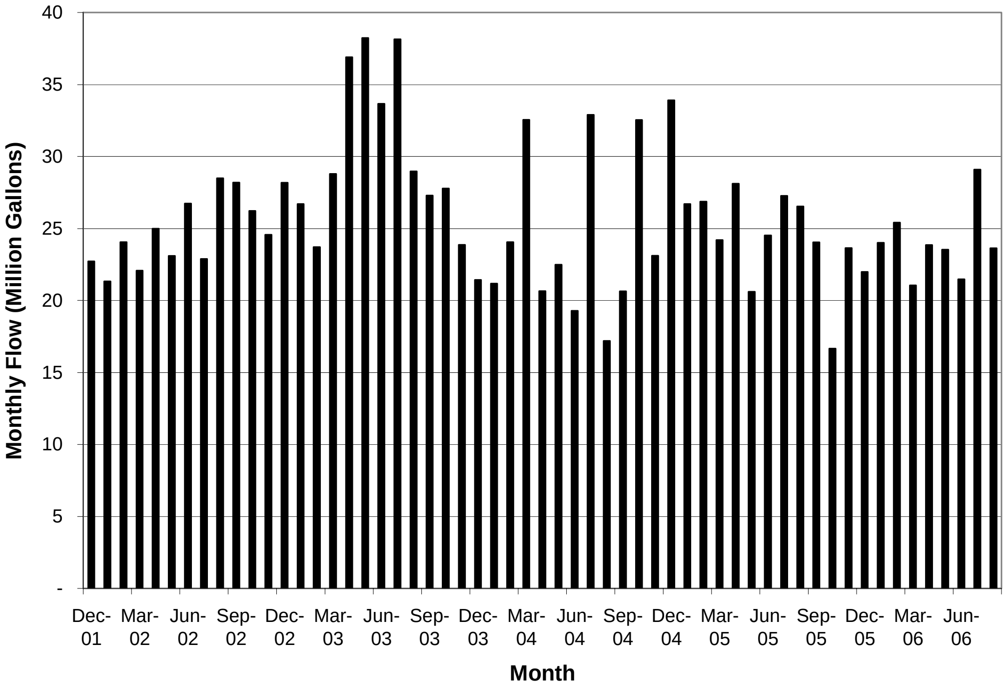

Monthly Flow (Million Gallons)
40
35
30
25
20
15
10
5
-
Dec-01
Mar-02
Jun-02
Sep-02
Dec-02
Mar-03
Jun-03
Sep-03
Dec-03
Mar-04
Jun-04
Sep-04
Dec-04
Mar-05
Jun-05
Sep-05
Dec-05
Mar-06
Jun-06
Month

Fig 4

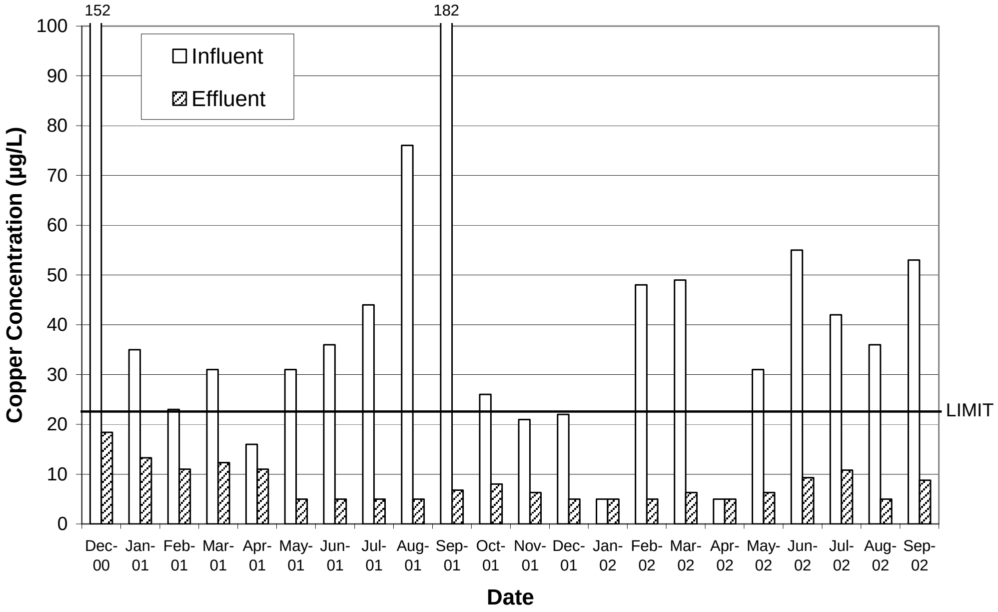

152
182
100
90
80
70
60
50
40
30
20
10
0
Copper Concentration (µg/L)
□ Influent
▨ Effluent
LIMIT
Dec-00
Jan-01
Feb-01
Mar-01
Apr-01
May-01
Jun-01
Jul-01
Aug-01
Sep-01
Oct-01
Nov-01
Dec-01
Jan-02
Feb-02
Mar-02
Apr-02
May-02
Jun-02
Jul-02
Aug-02
Sep-02
Date

Fig 5

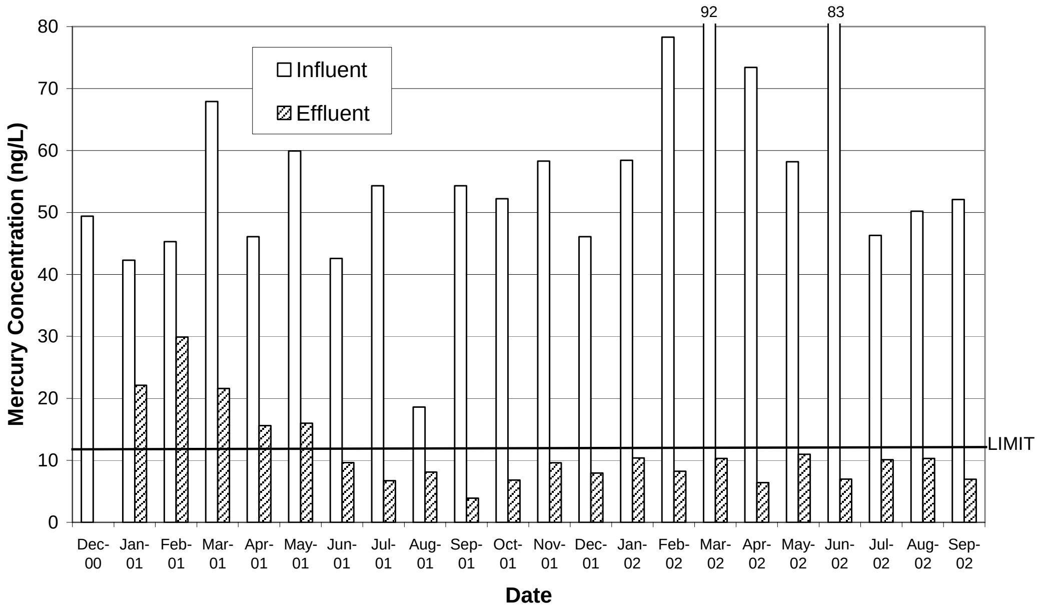

92
83
80
70
60
50
40
30
20
10
0
Influent
Effluent
Mercury Concentration (ng/L)
LIMIT
Dec-00
Jan-01
Feb-01
Mar-01
Apr-01
May-01
Jun-01
Jul-01
Aug-01
Sep-01
Oct-01
Nov-01
Dec-01
Jan-02
Feb-02
Mar-02
Apr-02
May-02
Jun-02
Jul-02
Aug-02
Sep-02
Date

Fig 6

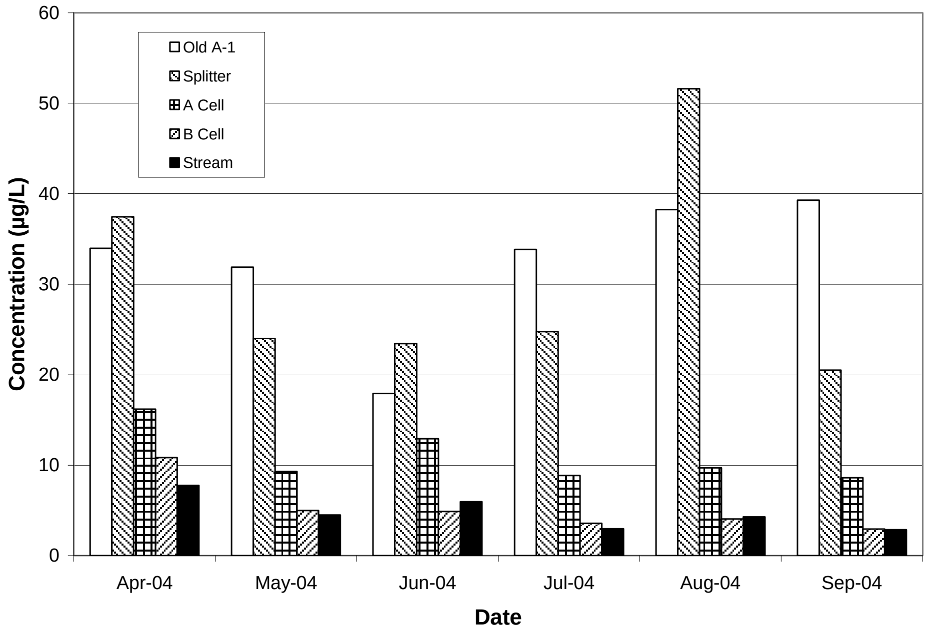

60
50
40
30
20
10
0
Old A-1
Splitter
A Cell
B Cell
Stream
Concentration (µg/L)
Apr-04
May-04
Jun-04
Jul-04
Aug-04
Sep-04
Date

Fig 7

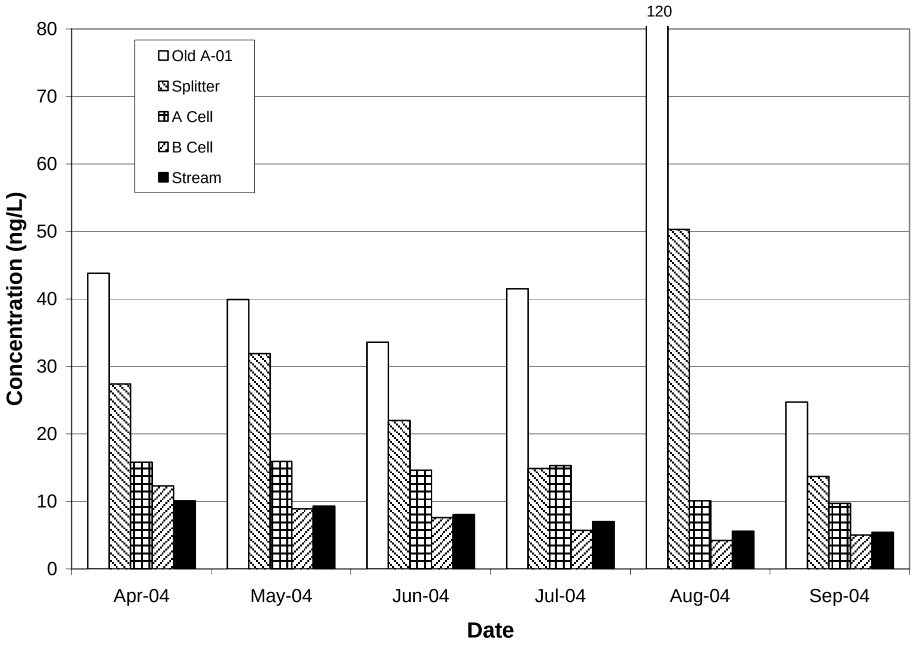
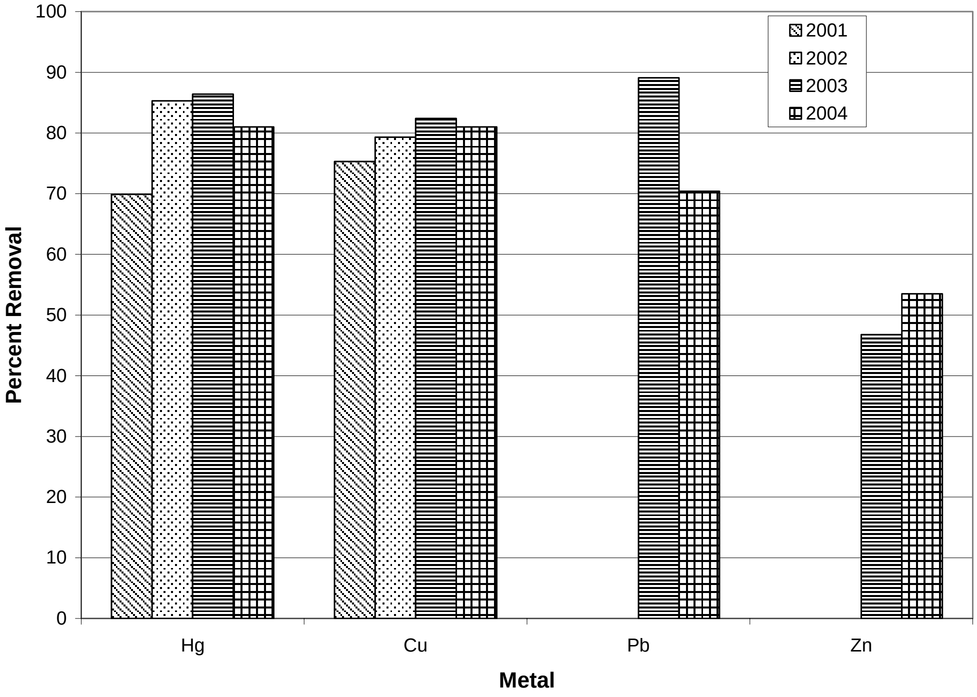

120
80
70
60
50
40
30
20
10
0
Concentration (ng/L)
Old A-01
Splitter
A Cell
B Cell
Stream
Apr-04
May-04
Jun-04
Jul-04
Aug-04
Sep-04
Date

Fig 8


100
90
80
70
60
50
40
30
20
10
0
Percent Removal
2001
2002
2003
2004
Hg
Cu
Pb
Zn
Metal