Evaluating performance of a constructed wetland treatment system designed to decrease bioavailable copper in a waste stream

Cynthia L. Murray-Gulde, William C. Bridges, and John H. Rodgers Jr.

ABSTRACT

Published literature has indicated that when properly designed and maintained, constructed wetlands provide predictable water-quality improvement. However, because of the complexity or heterogeneity of wastewaters and the lack of quality data (both temporal and spatial) currently available from full-scale constructed wetland treatment systems, many constructed wetland designs fail to provide predictable water-quality improvement. By understanding internal thermodynamic processes and design criteria that affect the removal of targeted constituents in constructed wetlands, constructed wetland technology can be accurately and reliably transferred from site to site. Specific design parameters that should be identified when designing a constructed wetland include (1) character of the wastewater including the targeted constituents, (2) performance goals or desired levels of treatment, (3) transfer and transformation pathways, (4) flow rates and retention time required to achieve treatment, and (5) climate (i.e., temperature and precipitation). Using these guidelines, this research evaluated the performance of a constructed wetland treatment system for treatment of a copper-contaminated wastewater. Specifically, this system was designed to achieve a regulatory limit of $\leq$22 µg/L total recoverable copper and eliminate toxicity in a waste stream by coupling the copper, sulfur, and carbon cycles, so that copper will be precipitated from the water column and sequestered in the sediment in nonbioavailable forms. In this constructed wetland treatment system, average acid-soluble copper concentrations decreased by 85%, and soluble copper decreased by 83% from upstream of the system to downstream, and the toxicity associated with the bioavailable fraction of copper was effectively removed.

DOI:10.1306/eg.07110707008

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INTRODUCTION

When designing site-specific constructed wetland treatment systems for the treatment of wastewater, more comprehensive performance information on existing constructed wetlands can lead to more effective and efficient transfer of this technology from site to site. Constructed wetlands have been used for mitigating risks from a variety of point sources (e.g., industrial process wastewater, municipal wastewater) for downstream biota. When non-point sources of metals, such as stormwater, can be coalesced into a common stream (e.g., ditch), strategies for mitigation of risks associated with those non-point sources can be developed. The success or failure of remediation or risk mitigation strategies such as constructed wetlands is commonly characterized by simple measures of performance. In many cases, the targeted constituents are measured from the inflow, and the outflow of a constructed wetland treatment system and performance is expressed as percent removal (Dortch and Gerald, 1995; Knight et al., 1999; Carleton et al., 2000; USEPA, 2000; Goulet et al., 2001). Although somewhat informative, this approach provides limited information regarding components or thermodynamic processes contributing to system performance and can be problematic especially in situations where inflow concentrations vary widely. Therefore, this cursory or summary information does not readily permit scaling of these systems from site to site. Measures of both gross or simple performance and internal functions or kinetics are needed to accurately and consistently apply this technology widely.

Many types of design guidelines have been published for the use of constructed wetlands (USEPA, 2000). However, because of the complexity or heterogeneity of wastewaters and the lack of quality data (both temporal and spatial) of sufficient detail currently available from full-scale constructed wetlands, many constructed wetland designs fail to provide predictable water-quality improvement (Knight et al., 1999; Goulet et al., 2001). Because of the minimal amount of full-scale data available, design parameters for constructed wetlands have commonly been derived by aggregating performance information from a variety of wetlands. This information is frequently the result of combining data from wetlands having different sizes or dimensions, mass loadings, design elements, and varying data collection techniques (USEPA, 2000). Because no standardization in reporting has been developed, the available wetland databases, from which design equations are derived, commonly lack essential design criteria such as strategic thermodynamic pathways included in the design, flow rates, and retention time information; climate (i.e., temperature, precipitation, and evapotranspiration); and characterization of the wastewater, including the targeted constituents the constructed wetland was designed to treat (USEPA, 2000). Without this information, constructed wetland technology cannot be accurately or reliably transferred from site to site.

Although simple performance information is necessary to characterize the efficiency of a constructed wetland treatment system, limited information is gained regarding the internal components or processes that contribute to the observed constructed wetland performance. The transfers (e.g., sorption, filtration, ion exchange, volatilization) and transformations (e.g., photolysis, biotansformation) that contribute to wetland performance are well known. However, few studies have provided an integrated assessment of interactions of the physical, chemical, and biological components within a constructed wetland to make the transfer and transformation of targeted constituents both possible and likely. An understanding of internal function as well as the kinetics of processes that affect the disposition of targeted constituents in constructed wetlands and contribute to the overall performance is necessary to move constructed wetland designs from site to site.

This research measured the performance of a constructed wetland treatment system designed to decrease bioavailable copper in a waste stream and to mitigate risks for receiving water biota. In 1999, a revised National Pollutant Discharge Elimination System permit was established for a waste stream that discharged into an unnamed tributary of Tim's Branch, a stream flowing into the Savannah River that borders Georgia and South Carolina. Subsequent to the issuing of the revised permit, samples collected from the waste stream consistently exceeded the criteria of 22 μg/L total recoverable copper and no chronic toxicity to *Ceriodaphnia dubia* (USEPA, 1998). A constructed wetland treatment system was designed to collect the stormwater and effluent that comprises the waste stream and decrease the concentration of copper in wastewater, so that risks to receiving stream biota are removed prior to the waste stream discharging into Tim's Branch (USEPA, 1998). A toxicity identification evaluation (TIE) conducted on the waste stream identified copper as the causative agent of the observed toxicity (USEPA, 1992a).

Copper's lithic biogeochemical cycle and its integration with sulfur and carbon cycles constitute the theory behind the design of this constructed wetland treatment system. Copper bioavailability and potential toxicity in aquatic systems are related to both the oxidation state and copper speciation with the free divalent ion, Cu^{2+}, apparently the most bioavailable species (Nor, 1987; Lewis, 1992; Deaver and Rodgers, 1996). However, under conditions of most surface waters, Cu^{2+} readily reacts with other components of aquatic systems, forming less bioavailable copper species such as sulfide minerals (Morse, 1995; Deaver and Rodgers, 1996; Huggett et al., 1999). Therefore, in this constructed wetland, HS^- (available for binding with Cu^{2+}) is produced during the oxidation of organic matter by sulfate-reducing bacteria. Using this background knowledge of the biogeochemistry of copper, sulfur, and carbon, a constructed wetland treatment system was designed to precipitate copper from the water column and sequester it in the sediment in nonbioavailable forms.

The overall objective of this constructed wetland treatment system was to achieve a regulatory limit of ≤22 µg/L total recoverable copper and eliminate toxicity in a waste stream comprised of a point source and stormwater runoff. Supporting the overall objective, the specific objectives of this research are (1) to characterize the waste stream and measure design parameters that may influence performance, (2) to measure parameters (e.g., acid-volatile sulfides [AVS], oxidation reduction potential [redox], biomass production and decomposition, and sediment accretion rates) indicative of performance pathways incorporated into the design of this constructed wetland treatment system, (3) to measure the rate and extent of changes in aqueous copper concentrations from the inflow (upstream) of the constructed wetland treatment system to the outflow (downstream); (4) to measure changes in the bioavailable fraction of copper (as defined by toxicity to C. *dubia*) in water samples collected from the inflow (upstream) to the outflow (downstream) of the constructed wetland treatment system; and (5) to evaluate variability between constructed wetland cells and in the seasonal performance of the constructed wetland treatment system using a first-order removal model.

MATERIALS AND METHODS

Study Site

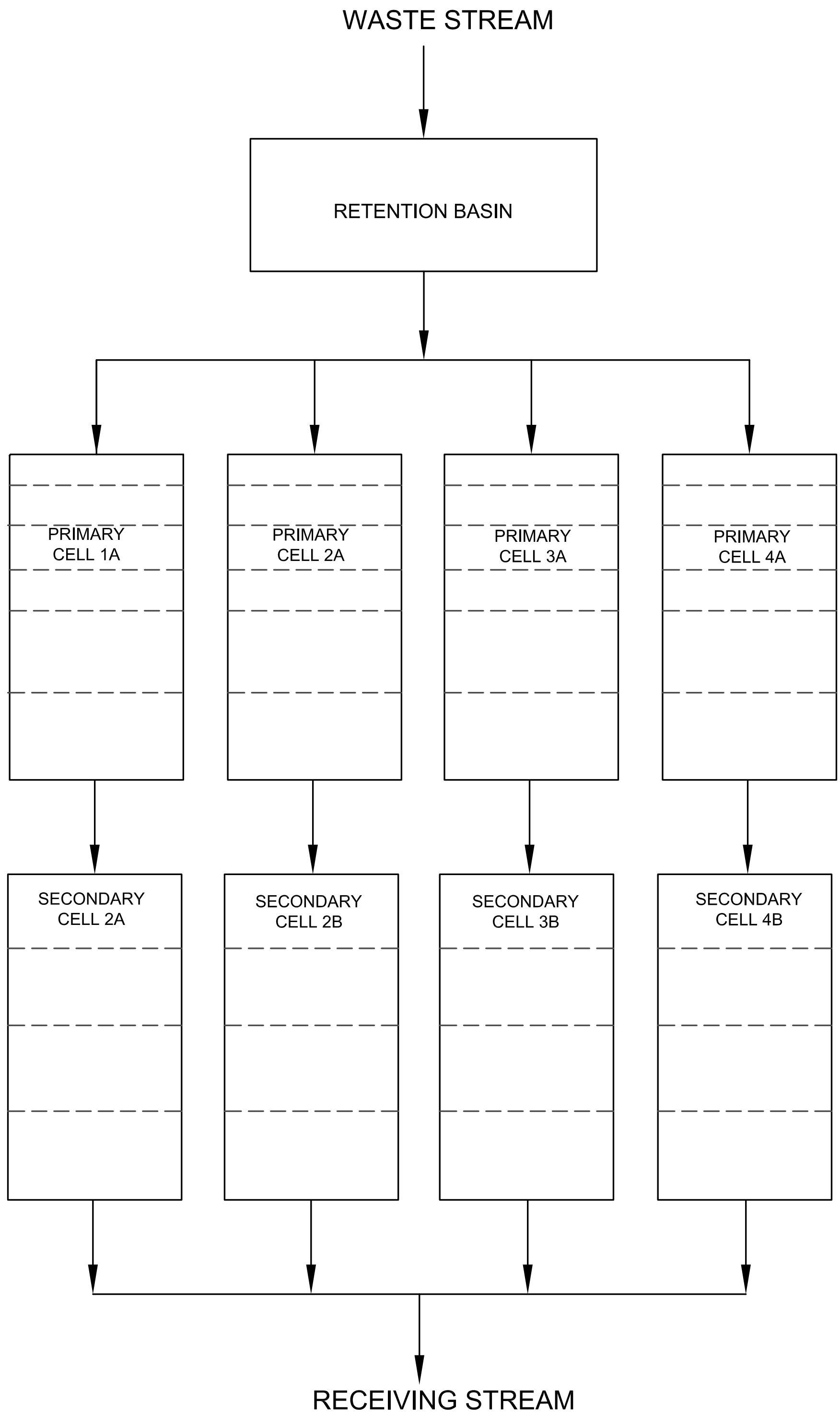
The constructed wetland used in this research is located on the U.S. Department of Energy's Savannah River Site (SRS), which occupies some 300 mi^2 (776 km^2) in Aiken and Barnwell counties, South Carolina. This constructed wetland was designed to treat the A-01 outfall, a waste stream comprised of process wastewater from technical facilities (58% of total flow) and stormwater runoff (42% of total flow) from a 77-ha (190-ac) watershed located within the SRS. The waste stream is discharged into an unnamed tributary that flows into Tim's Branch, which subsequently flows into the Savannah River (USEPA, 1998). The initial component of the constructed wetland treatment system was an upstream retention basin (1) to control water flow to the constructed wetlands and (2) to decrease variance in influent copper concentrations. The remaining treatment components included eight wetland cells that flow into the receiving stream (Figure 1). The system was designed to provide a 48-hr hydraulic retention time (HRT) at normal flow with one pair of cells offline (in case of needed maintenance). Hydrosoil for the full-scale wetland system consisted of local soils amended with pine mulch to achieve 3 to 5% organic matter by weight, agricultural lime to neutralize pH (49 g/m^2; 0.01 lb/ft^2), gypsum as a source of sulfur (0.5% sulfur per top 10 cm [4 in.] hydrosoil), and Osmocote time-release fertilizer (300 g/m^2; 0.061 lb/ft^2). Wetland cells were planted from May to July 2000 with *Schoenoplectus californicus* (C.A. Meyer) Palla (giant bulrush) on approximately 1-m (3.28-ft) centers. Plants were obtained from an aquatic plant nursery as root stock, with shoots cut to approximately 30–45 cm (11.8–17.7 in.) in length.

Waste-Stream Characterization

Crucial to this and every constructed wetland treatment system is flow management. The primary concerns for stormwater surges are the hydraulic force exerted and the maintenance of the structural integrity of the constructed wetlands. Because this waste stream comprises process flow from technical facilities (i.e., noncontact cooling water, steam condensate, laboratory drain waste, cooling tower overflow, steam cleaning rack waste, and air stripper effluent) and stormwater runoff, a flow management basin (i.e., retention basin or equalization basin) was constructed (1) to release the volume of stormwater gradually over time and assure that water is provided to the constructed wetlands during summer dry months when rainfall is minimal; and (2) to stabilize the concentration of constituents entering into the wetlands (i.e., dampen fluctuations in the concentrations of copper [range from nondetectable to nearly 0.1 mg/L] that enter the constructed wetland).

Base flow from the technical facilities and stormwater volume were calculated to determine the size of

Figure 1. Schematic flow diagram for constructed wetland treatment designed to remove copper from a waste stream. The sampling locations are the same for each series. The dashed lines represent the estimated HRT (0, 4, 8, 12, 16, 20, 28, 36, 44, 52, and 60) where samples were collected based on approximate linear flow.



the retention basin and account for high flow and minimum flow situations (Lehman et al., 2002). The annual rainfall and seasonal distribution of rainfall were also considered in these calculations (EarthInfo, 1995; Eliasson, 1997). Design criteria for the retention basin included retaining runoff from a 25-yr recurrence interval storm over a 24-hr period and release of the water from the retention basin to the constructed wetlands as necessary to maintain a relatively constant depth of 30 cm (11.81 in.) (Huddleston, 2001; Lehman et al., 2002).

The concentration, form (i.e., species), and bioavailability of divalent metals (such as copper) present in an aqueous system depend on several parameters,

Table 1. Chemical, Physical, and Toxicological Methods Used to Evaluate Performance of Full-Scale Constructed Wetland Treatment System

Analysis	Method
Acid-soluble copper in water samples	Method 200.1 (USEPA, 1996a)
Soluble copper in water samples	Method 220.1 (USEPA, 1983) and Method 3005A (USEPA, 1992b)
Total recoverable copper in plant tissue	Method 3052 using an ETHOS Microwave Digestion Station (USEPA, 1996b)
Total recoverable copper in sediments	Method 3051 using an ETHOS Microwave Digestion Station (USEPA, 1996b)
Hydrosoil redox potential	In-situ platinum electrodes (four per wetland cell, 2–6 cm (0.8–2.3 in.) depth) (Faulkner et al., 1989)
AVSs	Purge and trap method (Allen et al., 1991)
pH	Orion® Model 410 pH meter with Triode® electrode
Hardness	APHA et al. (1995)
Alkalinity	APHA et al. (1995)
Conductivity	Orion® Model 142 conductivity meter
Dissolved Oxygen	YSI® Model 52 dissolved oxygen meter
Toxicity	*C. dubia*, (USEPA, 1994a); *H. azteca* (USEPA, 1994b)

including alkalinity, hardness, pH, ionic strength, and dissolved organic carbon (DOC) (Deaver and Rodgers, 1996). Therefore, in constructed wetlands with copper as a targeted constituent, the waste stream must be adequately characterized. Aqueous copper was measured using two analytical techniques, acid-soluble copper and soluble copper (Table 1). Measurement of acid-soluble copper is designed to measure species of copper that are loosely bound to suspended particles and, therefore, may be potentially toxic to aquatic biota or readily converted to toxic forms. The measurement of soluble copper (USEPA, 1992b) is designed to measure the species of copper in the water column that are most likely to be bioavailable. Grab samples for copper analysis were collected in Nalgene high-density polyethylene bottles and analyzed for copper using a Perkin-Elmer Analyst 800 graphite furnace atomic absorption spectrometer (APHA et al., 1995). Copper standards were prepared using copper reference standard solution (Fisher Scientific) diluted in Milli-Q water. Standards were analyzed immediately before and after sample analysis, with a quality control standard analyzed every 10 samples. Lower detection limit was 2 μg/L.

Other parameters such as dissolved oxygen, pH, conductivity, temperature, alkalinity and hardness, and specific ions (e.g., calcium, chloride, iron, magnesium, nitrogen, phosphate, potassium, and sodium) were monitored in the wetland cells throughout the study. Water characteristics (i.e., dissolved oxygen, pH, conductivity, temperature, alkalinity, and hardness) were measured for each toxicity experiment conducted.

Parameters Influencing Performance

Oxidation-reduction (redox) potential and AVS production in wetland hydrosoil were measured monthly to ascertain that the system was poised for dissimilatory sulfate reduction (Table 1). Redox was measured monthly at four sampling sites within each cell. Redox probes were placed along a diagonal throughout each wetland cell in November 2000 and left in situ for the remainder of the study with periodic maintenance as needed. Redox measurements were made against an Accumet calomel reference electrode using a Fluke 77 III voltage meter. Acid-volatile sulfides in the wetland hydrosoil were measured according to Allen et al. (1991). A composite sediment sample was collected monthly from each cell and held in a 1-L glass jar with water to ensure no head space. The samples were placed on ice for transport to the laboratory and maintained at 4°C (39.2°F) until analysis.

The density of *S. californicus* was measured monthly during the initial growing season and bimonthly as plant growth, and density began to stabilize using a 125-ft (38.1-m) line transect and counting all visible shoots within 15 cm (0.49 ft) of the transect (Smeins and Slack, 1978). Estimates of the change in biomass (g/m^2) over time were accomplished by determining above-ground and below-ground weight and multiplying by the mean density for each sampling date (Hanson, 1987). In-situ decomposition of *S. californicus* was estimated using nylon net litter bags and measuring weight loss over time of dried plant material (Rodgers et al., 1975; Hammerly et al., 1989). Sediment deposition was measured in each cell using cylindrical sediment traps and analyzed to determine the rates of accretion for each wetland cell and the organic matter content of the trapped solids. Organic matter content was estimated by loss on ignition (Nelson and Sommers, 1996).

Performance Evaluation

Two fundamental parameters were important in ascertaining the performance of this system: (1) decreases in aqueous copper concentrations in samples collected from upstream and downstream of the constructed wetland treatment system and from inflow to outflow of the wetland cells (Figure 1) and (2) toxicity measured in 7-day tests using C. *dubia* (survival and reproduction) in samples collected from the same locations. Construction of the wetland treatment system was completed in October 2000, and compliance monitoring began in January 2001. Performance evaluation for this study began in March 2001 and continued until April 2002. For this performance evaluation, aqueous grab samples were collected monthly for copper analysis (acid soluble and soluble) and for toxicity assessment from the waste stream (upstream of the constructed wetland treatment system), the retention basin, inflow of each wetland cell, and 10 locations from inflow to outflow of each wetland series, as well as from the receiving stream (i.e., downstream) (Figure 1). Samples were collected in Nalgene high-density polyethylene bottles and held at 4°C (39.2°F) until analysis.

Toxicity Experiments

C. *dubia* was used in 7-day static and renewal toxicity tests to determine the toxicity of the collected samples to C. *dubia*. C. *dubia* is a freshwater microcrustacean associated with the water in lentic freshwater systems throughout the world. C. *dubia* is commonly used as an USEPA test species because of (1) its worldwide distribution, (2) ease of culturing, (3) time to reproduction, and (4) its relative sensitivity to copper when compared to other test species such as *Daphnia magna* or *Pimephales promelas* (USEPA, 1985; Belanger et al., 1989; Suedel et al., 1996). Tests were conducted by placing one less than 24-hr-old C. *dubia* in each of 10 replicates containing 15 mL (0.91 in.^{3}) of undiluted sample collected from each location. For each toxicity experiment, a control using moderately hard well water was also tested. This protocol was adapted from the USEPA protocol for chronic toxicity of effluents and receiving waters to freshwater organisms (USEPA, 1994a) (Table 1). The end points for C. *dubia* were reproduction and mortality. Daily renewals and feeding were conducted throughout the toxicity experiments, and water quality (i.e., dissolved oxygen, pH, conductivity, temperature, alkalinity, and hardness) was monitored. C. *dubia* were fed 0.1 μL of *Raphidocelis subcapitata* and yeast-cerophyll-trout chow daily.

Potential toxicity of the hydrosoil was determined using *Hyalella azteca* in 10-day static, whole sediment laboratory toxicity experiments (USEPA, 1994b). *H. azteca* is an epibenthic detritavore that inhabits aquatic systems throughout North and South America. *Hyalella* are commonly used as an USEPA benthic test organism for sediments because of their ease of culture and ability to tolerate a wide range of water characteristics and substrates. At test initiation, approximately 50 mL (3.1 in.^{3}) of sediment collected quarterly from four locations, approximately every 35 m (114.8 ft) within each wetland cell, was placed into borosilicate glass beakers (exposure chambers). Water collected from downstream of the constructed wetland was immediately placed over the sediment, and the exposure chambers were allowed to equilibrate for 24 hr prior to the addition of organisms. A control consisting of moderately hard water and reference sediments, as well as a water-only control of downstream water was also tested. Ten 2–3-week-old *H. azteca* were added to each exposure chamber and maintained at 25 ± 2°C (77 ± 4°F) with a 16-hr-light–8-hr-dark photoperiod. Test organisms were fed leached maple leaves (three 7-mm [0.28 in.] disks, *Acer rubrum*). The end points for *H. azteca* were survival and growth.

Statistical Analysis

Statistical analyses for performance based on decreasing concentrations of copper were conducted using SAS®. Nonlinear regression analysis (Gauss-Newton) was conducted to test the goodness of fit of the measured concentrations from within the wetland cells to the first-order removal model. For each nonlinear regression analysis, power analysis, univariate procedures, and Shapiro-Wilks test for normality were conducted. A two-way repeated-measures analysis of variance (ANOVA) and *F* distribution ($\alpha = 0.05$) were conducted to compare monthly performance between cells and seasonal performance.

The statistical analysis of organism survival and reproduction was performed to determine if differences existed between groups exposed to upstream, retention basin, and downstream water and samples collected from each location (inflow to outflow) within the wetland cells. Data normally distributed with homogeneous variance were analyzed using the Fisher's exact test followed by ANOVA ($\alpha = 0.05$) and Dunnett's test. Data not meeting these criteria were analyzed using one-way ANOVA on ranks. Differences, if any, were determined with multiple range tests, with $\alpha = 0.05$. Tests for normality and homogeneity of variance were performed using the Shapiro-Wilks test and Bartlett's test, respectively. Toxicological calculations were performed using TOXSTAT 3.5 (Western, Inc and Gulley, 1996).

RESULTS

Characterization of the Waste Stream

Total process flow was estimated at 3369 m^3/day (890,000 gal/day). The stormwater retention basin was designed to retain runoff from a 25-yr recurrence interval storm over a 24-hr period, with stormwater volume estimated at 52,996 m^3 (1,871,539 ft^3) in a 24-hr period based on 15.5 cm (6.10 in.) of rain over a 24-hr period (EarthInfo, 1995; Eliasson, 1997). Using these estimates, the retention basin was designed for a capacity of 79,540 m^3 (2.8 million gal). Based on these calculations and the time required to achieve treatment of copper (<24-hr through binding with AVS and sorption to inorganic and organic ligands), the HRT needed for this constructed wetland system was 48 hr at a 30-cm (11.81-in.) water depth. This allowed an average daily flow to the wetland cells of approximately 0.04 m^3/s (0.97 million gal/day), with low flow of 0.01 m^3/s (250,000 gal/day) and peak flow of 0.11 m^3/s (2.6 million gal/day).

As stated previously, the form (i.e., species) and bioavailability of copper in an aqueous system is dependent on the characteristics of that system, including alkalinity, hardness, pH, ionic strength, and DOC. Table 2 lists ranges of concentrations for water samples collected from upstream of the constructed wetland treatment system (i.e., from the A-01 waste stream), the retention basin, within the constructed wetland cells, and downstream of the wetland cells (i.e., in the receiving stream). This waste stream could be categorized as soft water, with an average alkalinity and hardness of 16 mg/L (range = 8–20 mg/L) as $CaCO_3$ and 7 mg/L (range = 4–16 mg/L) as $CaCO_3$, respectively (Table 2). Temperature for the 14 months of the study ranged from lows of 0.6–24°C (33–75.2°F) to highs of 14.0–35.0°C (57.2–95°F)

Table 2. Water Characteristics*

	In situ	Characteristics of Water Used in Toxicity Experiments				
Parameter	Wetland Cells	Upstream	Retention Basin	Primary Constructed Wetland Cell	Downstream	Moderately Hard Well Water
Temperature (°C)	18.9 (5.4–35.6)	21.6 (20.0–23.1)	21.5 (20.1–22.3)	21.4 (18.3–23.1)	21.5 (19.6–22.4)	21.9 (19.9–24.0)
pH	5.9 (4.7–8.7)	7.5 (7.3–7.6)	7.4 (7.2–7.5)	7.6 (6.6–8.8)	7.7 (7.5–7.8)	8.2 (7.8–8.6)
Hardness (mg/L as CaO_3)	NA	7 (4–8)	7 (5–8)	14 (4–38)	6 (4–8)	81 (60–94)
Alkalinity (mg/L as $CaCO_3$)	NA	16 (8–20)	19 (17–20)	20.3 (10–24.2)	16 (10–20)	82 (68–100)
Conductivity (μmhos/cm)	48.3 (19.4–114.7)	65.5 (31.0–112.0)	66 (39.0–110.0)	49 (32.7–72.4)	41 (35.0–47.0)	272.4 (219.0–309.0)
Dissolved oxygen (mg/L)	6.8 (1.6–18.0)	8.8 (7.4–11.2)	7.9 (7.4–8.2)	8.5 (7.0–11.2)	8.3 (7.4–7.9)	8.3 (7.7–8.8)

*Mean and ranges of in-situ constructed wetland waters and waters collected from the constructed wetland treatment system for toxicity experiments.

Table 3. Temperature Log for Constructed Wetland Treatment System at SRS, Aiken, South Carolina

Date	Temperature, °C (°F)		Precipitation, cm (in.)
	Low	High	
March 2001	5.6 (42.1)	16.7 (62.1)	ND*
April 2001	8.0 (46.4)	22.0 (71.6)	0.13 (0.05)
May 2001	12.2 (54.0)	30.6 (87.1)	0.99 (0.39)
June 2001	21.0 (69.8)	33.2 (91.9)	3.20 (1.26)
July 2001	22.0 (71.6)	32.7 (91.0)	0.56 (0.22)
August 2001	24.0 (75.2)	35.0 (95.0)	ND
September 2001	10.6 (51.1)	27.0 (80.6)	ND
October 2001	12.8 (55.0)	29.4 (84.9)	0.07 (0.03)
November 2001	15.6 (60.1)	28.2 (82.9)	0.25 (0.10)
December 2001	6.7 (44.1)	14.0 (57.2)	2.00 (0.79)
January 2002	0.6 (33.1)	33.7 (92.7)	ND
February 2002	11.7 (53.1)	22.2 (72.0)	0.48 (0.19)
March 2002	14.0 (57.2)	29.4 (84.9)	0.64 (0.25)
April 2002	12.8 (55.0)	30.0 (86.1)	ND

*ND = below trace amounts.

(Table 3). Average rainfall ranged from nondetectable to 3.2 cm (1.26 in.) (Table 3).

Parameters Influencing Performance

Redox potential and AVS concentrations measured in wetland hydrosoil indicated that this constructed wetland treatment system could support dissimilatory sulfate reduction over time, which is necessary for this system to continue to precipitate copper from the water column as copper sulfide minerals. The average redox of the constructed wetlands was -133 ± 27 mV (range = -17 to -261 mV), which is within the desired range of -75 to -250 mV. Acid-volatile sulfides are another measurement indicative of wetland function for removing copper from aqueous phase and limiting copper bioavailability. Average AVS and simultaneously extractable copper (SECu) was 1.4 ± 0.71 and 0.06 ± 0.05 μmol/g, respectively (Figure 2). The mean concentration of copper sorbed to sediments was 5.2 ± 1.3 mg/kg (ranging from 59 mg/kg at the inflow of the primary cell to 4 mg/kg at the outflow of the secondary cell).

The mean density of *S. californicus* increased from 9.4 shoots/m^2 (0.94 shoots/ft^2) to 24.2 shoots/m^2 (2.26 shoots/ft^2) in the first growing season and declined to 2 shoots/m^2 (0.17 shoots/ft^2) at the end of winter. During the second growing season, the density increased to 70 shoots/m^2 (6.54 shoots/ft^2) by July 2002 (Figure 3).

Material collected in sediment traps provided a conservative measure of the quantity of sedimenting solids and the associated organic matter content of particulates settling from the water column. The mean sedimentation rate for the 11 months studied was 14 ± 0.5 kg/m^2/yr (Table 4), with an average deposition of suspended particulates of 38.5 ± 1.4 g/m^2/day. Assuming an average silt/clay bulk density of 1.3 g/cm^3 (Fennessy et al., 1994), 1.1-cm/yr (0.43-in./yr) accumulation is predicted before compaction. From August 2001 to April 2002, sediment trap contents were analyzed for percent organic matter to assess relative contributions of primary production to sediment accumulation (Fennessy et al., 1994). Mean organic matter fraction ranged from 15.2 to 48% for the 8 months tested (Table 4). From the data collected, the organic matter content in the depositing sediments peaked during the time *S. californicus* senesced (November to March) and declined during the growing season (August and September).

Organic matter present in this system is oxidized by sulfate-reducing bacteria in the reduction of sulfate and provides organic ligands for binding copper as well. If the rate of growth of sediments or hydrosoil caused by organic matter accretion exceeds the rate of accumulation of copper in the sediments, then the concentration of copper (in units of milligrams of Cu per kilogram of sediment) should not increase to levels of concern. Using the mass loading of copper to the system (8 g/day) and the average deposition of solids, the estimated concentration of copper in the active layer of the constructed wetland hydrosoil is less than 25 mg Cu/kg sediment. Using the mass of copper loaded to the system during the study period and the mass of copper associated with the sediment and vegetation, 61% of the copper was partitioned to the sediments (of which 36% was associated with AVSs), and 7% of the copper was sorbed by *S. californicus*. Fifteen percent of the copper that entered the wetland was measured in the outflow. The remaining 17% was not accounted for in these measurements.

Performance Evaluation

To determine the rate and extent of change in copper concentrations, copper was measured in samples collected from upstream of the constructed wetland treatment system, 11 locations from inflow to outflow within the constructed wetland cells and in the receiving stream

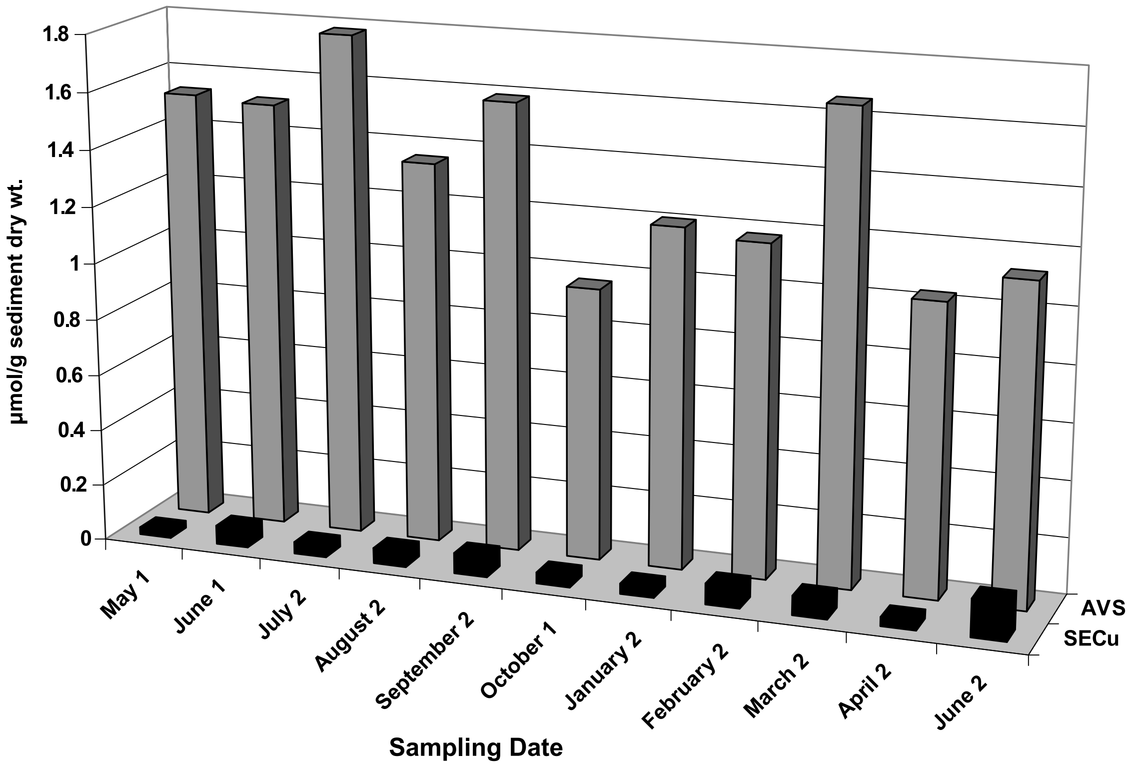


Figure 2. Acid-volatile sulfide and SECu concentrations measured in hydrosoil collected from constructed wetland treatment system designed to treat a copper-contaminated waste stream. Values presented are the mean of composited samples collected from primary and secondary cells of each series (May 2001 to June 2002).

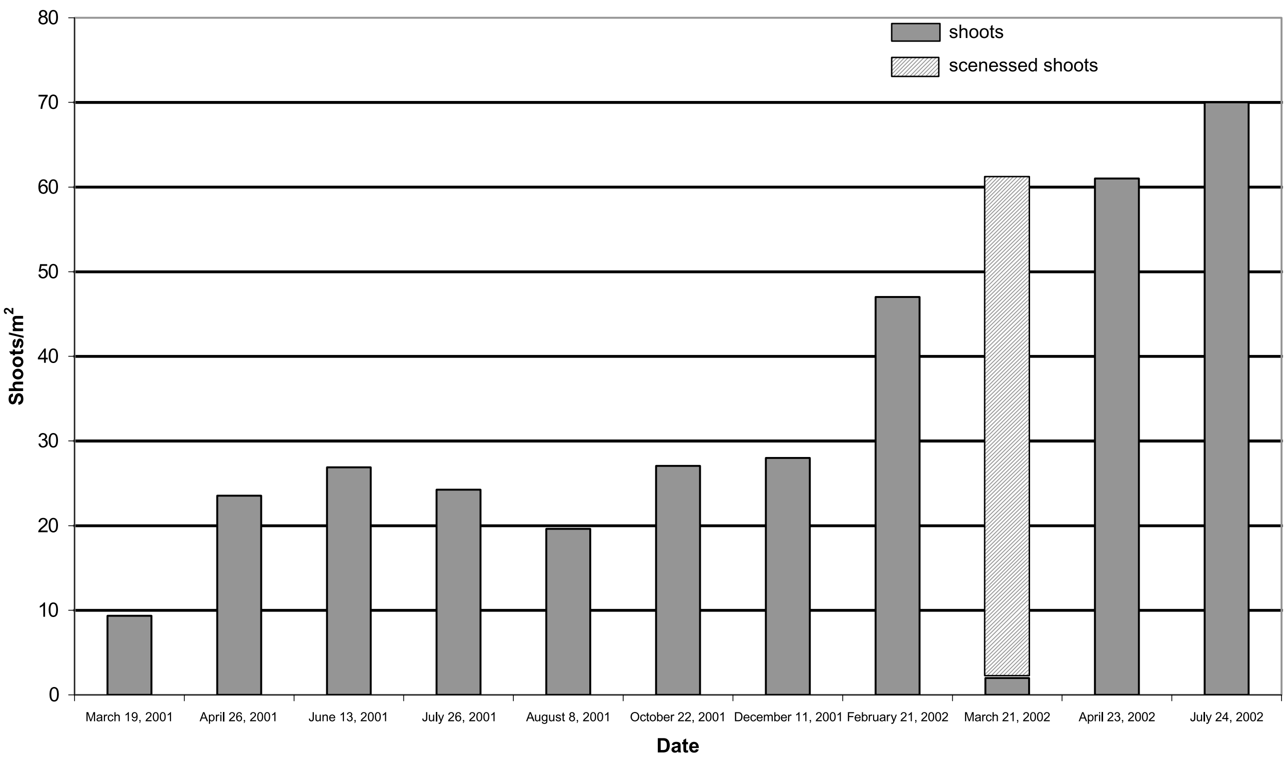


Figure 3. Mean stem density of *S. californicus* in a constructed wetland designed to decrease the concentration of bioavailable copper in a waste stream. Initial stem density at planting 1 plant/m^2 (May–July 2000).

Table 4. Mean Sedimentation Rate and Organic Matter Content*

Date	Mean Sedimentation Rate ($g/m^2/day$)	Mean Organic Matter (%)
May 2001	28.6 (8.5–42.2)	NA
June 2001	6.1 (2.5–9.5)	NA
July 2001	5.2 (4.1–8.7)	NA
August 2001	7.1 (3.7–12.5)	19.6 ± 5.2
September 2001	3.0 (0.9–8.0)	15.2 ± 3.0
October 2001	2.2 (0.9–4.1)	24.1 ± 8.7
November 2001	5.8 (0.3–8.1)	48.0 ± 22.4
December 2001	3.4 (1.7–6.5)	31.9 ± 14.1
January 2002	5.4 (1.1–9.5)	34.7 ± 10.0
February 2002	3.4 (1.6–7.2)	38.7 ± 24.0
March 2002	5.7 (1.2–15.1)	32.6 ± 7.8
Average deposition ± S.D. ($g/m^2/day$)	38.5 ± 1.4	
Average organic matter (%)		30.6 ± 10.7
Total deposition ($kg/m^2/yr$)	14.1 ± 0.5	

*From sediment trap samples collected from constructed wetland treatment system designed to remove copper from a waste stream.

(Figure 4). In all cases, downstream concentrations of the constructed wetland treatment system were significantly decreased compared to upstream concentrations ($\alpha < 0.05$), and the permit criterion of ≤22 μg/L was achieved. Average acid-soluble Cu concentrations (±S.D.) were 31 ± 10 μg/L (range = 10–47 μg/L) and 6 ± 3 μg/L (range = 3–11 μg/L) in the upstream (i.e., inflow to the constructed wetland prior to the retention basin) and downstream (i.e., outflow to the receiving stream) of the constructed wetland treatment system, respectively (Table 5; Figure 4). Soluble copper concentrations were 15 ± 7 μg/L (range = 5–25 μg/L) and 3 ± 2 μg/L (range = nondetectable to 5 μg/L) for upstream and downstream (Table 5; Figure 4). During the 13 months of this study, copper concentrations varied significantly in the waste stream from month to month. Percent removal for each month as measured by simple performance (i.e., $\text{concentration}_{\text{in}}$ versus $\text{concentration}_{\text{out}}$) ranged from 54 to 92% for acid-soluble copper removal and 50–94% for soluble copper.

Average inflow concentrations to the first wetland cell (cell A) were 31 and 14 μg/L for acid-soluble and soluble copper, respectively. The average outflow concentrations from the first cell and, therefore, the inflow concentrations to the second cell (cell B) were 9 and 5 μg/L for acid-soluble and soluble copper, respectively. Outflow concentrations for the second cell (cell B) are 6 and 3 μg/L for acid-soluble and soluble copper, respectively (Figure 4).

Rate coefficients for copper transfer and transformations were estimated by two methods: (1) the first-order model: $C_t = C_i e^{-kt}$ where C_t and C_i are average acid-soluble copper concentrations at time t (i.e., 6 μg/L at 64 hr) and average initial concentration (i.e., 31 μg/L), respectively; and (2) by nonlinear regression analysis using measured acid-soluble copper concentrations for each of the eight locations in cell A (i.e., first cell in wetland series) and four locations in cell B (i.e., second cell in wetland series) (Figure 1). A rate coefficient for copper removal was also determined by regression analysis using the 11 samples from inflow to outflow of the wetland cells. Removal rates were estimated for each of the four series of wetland cells and using an average from the four series. In both models, k is the overall copper transfer and transformation (i.e., removal) rate coefficient with units of t^{-1}. This k can be expressed as the transfer or transformation half-life ($t_{1/2}$) or the time required to decrease the inflow copper concentration by 50% given the equation $T_{1/2} = \ln 2/k = 0.693/k$. Using the first-order model, the resulting k for this system was 0.026 hr^{-1}, with a transfer and transformation half-life of 26.7 hr based on flow. Using nonlinear regression analysis, the average k for the 13-month study was 0.029 hr^{-1}, with a transfer and transformation half-life of 23.6 hr. This corresponds to a distance of 96 m (314 ft) from the inflow of the primary cell. Because an exponential decrease in copper concentrations occurs in the first cell, separate rate coefficients and half-lives were calculated for each of the two cells of the treatment series. The results for these analysis were k_A = 0.039 hr^{-1} ($t_{1/2}$ = 18.0 hr) and k_B = 0.013 hr^{-1} ($t_{1/2}$ = 54.6 hr) for the primary and secondary cell, respectively.

Toxicity Experiments

Survival and reproduction of C. *dubia* in 7-day exposures to upstream and downstream waters were also used as measures of treatment performance. With the exception of April and May 2001, 100% mortality was observed in toxicity experiments with C. *dubia* exposed to upstream waters (March 2001–April 2002). No mortality was observed in samples collected in either April or May 2001; however, reproductive effects were observed in May ($\alpha = 0.05$). During these 2 months, soluble copper concentrations were 4.5 and 6.5 μg/L, respectively. During the 13 months of the study, no toxicity to C. *dubia* in terms of survival or

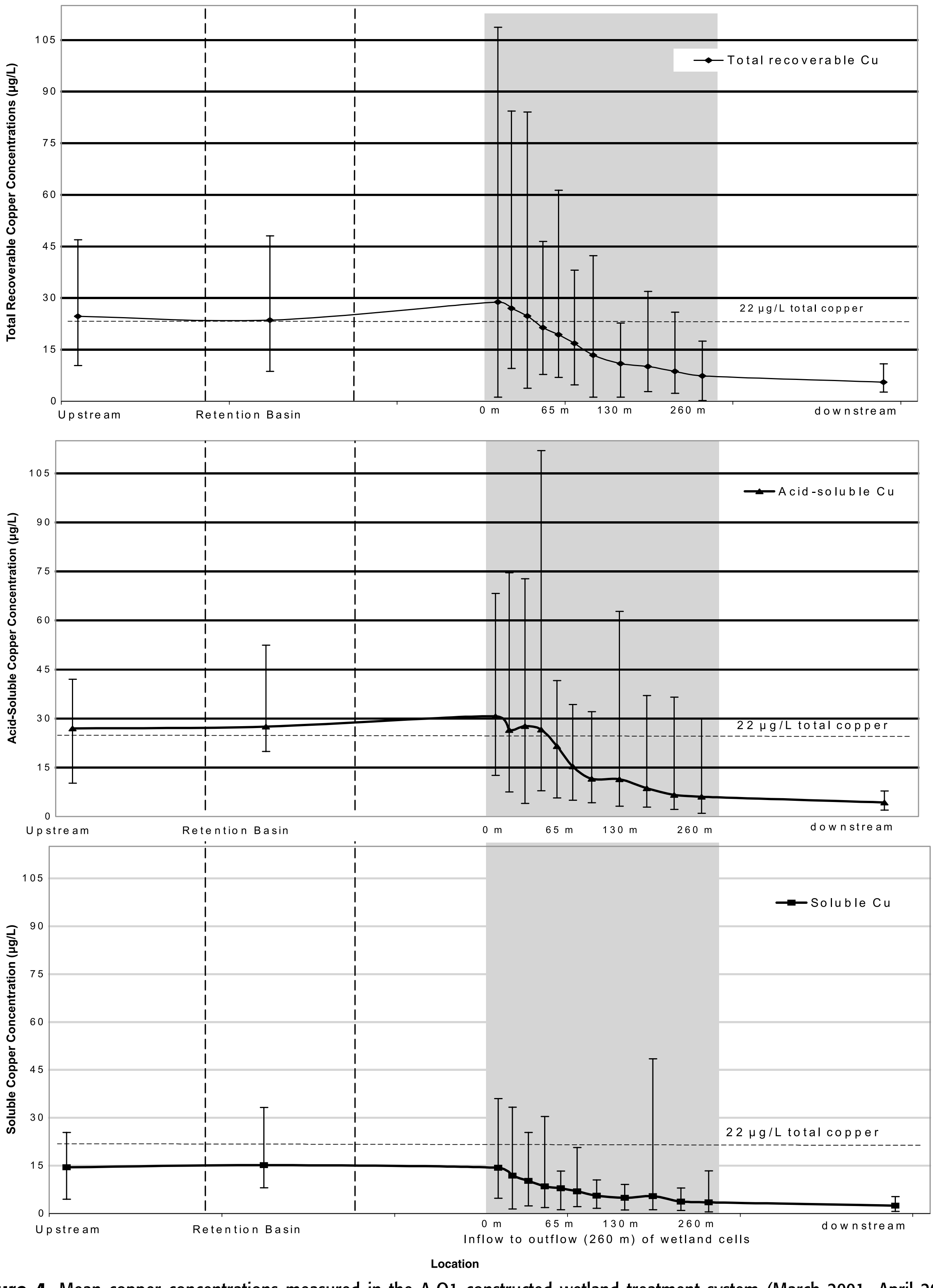


Figure 4. Mean copper concentrations measured in the A-O1 constructed wetland treatment system (March 2001–April 2002). Error bars represent range of values measured from March 2001 to April 2002. Concentration within the dashed lines represents the retention basin, and the shaded gray area represents samples collected from within the wetland cells.

Table 5. Monthly Copper Measurements in the Inflow (Upstream–above Retention Basin) and Outflow (Downstream) of the Constructed Wetland Treatment System

Date	Acid-Soluble			Soluble		
	Inflow (μg Cu/L)	Outflow (μg Cu/L)	% Removal	Inflow (μg Cu/L)	Outflow (μg Cu/L)	% Removal
March 2001	10.2	2.1	80	7.2	1.2	83
April 2001	25.6	2.7	89	4.5	0.7	84
May 2001	22.8	3.9	83	6.5	1.5	77
June 2001	33.5	2.6	92	23.5	1.5	94
July 2001	42.0	4.1	90	12.4	1.9	85
August 2001	24.6	3.1	87	15.5	1.2	94
September 2001	27.3	5.1	81	15.7	1.5	90
October 2001	19.6	4.1	79	11.4	2.5	78
November 2001	22.9	6.9	70	12.2	2.6	79
December 2001	29.0	4.6	84	17.6	4.8	73
January 2002	20.2	9.2	54	10.3	5.1	50
February 2002	18.6	8.1	56	9.6	4.2	56
March 2002	39.2	7.8	80	25.4	5.3	79
April 2002	14.5	3.2	78	7.3	2.3	71

reproduction was observed following 7-day exposures to downstream waters.

Survival and reproduction for C. *dubia* were also measured at 11 sample locations from inflow to outflow of the wetland cells (Figures 1, 5). However, because toxicity was removed within the first cell, only results from the primary cells are reported (i.e., no significant mortality or reproductive effects were observed in the second cell). Survival in waters collected from the inflow to the first wetland cell averaged 20% (range from 0 to 90%) during the 13 months of the study. Survival of C. *dubia* increased in samples collected as the water flowed through the first cell, averaging 91% survival (range = 70–100%) in samples collected at the outflow to the primary cell. Average survival for the control organisms was 98%. Reproduction similarly increased as water flowed from inflow to outflow of the wetland cells, and the concentration of soluble copper decreased (Figure 5). The average of eight neonates per female in waters collected from the inflow of the primary cell (cell A) increased to an average of 24 neonates per female in waters collected from the outflow of the primary cell. This reproduction in waters collected from the outflow of the primary cells was not significantly different from the reproduction observed for control organisms (average control = 26 neonates/female). In samples where significant partial mortality occurred (>30% mortality), the surviving organisms were still able to reproduce, although the number of offspring was significantly less than control organisms. During the 13 months of the study, the pH of the test waters ranged from 6.6 to 8.8, hardness ranged from 4 to 8 mg/L as CaO_3, alkalinity ranged from 8 to 20 mg/L as CaO_3, and conductivity was between 35 and 112 μmhos/cm.

In addition to aqueous toxicity experiments, sediment samples were collected from several locations within the primary (0–16, 48, 81, and 114 m [0–52, 158, 265, and 374 ft] from inflow) and secondary (146, 178, 211, and 243 m [479, 584, 692, and 797 ft] from inflow) wetland cells and subjected to sediment toxicity experiments in the laboratory using *H. azteca* in 10-day static exposures (Table 6). The mean percent survival for the 24 samples tested ranged from 81 to 96%, with significant mortality ($\alpha = 0.05$) observed in only two samples tested. Survival of organisms in the moderately hard controls and in the downstream controls was 95 and 96%, respectively. No significant differences in growth relative to the control were observed in any of the experiments conducted. In samples collected on October 22, 2001, and January 17, 2002, from the primary cells in series 2, survival of *H. azteca* was 60 ± 3 and 65 ± 3%, respectively. Survival of organisms exposed to control sediments was 95 ± 3% survival and 100% survival for each of these sampling dates, respectively. Following the exposures where mortality was observed, the pH of the overlying water ranged from 4.3 to 5.3 in these treatments compared to a range of 5.5–7.3 observed in the overlying water from the rest

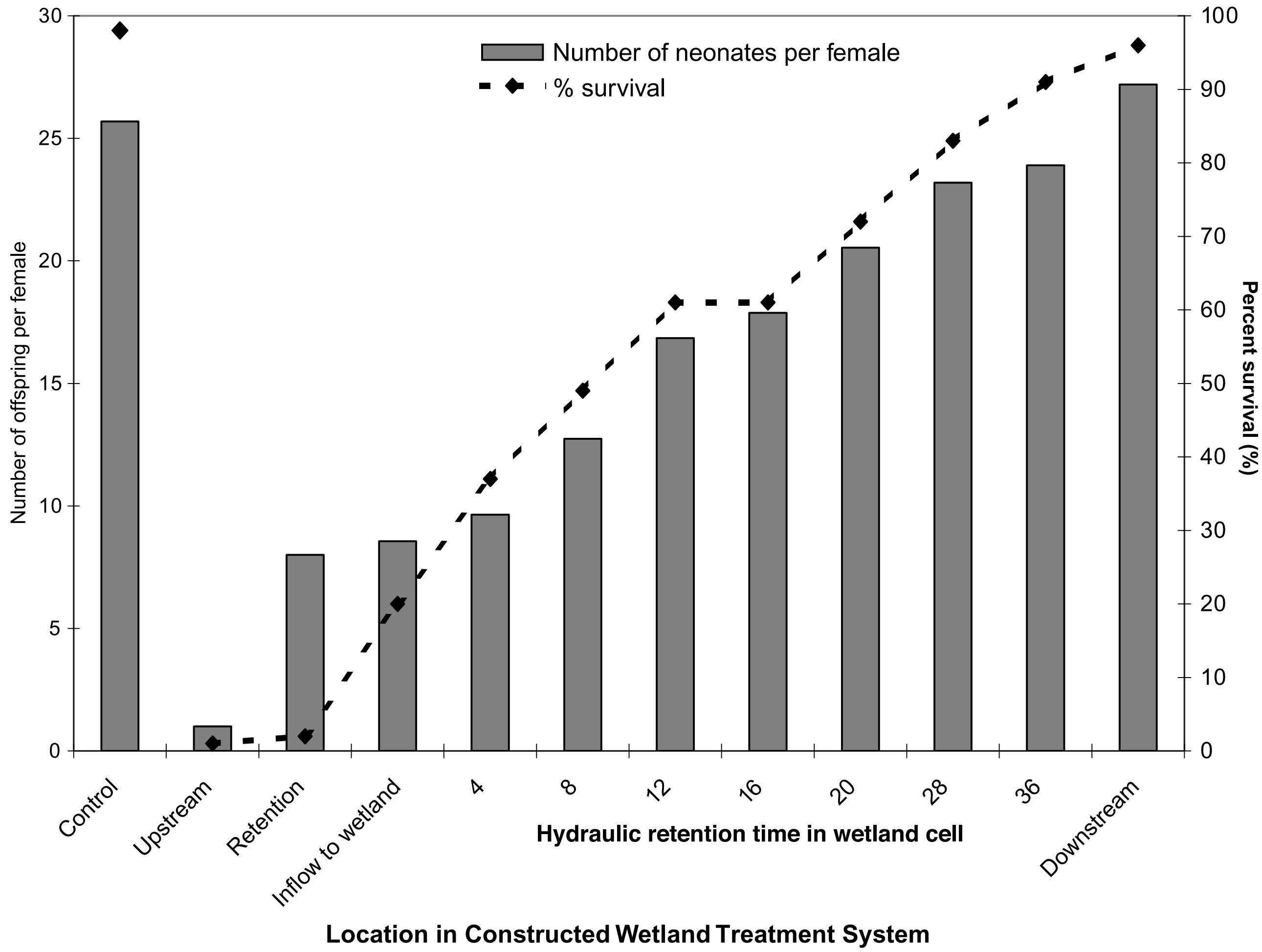


Figure 5. *C. dubia* survival and reproduction measured in aqueous samples collected from upstream, retention basin, inflow to outflow of constructed wetland cell A, and downstream of the constructed wetland treatment system designed to decrease bioavailable copper in a wastewater stream.

of the treatments (Table 7). Because of the fact that the copper concentrations measured in the overlying water were less than 5 µg/L and the concentrations of copper measured in the hydrosoils from these cells ranged from 3 to 27 mg/kg, the observed mortality was likely caused by the change in water chemistry that occurred during the experiment and was not a result of the copper concentrations in the sediments (Table 7). The dissolved oxygen remained above 6.2 mg/L throughout the toxicity experiments.

Variability between Constructed Wetland Cells and Seasonal Performance

Because four series of wetland cells (i.e., four replicate pairs of cells) in this constructed wetland system are present, an ANOVA between the performance of each series of cells was conducted to determine if wetlands constructed in a similar manner would behave similarly. Based on the rate of removal of copper from the aqueous phase measured for each cell, a significant difference in the performance of the four cells was observed in only 1 of the 13 months of the study. In October, because of variance in copper concentrations within the primary and secondary cells, one set of wetland cells was different. However, the measured outflow concentration was similar to the other cells (approximately 3 µg/L acid-soluble copper). Variability in seasonal performance was also evaluated in this study. Based on average rate coefficients determined for each season (where spring = March, April, May; summer = June, July August; etc.), no significant difference ($\alpha = 0.05$) was observed in the seasonal performance of this constructed wetland treatment system. However, individual declines of performance in colder months indicate the need for caution and adjustment of rate coefficients for biotic processes such as dissimilatory sulfate reduction.

Table 6. Survival of *H. Azteca**

Cell	% Survival ± S.D.				
	October 22, 2001	January 10, 2002	April 22, 2002	July 24, 2002	Average
Control	95 ± 3	100	95 ± 1	98 ± 1	96 ± 2
Downstream water**	93 ± 3	90 ± 2	98 ± 1	100	95 ± 2
Cell 1A	88 ± 3	85 ± 2	95 ± 1	97 ± 2	92 ± 6
Cell 1B	NT†	NT	95 ± 1	97 ± 1	96 ± 2
Cell 2A	60 ± 3††	65 ± 3††	93 ± 1	97 ± 1	81 ± 19
Cell 2B	NA‡	NA	85 ± 1	93 ± 1	88 ± 6
Cell 3A	90 ± 1	93 ± 2	85 ± 2	80 ± 1	87 ± 6
Cell 3B	NT	NT	78 ± 1	93 ± 1	83 ± 10
Cell 4A	90 ± 1	93 ± 1	95 ± 1	100	95 ± 4
Cell 4B	NT	NT	90 ± 2	97 ± 1	92 ± 5

*Exposed (10 days) to sediments collected from inflow to outflow of a constructed wetland treatment system designed to remove copper from a waste stream.
**Downstream water collected from the receiving stream was used as the overlying water in *H. azteca* experiments.
†NT = toxicity test was not conducted for secondary cell for this sampling date.
††Statistically different from control (α = 0.05).
‡NA = not applicable.

DISCUSSION

As stated previously, an understanding of internal thermodynamic processes and design criteria that affect the removal of targeted constituents in constructed wetlands and contribute to the overall performance is necessary to transfer constructed wetland technology accurately or reliably from site to site. Specific design parameters that should be identified are (1) character of the wastewater, including the targeted constituents; (2) performance goals or desired levels of treatment; (3) transfer and transformation pathways; (4) flow rates and retention time required to achieve treatment; and (5) climate (i.e., temperature and precipitation).

The constructed wetland used in this research was specifically designed to treat a waste stream that occasionally failed to meet the numeric criterion of ≤22 μg total copper/L and consistently failed to achieve the narrative criterion of "no chronic toxicity to C. *dubia*." Therefore, the goal of this treatment system is to decrease the fraction of copper that exists in the waste stream as free divalent ion (Cu^{2+}) by promoting copper

Table 7. Characteristics of Overlying Water*

Parameter	Control	Date			
		October 22, 2001	January 10, 2002	April 22, 2002	July 24, 2002
pH (overlying water)	6.8–8.2	4.7–7.2	4.3–6.5	6.4–6.6	7.2–8.0
Dissolved oxygen (overlying water) (mg/L)	6.8–8.3	6.3–6.9	6.2–7.2	6.5–7.2	6.7–7.6
Conductivity (overlying water) (μmhos/cm)	219–309	39–93	31–78	40–68	52–94
Alkalinity (overlying water) (mg/L as $CaCO_3$)	68–100	8–20	10–24	10–20	8–22
Hardness (overlying water) (mg/L as $CaCO_3$)	60–94	4–8	5–8	4–8	4–10
Soluble Cu in overlying water, μg/L (range)	ND**	2.9 (2–4)	1.7 (1–3)	3.3 (2–5)	2.3 (1–4)
Acid-soluble Cu in overlying water, μg/L (range)	ND	3.9 (3–5)	4.8 (4–6)	5.2 (4–8)	4.4 (3–8)
Cu in hydrosoil primary cell, mg/kg (range)	ND	6 (3–26)	4 (2–8)	6 (1–44)	26 (4–111)
Cu hydrosoil secondary cell, mg/kg (range)	ND	3 (2–6)	3 (2–7)	4 (3–5)	NA

*Measured at test termination in experiments conducted with *H. azteca* exposed to sediments collected from inflow to outflow of a constructed wetland treatment system designed to remove copper from a waste stream.
**ND = below detection limit.

interactions with wetland macrofeatures, including hydrosoil, vegetation, and hydroperiod (Hawkins et al., 1997; Gillespie et al., 2000; Huddleston et al., 2000). Together, these macrofeatures contribute to the thermodynamic transfers and transformations of contaminants in wastewater to less toxic forms (Mitsch and Gosselink, 1993). Specific contributions of the macrofeatures to this constructed wetland treatment system have been explored in previous publications (Murray-Gulde et al., 2005, in press). For this constructed wetland, copper's lithic biogeochemical cycle was coupled with the sulfur and carbon cycles to remove copper from the water column and sequester it in the sediments. According to the Cu-C-S-O-H model developed by Brookins (1988), CuS and Cu_2S should be the dominant copper species in wetland hydrosoil given a sufficiently negative redox (< -75 mV) and circumneutral pH. To ensure the formation of CuS and Cu_2S, sufficient sulfides must be present in the system. Sulfides are produced when sulfate in the constructed wetland is reduced during the oxidation of organic matter by sulfate-reducing bacteria. To decrease the concentrations of bioavailable copper over a period of time, sulfide production must occur at a rate that exceeds the rate of copper loading to the system. By using AVSs as a measurement of sulfide production and determining the concentration of copper simultaneously extracted from the hydrosoil sample, an estimate of the proportion of copper loaded to the constructed wetland system that is likely bound as insoluble sulfide minerals and unavailable to aquatic organisms can be obtained (Di Toro et al., 1990; Ankley et al., 1996; Berry et al., 1996). In this study, AVS exceeded SECu in all cases, indicating an adequate pool of AVS for binding the available metal.

From calculations of copper partitioning in this system, sediments account for 61% of the copper loaded to the system, with AVSs sequestering 36% of the copper from the water column and the remaining 25% sorbing to other sediment fractions. Of the copper sorbed to other fractions, the organically bound and residual fractions (i.e., detrital silicate minerals, resistant sulfides, and refractory organic material) constitute the highest percentage (~50–60%) of measured copper (Murray-Gulde et al., in press). Copper bound to these fractions is unlikely to be mobilized and can be considered nonbioavailable (Tessier et al., 1979; Dollar et al., 2001; Morera et al., 2001). In toxicity experiments conducted by exposing *H. azteca* to hydrosoil collected from within the wetland cells, no effects on growth or survival of *H. azteca* exposed to wetland hydrosoils were detected, with the exception of samples collected in October 2001 and January 2002 from wetland primary cell 2. However, the toxicity observed in these two samples was attributed to low pH in the overlying water (i.e., pH < 5). This low pH was likely caused by the liberation of H^+ ions as copper reacted with hydrogen sulfide present in the sample, forming sulfuric acid (Huddleston, 2001). *S. californicus* roots and shoots retained 7% of the copper loaded to the system. Of the copper associated with the sediments and plants, a trend of declining concentrations was observed in the sediments and roots from wetland inflow sites to outflow sites (i.e., concentrations were not evenly distributed through the wetland cells). A trend was not observed for shoots because significant amounts of copper were not translocated from roots to shoots.

The productivity and decomposition of *S. californicus* are important in this system to drive dissimilatory sulfate reduction producing HS^- that precipitates copper as stable sulfide minerals. A general increase in above- and below-ground biomass was observed throughout the study, and detritus decomposition in this constructed wetland system was sufficiently slow that residual biomass from previous growing seasons (approximately 23%) exists at the time of senescence of the present standing crop. Therefore, organic matter will accrete over time within the constructed wetland system (Johnston, 1991; Vymazal et al., 1998). Based on the sedimentation rates measured in this system, an estimated 1.1-cm/yr (0.43-in./yr) accumulation is predicted before compaction. Because this constructed wetland is designed to remove copper by precipitation from the water column and sequestration in the sediment, an accreting system will ensure an organic carbon source for sulfate-reducing bacteria over time (Johnston, 1991; Moshiri, 1993; Mitsch and Wise, 1998) and allow for the mass of sediments within the system to grow at a rate that exceeds the mass of metal entering the system.

In addition to understanding the fundamental design principles and pathways invoked in this constructed wetland, an analysis of the specific character of this waste stream is required. Because this constructed wetland treatment system was designed to treat stormwater runoff, a retention basin was built to lessen the hydraulic force of stormwater surges that may weaken the stability of downstream structures or short circuit the retention time required for treatment of the target constituents (24 hr for copper). In addition to using the retention basin as a flow management structure, it also serves to stabilize the copper concentrations that, during the course of this study, fluctuated between 10 and 42 µg

Cu/L in the waste stream. When calculating performance of a constructed wetland system, if the inflow concentrations are highly variable and the percent removal for the system remains the same over time, the outflow concentrations will also be highly variable, making the performance of the system difficult to assess.

In addition to characterizing the stream physically and chemically, if aquatic organism toxicity is a treatment criterion, the waste stream must be assessed toxicologically (Belin et al., 2000). For constituents such as metals, where changes in both the concentration and form of metal are necessary to achieve changes in bioavailability manifested as changes in toxicity (Erickson et al., 1996), analytical measurements of total or general constituent concentrations commonly fail to provide an accurate assessment of treatment performance. This was observed in 5 of the 14 samples from this study where the waste stream (prior to treatment) met the regulatory limit of less than 22 μg Cu/L; however, significant toxicity was observed. In each of these cases, toxicity was removed following treatment by the constructed wetland.

In this constructed wetland treatment system, average acid-soluble copper concentrations decreased by 85%, and soluble copper decreased by 83% from upstream of the system to downstream, illustrating the ability of this constructed wetland design to function in transferring (removing) and/or transforming Cu associated with the water column. In addition to decreasing concentrations of copper, this system also effectively removed the toxicity associated with the bioavailable fraction of copper. In most cases, the aqueous samples collected from the waste stream prior to entering the constructed wetland treatment system were toxic to C. *dubia*. However, no toxicity was observed in the downstream samples collected from the outflow to the receiving stream, demonstrating the removal of bioavailable copper within the treatment system.

Although this simple performance information (inflow versus outflow) may be useful for a cursory evaluation of this constructed wetland treatment system, a more thorough characterization of internal treatment performance is necessary to transfer this technology from site to site. In other words, traditional performance will indicate the achievement of the desired treatment efficiency of the constructed wetland (in this case, $\leq$22 μg Cu/L and no chronic toxicity to C. *dubia*), but it does not provide information on where within the constructed wetland treatment objectives are accomplished. Because every waste stream is a mixture of constituents, every waste stream is inherently different in terms of initial water characteristics. If the character of the water differs from site to site, it is unreasonable to assume that a constructed wetland design can be moved from site to site without accounting for the difference in the initial character of the water. Therefore, the accurate and reliable transfer of constructed wetland technology from site to site requires the understanding of the transfer and transformation pathways invoked in the constructed wetland and scaling of these pathways to fit the characteristics of the waste stream.

In this constructed wetland system, the bioavailable fraction of copper was removed within the primary wetland cell. Therefore, it is expected that the performance measured for the primary cells differ from the secondary cells because the initial conditions for each cell are different. In the primary cells, the concentration of copper (i.e., 31 μg acid-soluble Cu/L) as well as the soluble fraction (i.e., 14 μg /L assumed bioavailable) of copper entering the wetland cell is significantly greater than the concentration (11 μg acid-soluble Cu/L) and form (5 μg soluble Cu/L) entering the secondary cells. Therefore, the performance of the primary cells differs from the performance of the secondary cells (64% and 45%, respectively). Analysis of the rate coefficients and half-lives of aqueous copper for each cell indicates that they are also different. For the primary cells, k_A = 0.039 hr^{-1} ($T_{1/2}$ = 18.0 hr), and for the secondary cells, k_B = 0.013 hr^{-1}($T_{1/2}$ = 54.6 hr). From this information, the first cell of the system is responsible for most of the copper removal observed in this system, and the second cell is serving as a buffer for cases where copper concentrations or flow could increase significantly. This information is essential when scaling a similar system for another site. From the ANOVA between cells, as long as environmental conditions are similar, a constructed wetland treatment system of similar design built at another site to treat a similar waste stream would be expected to provide the same level of treatment (Kuehn and Moore, 1995). If environmental conditions such as precipitation, evaporation, and temperature are not similar, then seasonal trends would influence the overall performance of the system (Carleton et al., 2000; Goulet et al., 2001).

CONCLUSION

As reported in previous articles, constructed wetlands may fail to meet their performance criteria because they are designed with limited understanding of the variables that affect the cycling of target constituents within the wetland (Wood, 1995; Goulet et al., 2001). In most cases, wetlands are designed based on hydrological and sizing considerations (Wood, 1995; Knight et al., 1999; Goulet et al., 2001). However, because all waste streams have different water characteristics, constructed wetland treatment systems must be designed based on those specific wastewater characteristics to consistently achieve performance objectives. When evaluating traditional performance (concentration$_{in}$ versus concentration$_{out}$) of a constructed wetland for transfer of a design to another site, simple performance without knowing internal factors (i.e., biological, physical, and chemical) and external factors (e.g., precipitation and temperature) that influence overall performance will not provide the design criteria necessary to move constructed wetland technology from site to site. Specific parameters that influence design include (1) the character of the wastewater, including the targeted constituents; (2) performance goals or desired levels of treatment; (3) transfer and transformation pathways; (4) flow rates and retention time required to achieve treatment; and (5) climate (i.e., temperature and precipitation).

In addition, when toxicity is a performance criterion, analytical speciation may provide valuable insight into the performance of the system but, unlike toxicity experiments, cannot accurately measure bioavailability. Having an understanding of how targeted transfers and transformations are achieved within a constructed wetland facilitates the operational scaling of a constructed wetland treatment system from one site to another.

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