Design of a constructed wetland system for treatment of copper-contaminated wastewater

George M. Huddleston III and John H. Rodgers Jr.

ABSTRACT

This research provided an approach for designing a constructed wetland system for treatment of copper-contaminated wastewater and was mostly based on (1) a review of scientific literature, (2) theoretical modeling, and (3) verification of performance via a pilot system. The pilot system consisted of five pairs of 378-L (100-gal) wetland cells, each pair arranged in series with a 48-hr hydraulic retention time. Four pairs received local municipal water amended with 50 μg Cu/L (nominal) as $CuSO_4 \cdot 5H_2O$. The remaining pair received only municipal water, which provided an untreated control. Wetland hydrosoil was 85% sand and 15% silt and clay-size particles amended with agricultural lime ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and Osmocote time-release fertilizer. Organic matter content was 3% by weight. Hydrosoil and overlying water depths were 30 cm (12 in.) each. Wetland vegetation was *Schoenoplectus californicus* (giant bulrush). Performance objectives were to decrease total copper to less than 22 μg/L and to eliminate toxicity to *Ceriodaphnia dubia* based on organism survival and reproduction. Total (acid-soluble) copper concentrations associated with wetland inflow averaged 46 ± 9 μg/L, whereas outflow concentrations were 12 ± 7 μg/L. Overall total copper removal from influent water was 73 ± 14%. Although inflow water was toxic to *C. dubia*, no toxicity was observed in outflow water after 1 month. Diagnostic measurements of wetland function (e.g., hydrosoil redox potential and sulfide formation) indicated that copper bioavailability was likely limited by copper precipitation as sulfidic minerals. This constructed wetland design was implemented at the U.S. Department of Energy's Savannah River Site to mitigate risks to receiving-water biota.

INTRODUCTION

Constructed wetlands are a viable alternative for treating wastewaters from a variety of sources (Moshiri, 1993; Kent, 1994). Concentrations of divalent metals such as copper and zinc can be decreased

AUTHORS

George M. Huddleston III ~ *ENTRIX, Inc., 102 East Main Street, Pendleton, South Carolina 29670; mhuddleston@entrix.com*

George M. Huddleston is project scientist at ENTRIX, Inc., and has 9 years of professional experience involving environmental toxicology and ecological risk management. He specializes in assessment of natural resources and development of strategies for mitigating ecological risks. He received his B.S. and M.S. degrees from Eastern Kentucky University and received his Ph.D. in 2001 from Clemson University.

John H. Rodgers Jr. ~ *Department of Forestry and Natural Resources, Clemson University, Clemson, South Carolina 29634; jrodger@clemson.edu*

John Rodgers received his Ph.D. from Virginia Polytechnic Institute and State University in 1977. Currently, he is a professor at Clemson University, director of the Ecotoxicology Program in the Department of Forestry and Natural Resources, and codirector of the Clemson Environmental Institute. His research involves a quest for accurate risk characterizations and development of sustainable risk mitigation tactics.

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significantly in wastewaters treated by constructed wetlands (Sinicrope et al., 1992; Hawkins et al., 1997; Gillespie et al., 1999, 2000). The purpose of this research was to design a constructed wetland system for copper-contaminated wastewater based on theoretical principles, published literature, and function and performance of a pilot-scale constructed wetland system. Implicit in this research was that risks to receiving-water biota would be mitigated by developing a system to allow copper in the waste stream to be transferred and transformed to less bioavailable forms.

The design of constructed wetlands for treatment of metal-contaminated wastewater generally includes some application of the biogeochemical principles of metal cycling within the wetland system (Sinicrope et al., 1992; Hawkins et al., 1997; Gillespie et al., 1999, 2000). For example, copper is bioavailable (and potentially toxic) in aquatic systems as free divalent ion, Cu(II) (Moore, 1990; Lewis, 1992; Deaver and Rodgers, 1996). However, under conditions of most natural waters, Cu(II) readily reacts with other components of the system, forming less bioavailable species such as sulfide and carbonate salts (Morse, 1995; Deaver and Rodgers, 1996; Huggett et al., 1999). Constructed wetlands can be designed to promote these biogeochemical transfers and transformations of copper so that risks to receiving-water biota are decreased.

Sources of information for constructed wetland design may include theoretical models, published literature, and studies using pilot-scale or wetland microcosm systems. Theoretical models such as equilibrium speciation programs (e.g., MINTEQ2A, MINEQL+) and E_h-pH relationships can predict the extent of metal transfers and transformations under specified environmental conditions in aquatic systems. The rates of metal transfers and transformations, and the influences that wetland macrofeatures (hydroperiod, hydrosoil, and vegetation) have on these reactions, can commonly be obtained from scientific literature. Pilot-scale constructed wetland systems that integrate design features can confirm the extent and rates of metal transfers and transformations, leading to enhanced and reliable full-scale constructed wetland design.

The purpose of this research was to design a constructed wetland treatment system for achieving a regulatory discharge limit of 22 µg/L total copper and eliminating toxicity from wastewater comprised of a point source and stormwater runoff at the U.S. Department of Energy's Savannah River Site in South Carolina. This constructed wetland design approach used theoretical modeling, information available in published scientific literature, and a pilot-scale constructed wetland system to confirm and enhance design characteristics before full-scale construction. This article provides an overview of the development of the conceptual design (based on theoretical modeling and published literature) and focuses on function and performance of the pilot-scale constructed wetland system.

MATERIALS AND METHODS

Study Site

The waste stream treated by the constructed wetland system was composed of process wastewater from technical and laboratory facilities (58% of total flow) and stormwater runoff (42% of total flow) from a 77-ha (190-ac) watershed located within the U.S. Department of Energy's Savannah River Site, South Carolina (Figure 1). Since the 1950s, operations at this facility have included production of weapons-grade nuclear material (primarily tritium and plutonium-239), ecological research, and environmental reclamation. Land coverage of the waste-stream drainage area included industrial development (47%), pavement (1%), grass (9%), gravel roads (1%), and forest (42%). Average daily process flow was approximately 0.97 million gal/day, with low flow of 0.25 million gal/day and peak flow of 2.6 million gal/day. The outfall (Table 1) was permitted under the National Pollutant Discharge Elimination System. However, the outfall occasionally exceeded the anticipated discharge limit for total copper (22 µg/L) and did not meet toxicity requirements using the freshwater crustacean *Ceriodaphnia dubia* (U.S. EPA, 1994).

Theoretical Modeling

This constructed wetland system was designed using an integrated approach, whereby principles of wetland biogeochemistry and influences from wetland hydrology, hydrosoil characteristics, and vegetation (macrofeatures) were synthesized to promote copper speciation to less bioavailable forms. The objective of theoretical modeling was to predict the extent to which copper speciation reactions would occur. Speciation models based on ambient pH (Sylva, 1976) and E_h-pH relationships (Brookins, 1988) in freshwater environments were used for predictions of potential forms of copper attainable in the constructed wetland system. Predictions of copper mass distribution among various species were facilitated using MINTEQA2 Version 3.0, a geochemical

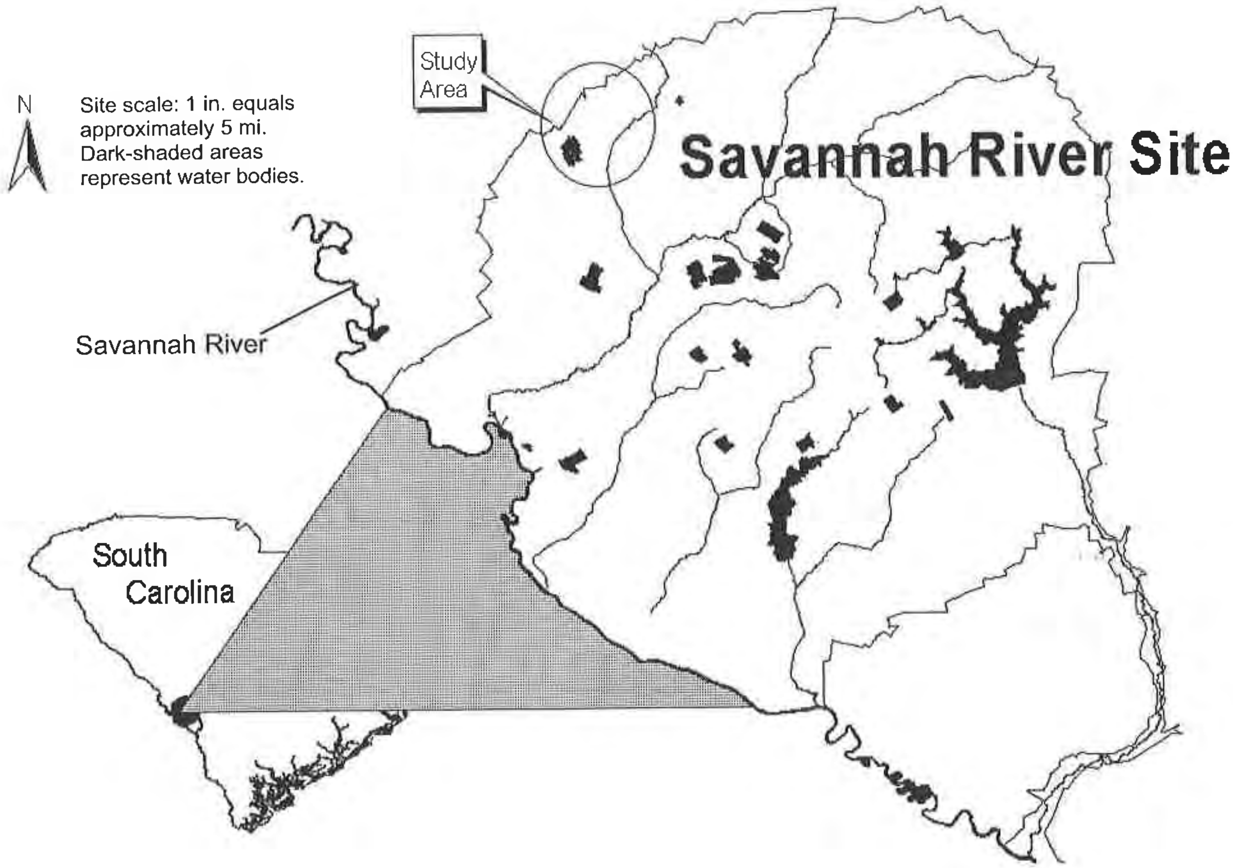

Figure 1. The Savannah River Site is a 310-mi^2 (802-km^2) U.S. Department of Energy facility established in South Carolina in 1950. The site is located in the southeastern United States coastal plain in the Savannah River watershed. This figure shows the administrative borders of the Savannah River Site and the location of the 190-ac (76-ha) study area described in the text.

equilibrium speciation model designed for calculating the equilibrium composition of dilute solutions containing trace metal in laboratory or natural aqueous systems (Allison et al., 1991).

Constructed Wetland Design Characteristics

A review of scientific literature provided information for determining the influence of wetland hydroperiod, hydrosoil, and vegetation on copper transfers and transformations. Areas of emphasis included copper biogeochemistry, copper bioavailability and toxicology, and constructed wetlands for treatment of metal-contaminated wastewaters.

Considerations for determining wetland hydroperiod included (1) kinetics of copper transfers and transformations in aquatic systems; (2) rates of inflow and copper mass loadings; (3) water quality characteristics

Table 1. Water Chemistry Characteristics (Ranges) Used in Constructed Wetland Design

Parameter	Wastewater to Be Treated by Full-Scale Constructed Wetland System	Municipal Water Used in Wetland Microcosm System
pH	5.3–7.8	6.0–7.8
Hardness (mg/L as $CaCO_3$)	4–28	12–16
Alkalinity (mg/L as $CaCO_3$)	21–59	18–24
Conductivity (μS/cm)	80–164	83–94
Dissolved oxygen (mg/L)	4.0–11.8	7.8–9.4

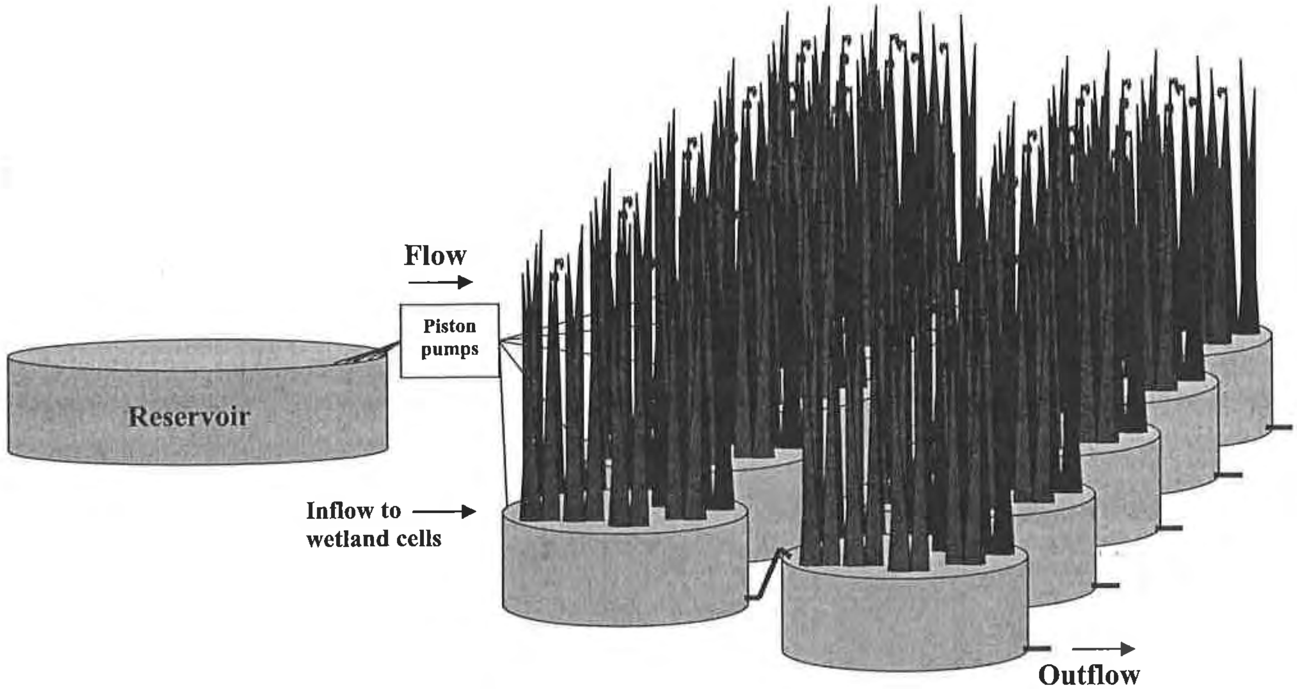

Figure 2. Schematic of a pilot-scale constructed wetland system at Clemson University used to establish design parameters for a full-scale wetland treatment system at the Savannah River Site.

(e.g., pH, hardness); and (4) water depth necessary to achieve the desired copper transfers and transformations. The wetland hydroperiod included in the conceptual design consisted of a 48-hr hydraulic retention time (HRT) and 30-cm (12-in.) water depth (based on empty bed volume).

Criteria for selecting an appropriate hydrosoil included (1) availability, (2) compatibility with wetland vegetation, (3) nutrient availability, and (4) organic matter content. For constructing wetlands, hydrosoils are derived from upland soils that are altered by inundation and commonly amended to achieve desired transfers and transformations of wastewater constituents. Characterization of upland soils present at the wetland construction site indicated that these soils were suitable for use as hydrosoil, given appropriate amendments of agricultural lime (to neutralize pH), organic mulch (to drive reductive processes for copper precipitation), and plant fertilizer.

Wetland vegetation was evaluated based on (1) native occurrence in the area, (2) the plant's ability to support reduced hydrosoil, (3) its ability to provide an organic carbon source for anaerobic microbial respiration, and (4) sufficiently slow degradation of detritus for increasing organic binding sites for copper over time. Vegetation selected for this system was giant bulrush, *Schoenoplectus californicus* (C.A. Meyer) Steud.

Pilot-Scale Constructed Wetland System

The pilot-scale constructed wetland system was used to confirm the conceptual design, make modifications if necessary, and provide design characteristics for the full-scale constructed wetland system. The pilot study was conducted at Clemson University, South Carolina. Ten wetland cells (surface area: 0.69 × 0.64 × 0.61 m [2.26 × 2.10 × 2.00 ft]) were constructed using 378.5-L (100-gal) Rubbermaid® utility tanks (Figure 2). Cells were arranged in five pairs, each pair connected in series using polyvinyl chloride pipe. Hydrosoil consisted of flood-plain soil collected adjacent to Eighteen Mile Creek within the Clemson University Experimental Forest, Anderson County, South Carolina. The physical and chemical character of this soil was similar to soil collected from the full-scale construction site, consisting of 85% sand and 15% silt and clay. Agricultural lime (49 g/m^2) and Osmocote® (8.2% ammonia nitrogen, 5.8% nitrate nitrogen, 14% P_2O_5, and 14% K_2O) time-release fertilizer (144 g/m^2) were manually mixed with hydrosoil prior to planting. Each wetland cell contained hydrosoil at a depth of 30 cm (12 in.) planted with *S. californicus* on 15-cm (6-in.) centers. Plants were obtained from stock cultures maintained at Clemson University. Two months after initiating the flow of simulated wastewater to the pilot system, wetland cells were amended with agricultural-grade pelletized gypsum ($CaSO_4 \cdot 2H_2O$) equivalent to 0.5% sulfur (by weight) per top 10 cm (4 in.) of hydrosoil. In addition, a mixture of pond detritus and grass clippings were added to achieve an organic matter content of 3% (dry weight). These amendments were added directly to the water surface and distributed evenly throughout.

Wastewater was simulated by amending municipal water with reagent-grade copper sulfate ($CuSO_4 \cdot 5H_2O$, Sigma® Chemicals) to a nominal concentration of 50 µg/L. Local municipal water was used because of its similar character to the wastewater for which the constructed wetland treatment system was designed (Table 1). Water amended with copper was delivered to the system using piston pumps (Fluid Metering, Inc., Oyster Bay, NY) calibrated to provide a 48-hr HRT for each pair of wetland cells. Simulated wastewater was formulated in a 6867-L (1814-gal) reservoir, which was renewed weekly and amended with copper.

Samples for copper analysis were collected in Nalgene® high-density polyethylene bottles and immediately split for total and soluble copper determination. Samples for total (acid-soluble) copper analysis were acidified with concentrated trace metal-grade nitric acid (Fisher Scientific®) to pH ≤ 2, followed by filtration using 0.45-µm Millipore® nitrocellulose syringe filters (U.S. EPA, 1985). Wetland inflow copper concentrations were determined by sampling the reservoir in triplicate, whereas the outflow of each wetland cell was sampled to determine copper concentrations after 24 and 48 hr of treatment. Outflow samples for the respective HRTs were analyzed individually or composited prior to analysis. Copper concentrations were determined using a Varian® Spectra AA 20 Plus atomic absorption spectrometer and Varian® GTA 96 Plus graphite furnace. Quality assurance procedures included the analyses of method blanks, replicate samples, and standard additions to verify the absence of matrix effects. Calibration standards were prepared regularly using a copper reference solution (Fisher Scientific®) at 6.25, 12.5, 25, 50, and 100 µg/L. Standard curve R^2 values ranged from 0.94 to 0.99.

Toxicity of wetland inflow and outflow water was measured using *C. dubia* in 7-days, static, renewal exposures (U.S. EPA, 1994). Control organisms were exposed to both culture water and municipal water. Toxicity tests were initiated 1 day after mixing copper with municipal water (to decrease potential for toxic responses to chlorine). Toxicity tests were conducted monthly for 9 months after copper-contaminated water was introduced to the pilot system. Statistical analysis of organism survival and reproduction was performed to determine if differences existed between groups exposed to inflow and outflow water. Data normally distributed with homogeneous variance were analyzed by one-way analysis of variance (ANOVA). Data not meeting these criteria were analyzed using one-way ANOVA on ranks. Differences, if any, were determined with multiple range tests with $\alpha = 0.05$.

Oxidation-reduction (redox) potential of wetland hydrosoil was measured by placing five platinum-tipped electrodes (Faulkner et al., 1989) evenly spaced throughout each wetland cell at a depth of 2–6 cm (0.8–2.4 in.). Electrodes were standardized using the Zobel solution (APHA et al., 1995). Redox measurements were made against an Accumet® calomel reference electrode using a Fluke® 77 III voltage meter. Acid-volatile sulfides (AVS) in the wetland hydrosoil were measured according to Allen et al. (1993). Dissolved oxygen, pH, and conductivity of surface waters were measured using a YSI® Model 52 dissolved oxygen meter, Orion® Model 250A pH meter and Triode® electrode, and Orion Model 142 conductivity meter, respectively. Alkalinity and hardness of aqueous samples were determined according to the *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 1995). Particle size distribution of hydrosoils was determined by hydrometer method (Gee and Bauder, 1986). Hydrosoil organic matter content was determined by loss on ignition (Nelson and Sommers, 1996). Hydrosoil pH was measured according to Plumb (1981). The sediment oxygen demand (SOD) of this system was determined by incubating 10 g of wet surface sediment for 5 days under darkness at 20°C. Sediments were incubated in 300-mL biochemical oxygen demand bottles filled to volume with deionized water and were analyzed in triplicate. Deionized water containing no sediment was analyzed concurrently as a control.

RESULTS

Theoretical Modeling

Predictions of copper speciation under conditions anticipated for this constructed wetland system indicated the formation of predominantly copper sulfide mineral. For example, the Cu-C-S-O-H system described by Brookins (1988) (Figure 3) indicated that CuS and Cu_2S would be the dominant copper species in this system given sufficiently negative redox (−75 to −250 mV) and circumneutral pH. MINTEQA2 also predicted precipitation of copper as covellite (CuS) with the

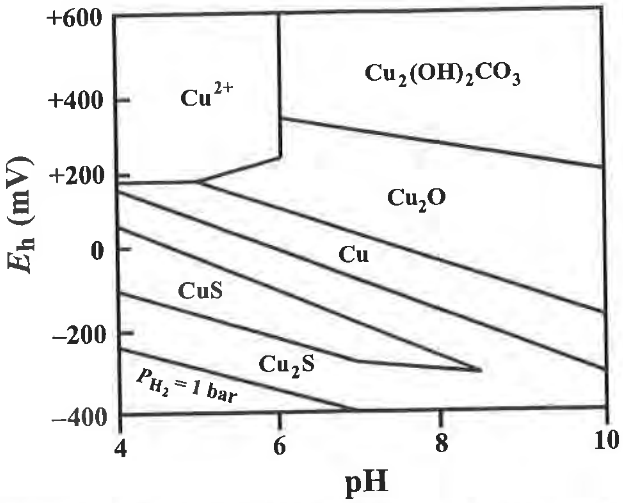

Figure 3. E_h-pH relationships for part of the system Cu-C-S-O-H (modified from Brookins, 1988). The diagram illustrates various copper species that can form in the constructed wetland system under given E_h and pH conditions.

equilibrated mass distribution of copper within the system as >99% precipitated. The remaining fraction (<1%) was dissolved or adsorbed.

Constructed Wetland Design Characteristics

Published literature provided information on functional roles of wetland hydroperiod, hydrosoil, and vegetation that were incorporated into the conceptual design (Table 2). Hydroperiod for this system was based on an HRT adequate for copper transfers and transformations to occur, given the character of the wastewater, and a water depth sufficient for maintaining reduced hydrosoil conditions. Published literature indicated that, given sufficient ligand concentrations, precipitation of copper with reduced sulfur and binding of copper to dissolved and particulate organic matter are relatively rapid (instantaneous to <24 hr) (Morel and Hering, 1993; Kim et al., 1999; Ma et al., 1999). Other constructed wetland studies reported that 24–48-hr HRT and 30-cm (12-in.) water depth were sufficient for the removal of divalent metals from wastewater (Sinicrope et al., 1992; Hawkins et al., 1997; Gillespie et al., 2000).

Previous studies provided evidence that hydrosoil used in combination with the hydroperiod described above could maintain circumneutral pH and redox potential within the range for sulfate reduction and support growth of *S. californicus* (Sinicrope et al., 1992; Hawkins et al., 1997; Gillespie et al., 1999; 2000). *S. californicus* was selected for this constructed wetland system based on (1) the plant's ability to maintain reduced hydrosoil (Josselyn et al., 1990; Sinicrope et al., 1992; Hawkins et al., 1997; Gillespie et al., 1999, 2000); (2) its ability to provide an organic carbon source for sulfate-reducing bacteria (Sinicrope et al., 1992; Araujo de Oliveira et al., 1994; Richardson et al., 1995); and (3) sufficiently slow degradation of detritus for increasing organic binding sites over time (Chendorain et al., 1998).

Table 2. Macrofeatures (Hydroperiod, Hydrosoil, and Vegetation) of a Pilot-Scale Constructed Wetland System Receiving Copper-Contaminated Water

Macrofeature	Functional Roles	Citations
Hydroperiod: 48-hr HRT 30-cm (12-in.) water depth; water character	HRT sufficient for transfer and transformation reactions to occur; sufficient water depth for maintaining reduced hydrosoil conditions; influence of aqueous chemical characteristics on copper speciation	Sylva, 1976; Sinicrope et al., 1992; Hawkins et al., 1997
Hydrosoil: Onsite soil with chemical amendments	Support aquatic vegetation; maintain redox range for dissimilatory sulfate reduction; maintain circumneutral pH	Sinicrope et al., 1992; Suedel et al., 1996; Hawkins et al., 1997; Gillespie et al., 1999, 2000
Vegetation: *S. californicus* (giant bulrush)	Maintains hydrosoil redox in the targeted range (−75 to −250 mV); provides organic carbon source for sulfate-reducing bacteria; sufficiently slow-degrading detritus for providing renewable organic binding sites	Josselyn et al., 1990; Sinicrope et al., 1992; Araujo de Oliveira et al., 1994; Richardson et al., 1995; Hawkins et al., 1997; Chendorain et al., 1998; Gillespie et al., 1999, 2000

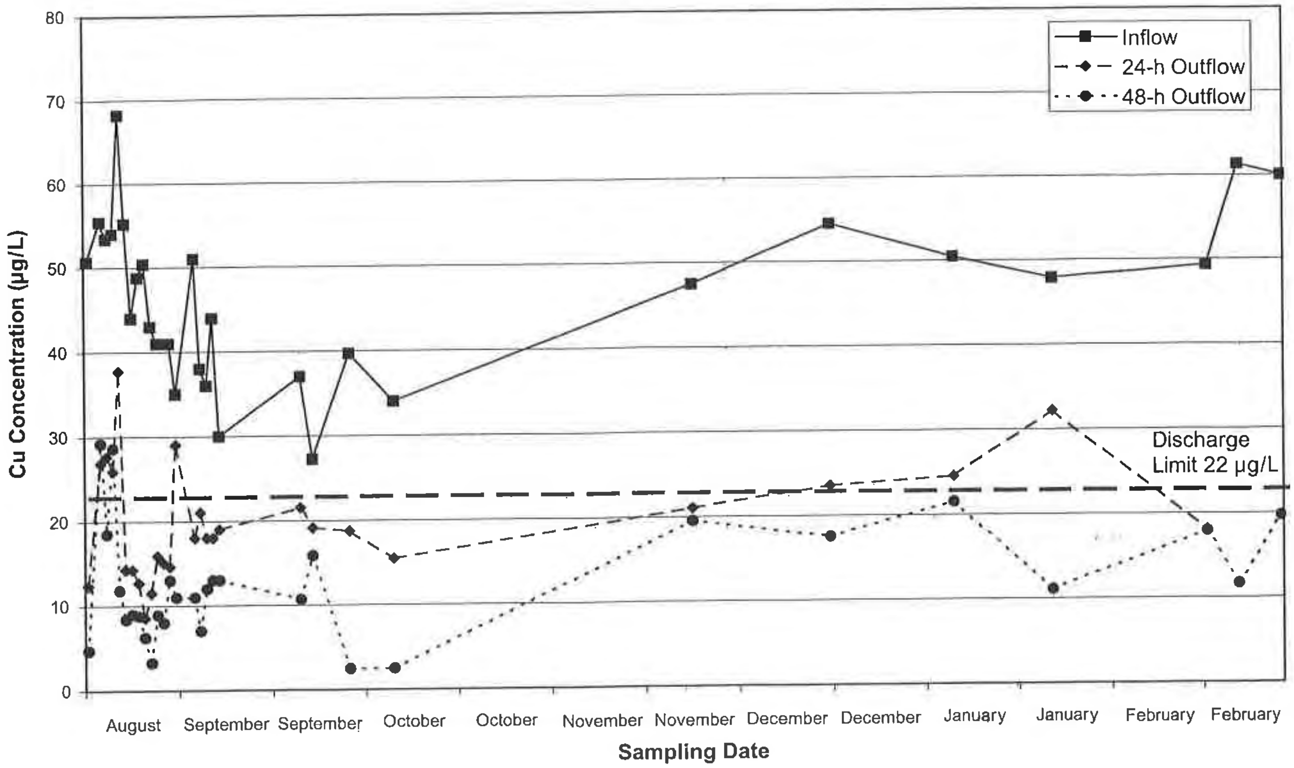

Figure 4. Total recoverable copper in inflow and outflow water from a pilot-scale constructed wetland system at Clemson University used to establish design parameters for a full-scale wetland treatment system at the Savannah River Site.

Pilot-Scale Constructed Wetland System

Acid-soluble copper in the inflows of the pilot system averaged 46 ± 9 µg/L (range = 27–68 µg/L) (Figure 4). Outflow concentrations averaged 12 ± 7 µg/L (range = 3–29 µg/L). On average, copper removal by the model wetland system was 73 ± 14%. Copper removal (transfer and transformation) rate approximated first-order kinetics ($K = 0.028$/h), with a predicted copper half-life in the aqueous phase of 24.8 hr. The measured average total copper concentrations after a 24-hr HRT was 20 ± 7 µg/L.

Survival and reproduction of C. *dubia* in 7-day exposures to inflow and outflow waters were also used to measure performance of the model constructed wetland system. Mortality in inflow water ranged from 40 to 100% and from 0 to 20% in outflow water. With the exception of the initial toxicity test, no significant difference ($\alpha = 0.05$) in reproduction was observed in test organisms exposed to control and outflow water. Thus, C. *dubia* toxicity was not detected in outflow water from the model wetland system.

Following hydrosoil amendments with gypsum and organic matter (Table 3), redox potential and AVS concentrations of wetland hydrosoils indicated that conditions supported dissimilatory sulfate reduction, promoting precipitation and coprecipitation of copper with sulfide and other pyritic minerals. Hydrosoil redox potential averaged −127 ± 47 mV and did not vary significantly between wetland cells. Redox remained within the range of sulfate reduction throughout the remainder of the study. Acid-volatile sulfides were measured prior

Table 3. Initial and Amended Hydrosoil Characteristics in a Pilot-Scale Constructed Wetland System Treating Copper-Contaminated Water

Parameter	Initial Characteristics	Following Amendments
pH	5.7	6.1–6.4
Organic matter content (percent dry weight)	2	3
Particle size distribution (%)		
Sand	85%	85%
Silt and clay	15%	15%
CEC (meq/100 g)	1.4	5.6

to and following hydrosoil amendments. Before additions of gypsum and organic matter, the AVS concentration was 0.49 ± 0.1 μmol/g, with 0.04 ± 0.1 μmol/g simultaneously extractable copper. Following hydrosoil amendments, AVS increased to 3.10 ± 0.11 μmol/g, whereas no change was detected in simultaneously extractable copper. Also following hydrosoil amendments, cation exchange capacity (CEC) increased from 1.4 to 5.6 meq/100 g.

From the time of planting (May) through the initial growing season (November), shoot length of *S. californicus* increased from approximately 1.5 to 2.7 m (5 to 9 ft). Shoot density increased from 30 to 242 shoots/m^2.

To evaluate the likelihood that anaerobic conditions would prevail in wetland hydrosoil, the net oxygen supply rate (NOSR) within the system (Kadlec and Knight, 1996) was estimated by

$$\text{NOSR} = K(\text{DO}_{\text{sat}} - \text{DO}_{\text{avg}}) - \text{SOD}$$

where K = mass oxygen transfer rate, 0.1 m/day (Langmuir, 1997); DO_{sat} = equilibrium dissolved oxygen concentration at 1 atm, 8.7 mg/L (g/m^3) (APHA et al., 1995); DO_{avg} = average dissolved oxygen concentration in overlying water, 8.0 mg/L (g/m^3); and SOD = experimentally determined sediment oxygen demand, 0.1 ± 0.01 mg O_2/day.

Using the equation above, the NOSR for this system was −685 mg O_2/day or net oxygen consumption.

DISCUSSION

The approach used in this research for constructed wetland design involved the development of a conceptual design based on theoretical modeling and review of published literature. The conceptual design was then implemented as a pilot-scale constructed wetland system used to evaluate wetland function and performance, thus confirming and modifying components of the full-scale design.

Copper speciation modeling indicated that circumneutral pH and redox potential in the range of −75 to −200 mV would allow copper to precipitate as a sulfide mineral, such as covellite (CuS). Copper sulfide is stable in aquatic systems; the CuS stability coefficient is 36.1, compared to, for example, 6.3 for CuOH (Morel and Hering, 1993). For sulfides to be available for copper binding, sulfate present in the system is reduced during oxidation of organic matter by sulfate-reducing bacteria. This process of dissimilatory sulfate reduction typically occurs near the sediment-water interface when oxygen is depleted because of organic matter decomposition (Wetzel, 1983; Mitsch and Gosselink, 1993). These biogeochemical processes and the conditions under which they occur formed the functional basis for the constructed wetland system design.

The next phase of the design process was to integrate characteristics of wetland macrofeatures (hydroperiod, hydrosoil, and vegetation) into a system where copper transfers and transformations were both possible and likely to occur. Information supporting the functional roles of wetland macrofeatures in establishing the conditions to support copper transfers and transformations in the constructed wetland system was provided mostly by published literature.

A primary criterion for establishing hydroperiod is transfer and transformation kinetics of the material(s) targeted for removal from wastewater. The kinetics of copper speciation in aqueous systems is generally less than 48 hr (Morel and Hering, 1993; Kim et al., 1999; Ma et al., 1999). Hawkins et al. (1997), working with approximately half the inflow copper concentrations as the present study, obtained 33% copper removal from aqueous phase using pilot-scale constructed wetlands, corresponding to a half-life of approximately 80 hr. The transfer and transformation half-life calculated in the present study was 25 hr. The shorter half-life obtained in this study was likely attributed to greater inflow copper concentrations and greater sulfides and organic matter associated with the hydrosoil. Sinicrope et al. (1992) reported that the most efficient copper removal (88%) by wetland microcosms was associated with a loading rate of 1.2 mg Cu/L at 96 L/day. Copper transfer and transformation half-lives calculated from Sinicrope et al. (1992) were 11–15 hr. Rates of copper removal are affected by initial conditions (e.g., copper concentration) and characteristics of the system (e.g., hydrosoil and hydroperiod properties). In this study, the constructed wetland system was designed with a 48-hr HRT, a conservative retention time sufficient for copper transfers and transformations to occur, assuming that aqueous and hydrosoil conditions are amenable for these processes to occur. Hydrosoil used in the pilot system was similar to the soil to be used for the full-scale system in terms of particle size distribution and organic content. After 2 months of operation of the pilot system, hydrosoil redox potential was not consistently achieving the range for sulfate reduction, copper concentrations were not reaching the target criterion (22 μg/L), and toxicity to *C. dubia* was observed. Although it is likely that the system would eventually stabilize and achieve the desired performance, time was critical in this case for meeting the project schedule. By adding gypsum and additional organic matter, wetland maturity time was compressed, and conditions favorable to copper sulfide precipitation were achieved, as indicated by redox potential and AVS measurements. Redox potential provided a measure of the reducing intensity of the hydrosoil, indicating that conditions were adequate for sulfate reduction. Acid-volatile sulfide measurements were a further indication of the reducing capacity or the amount of sulfide available for binding copper. The toxicity of cationic metals such as Cu, Cd, Ni, Pb, and Zn is influenced by the quantities of amorphous metal sulfides present in the system (Di Toro et al., 1990; Berry et al., 1996; Hansen et al., 1996). These studies have demonstrated that if the molar concentration of AVS extracted from sediment exceeds the molar sum of simultaneously extractable metal(s) (SEM), then those sediment metals will not be available to sediment-dwelling or overlying-water organisms. The theoretical foundation for SEM/AVS predictions of metal bioavailability and toxicity is that the sulfides of cationic metals, such as copper, have lower sulfide solubility coefficients than do the sulfides of iron and manganese, which are formed naturally in sediments as a product of bacterial oxidation of organic matter (Wetzel, 1983). As a result, these metals will displace manganese and iron whenever they are present, together with manganese and iron monosulfides (Di Toro et al., 1992). In prior studies, gypsum has been used to control metal bioavailability in sediments (Carbonell et al., 1999a, b).

Hydrosoils were also expected to provide adsorptive sites for copper attenuation in the constructed wetland system. Mineral particles less than about 1 µm in diameter have a significant percentage of their atoms at particle surfaces, providing important surface properties relative to interactions with ions in aqueous systems (Langmuir, 1997). These particles generally exhibit a net negative surface charge, or CEC, which can be affected by changes in pH (Langmuir, 1997). Electrochemical attractions between cationic copper species (e.g., Cu^{+2} or $CuOH^{+}$) and negatively charged particles function to bind these species, removing copper from solution and decreasing its bioavailability (Eisler, 2000).

S. californicus has been used previously in constructed wetlands designed for transfers and transformations of Cu, Pb, and Zn (Hawkins et al., 1997; Gillespie et al., 1999, 2000). These studies indicated that reduced hydrosoil could be maintained using this macrophyte, which does not translocate oxygen to the root zone to the extent that net oxidized conditions prevail in the hydrosoil. In addition, *S. californicus* was chosen for this constructed wetland system for contributing organic matter over time, supporting dissimilatory sulfate reduction and providing organic ligands (Elder, 1988; Kim et al., 1999; Ma et al., 1999). For this constructed wetland system, potential organic ligands not in solution included detritus and the submerged surfaces of wetland vegetation. As wetland vegetation senesces in winter, a part of the standing crop will be contributed to the detritus (Mitsch and Gosselink, 1993). If the decomposition rate (loss of biomass) of detritus is sufficiently slow (half-life greater than 6 months), the wetland system will accrete organic matter over time, providing additional sorbent material for copper each year.

The numerical criterion of 22 µg/L total copper and narrative criterion of no toxicity (based on the reproduction and survival of *C. dubia* under standard exposure conditions) were achieved by this pilot-scale constructed wetland system. This provided confirmation of some conceptual design characteristics and an opportunity to modify and enhance other design features (e.g., hydrosoil properties). The design could then be implemented in the field with empirical evidence that the system will function and perform as designed. This design approach is practical and repeatable and can be applied in a variety of wastewater treatment situations (e.g., industrial effluents, municipalities, stormwater management). Recognizing that this is but one approach to designing constructed wetland treatment systems, it offers a logical and practical path for providing an effective solution for wastewater treatment or water-quality improvement. Certainly, specific projects may require more robust equilibrium modeling, and as the science advances, more published information will be available as a resource for supporting constructed wetland design.

CONCLUSIONS

This research provided an approach to constructed wetland design for decreasing concentrations and bioavailability of copper in wastewater. This design was based on biogeochemical processes that transfer and transform copper to species with limited bioavailability. The integrated design process involved formulation of a conceptual design, which was then confirmed and enhanced using a pilot-scale constructed wetland system. By evaluating wetland function and performance at the pilot scale, empirical evidence was obtained that the full-scale constructed wetland system would operate effectively, mitigating potential risks of copper in wastewater to receiving waters.

REFERENCES CITED

Allen, H. E., F. Gomgmin, and B. Deng, 1993, Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments: Environmental Toxicology and Chemistry, v. 12, p. 1441–1454.

Allison, J. D., D. S. Brown, and K. J. Novo-Gradac, 1991, MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 user's manual: Athens, Georgia, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 106 p.

American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, 1995, Standard methods for examination of water and wastewater, 19th ed.: Washington, D.C., American Public Health Association, 1325 p.

Araujo de Oliveira, M. E., M. A. L. Verdade, and B. Carvalho, 1994, Effects of salinity and sediment features on two emergent macrophytes in a coastal environment in southern Brazil: International Journal of Ecology and Environmental Sciences, v. 20, p. 73–82.

Berry, W. J., D. J. Hansen, J. D. Mahony, D. L. Robson, D. M. Di Toro, B. P. Shipley, B. Rogers, J. M. Corbin, and W. S. Boothman, 1996, Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulfide and interstitial water normalizations: Environmental Toxicology and Chemistry, v. 15, p. 2067–2079.

Brookins, D. J., 1988, E_h-pH diagrams for geochemistry: New York, New York, Springer-Verlag, 176 p.

Carbonell, A. A., J. D. Porthouse, C. K. Mulbah, R. D. Delaune, and W. H. Patrick Jr., 1999a, Metal solubility in phosphogypsum-amended sediment under controlled pH and redox conditions: Journal of Environmental Quality, v. 28, p. 232–242.

Carbonell, A. A., R. Pulido, R. D. Delaune, and W. H. Patrick Jr., 1999b, Heavy metals in the environment: Soluble barium in barite and phosphogypsum amended Mississippi River alluvial sediment: Journal of Environmental Quality, v. 28, p. 316–321.

Chendorain, M., M. Yates, and F. Villegas, 1998, The fate and transport of viruses through surface water constructed wetlands: Journal of Environmental Quality, v. 27, p. 1451–1458.

Deaver, E., and J. H. Rodgers Jr., 1996, Measuring bioavailable copper using anodic stripping voltametry: Environmental Toxicology and Chemistry, v. 15, p. 1925–1930.

Di Toro, D. M., J. D. Mahony, D. J. Hansen, K. J. Scott, M. B. Hicks, S. M. Mayr, and M. S. Redman, 1990, Toxicity of cadmium in sediments: The role of acid volatile sulfide: Environmental Toxicology and Chemistry, v. 9, p. 1487–1502.

Di Toro, D. M., J. D. Mahoney, D. J. Hansen, K. J. Scott, A. R. Carlson, and G. T. Ankley, 1992, Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments: Environmental Science and Technology, v. 26, p. 96–101.

Eisler, R., 2000, Handbook of chemical risk assessment, health hazards to humans, plants, and animals: Metals: Boca Raton, Florida, Lewis Publishers, v. 1, 738 p.

Elder, J. F., 1988, Metal biogeochemistry in surface-water systems, a review of principles and concepts: U.S. Geological Survey Circular 1013, 43 p.

Faulkner, S. P., W. H. Patrick Jr., and R. P. Gambrell, 1989, Field techniques for measuring wetland soil parameters: Soil Science Society of America Journal, v. 53, p. 883–890.

Gee, G. W., and J. W. Bauder, 1986, Particle-size analysis, *in* W. C. Black, ed., Methods of soil analysis: Part I: Madison, Wisconsin, American Society of Agronomy, p. 383–411.

Gillespie Jr., W. B., W. B. Hawkins, J. H. Rodgers Jr., M. L. Cano, and P. B. Dorn, 1999, Transfer and transformations of zinc in flow-through wetland microcosms: Ecotoxicology and Environmental Safety, v. 43, p. 126–132.

Gillespie Jr., W. B., W. B. Hawkins, J. H. Rodgers Jr., M. L. Cano, and P. B. Dorn, 2000, Transfer and transformations of zinc in constructed wetlands: Mitigation of a refinery effluent: Ecological Engineering, v. 14, p. 279–292.

Hansen, D. J., J. D. Mahony, W. J. Berry, S. J. Benyi, J. M. Corbin, S. D. Pratt, D. M. Di Toro, and M. B. Ablē, 1996, Chronic effect of cadmium in sediments on colonization by benthic marine organisms: An evaluation of the role of interstitial cadmium and acid volatile sulfide in biological availability: Environmental Toxicology and Chemistry, v. 15, p. 2126–2137.

Hawkins, W. B., J. H. Rodgers Jr., A. W. Dunn, P. B. Dorn, and M. L. Cano, 1997, Design and construction of wetlands for aqueous transfers and transformations of selected metals: Ecotoxicology and Environmental Safety, v. 36, p. 238–248.

Huggett, D. B., W. B. Gillespie Jr., and J. H. Rodgers Jr., 1999, Copper bioavailability in Steilacoom Lake sediments: Archives of Environmental Toxicology, v. 36, p. 120–123.

Josselyn, M. N., S. P. Faulkner, and W. H. Patrick, 1990, Relationships between seasonally wet soils and occurrence of wetland plants in California: Wetlands, v. 10, p. 7–26.

Kadlec, R. H., and R. L. Knight, 1996, Treatment wetlands: Boca Raton, Florida, Lewis Publishers, 891 p.

Kent, D. M., 1994, Applied wetlands science and technology: Boca Raton, Florida, CRC Press, Inc., 436 p.

Kim, S. D., H. Ma, H. E. Allen, and D. K. Cha, 1999, Influence of dissolved organic matter on the toxicity of copper to *C. dubia*: Effect of complexation kinetics: Environmental Toxicology and Chemistry, v. 18, p. 2433–2437.

Langmuir, D., 1997, Aqueous environmental geochemistry: Upper Saddle River, New Jersey, Prentice Hall, 600 p.

Lewis, A. G., 1992, The biological importance of copper: A literature review: New York, New York, International Copper Association, Ltd., 400 p.

Ma, H., S. D. Kim, D. K. Cha, and H. E. Allen, 1999, Effect of kinetics of complexation by humic acid on toxicity of copper to *C. dubia*: Environmental Toxicology and Chemistry, v. 18, p. 828–837.

Mitsch, W. J., and J. G. Gosselink, 1993, Wetlands, 2d ed.: New York, New York, Van Nostrand Reinhold, 722 p.

Moore, J., 1990, Inorganic contaminants of surface water: New York, Springer-Verlag Inc., 334 p.

Morel, F. M. M., and J. G. Hering, 1993, Principles and applications of aquatic chemistry: New York, New York, John Wiley & Sons, Inc., 588 p.

Morse, J. W., 1995, Dynamics of trace metal interactions with authigenic sulfide minerals in anoxic sediments, *in* H. E. Allen, ed., Metal contaminated aquatic sediments: Ann Arbor, Michigan, Ann Arbor Press, Inc., p. 187–199.

Moshiri, G. A., 1993, Constructed wetlands for water quality improvement: Boca Raton, Florida, Lewis Publishers, 632 p.

Murray-Gulde, C. L., W. C. Bridges, and J. H. Rodgers Jr., 2008, Evaluating performance of a constructed wetland treatment system designed to decrease bioavailable copper in a waste stream: Environmental Geosciences Journal, v. 15, p. 21–28.

Nelson, D. W., and L. E. Sommers, 1996, Carbon and organic

matter: Loss on ignition method, *in* D. L. Sparks, ed., Methods of soil analysis: Part 3. Chemical methods: Madison, Wisconsin, Soil Science Society of America, Inc., American Society of Agronomy, Inc., p. 1001–1010.
Nelson, E. A., and J. B. Gladden, 2008, Full-scale treatment wetlands for metal removal from industrial wastewater: Environmental Geosciences Journal, v. 15, p. 39–48.
Plumb, R. H., 1981, Procedures for handling and chemical analysis of sediment and water samples. Technical Report EPA/CE-81-1: Vicksburg, Mississippi, U.S. Army Engineer Waterways Experiment Station, 501 p.
Richardson, J. R., T. T. Harris, and K. A. Williges, 1995, Vegetation correlations with various environmental parameters in the Lake Okeechobee marsh system: Archives of Hydrobiology: Special Issues in Advanced Limnology, v. 45, p. 41–61.
Sinicrope, T. L., R. Langis, R. M. Gersberg, M. J. Busnardo, and J. B. Zedler, 1992, Metal removal by wetland mesocosms subjected to different hydroperiods: Ecological Engineering, v. 1, p. 309–322.
Suedel, B. C., E. Deaver, and J. H. Rodgers Jr., 1996, Experimental factors that may affect toxicity of aqueous and sediment-bound copper to freshwater organisms: Archives of Environmental Contamination Toxicology, v. 10, p. 40–46.
Sylva, R. N., 1976, The environmental chemistry of copper (II) in aquatic systems: Water Research, v. 10, p. 789–792.
U.S. Environmental Protection Agency (U.S. EPA), 1985, Ambient water quality criteria for copper— 1984: EPA/440/5-84-031: Washington, D.C., 150 p.
U.S. Environmental Protection Agency (U.S. EPA), 1994, Short-term methods for estimating chronic toxicity of effluents and receiving waters to freshwater organisms, 2d ed.: EPA/600/4-91/002: Cincinnati, Ohio, 370 p.
Wetzel, R. G., 1983, Limnology: Orlando, Florida, Saunders College Publishers, 767 p.