Lead and Zinc Removal by Laboratory-Scale Constructed Wetlands

Ying Song, Mark Fitch, Joel Burken, Linda Nass, Somnath Chilukiri, Nord Gale, Chad Ross

ABSTRACT: Constructed wetlands have the potential to trap and remove metals in mine wastewater. To determine the effectiveness of constructed wetlands for treating selected heavy metals in neutral mine effluent typical of lead mines, eight laboratory-scale constructed wetlands were set up to treat a synthetic, slightly alkaline, mine water containing 34.2 mg/L sulfate (SO_4^{2-}), 50 μg/L lead (Pb), and 300 μg/L zinc (Zn). After 45 days, one of the wetlands was switched to treat a synthetic smelter effluent with a much greater load of SO_4^{2-}, sodium (Na^+), and Pb. Temperature, hydraulic loading, and substrate composition typically did not affect treatment efficiency. The pH of the effluent was reduced from 8.0 to 8.5 to near neutral. The average removal in the eight wetlands was 90% for Pb and 72% for Zn. In wetlands operating on synthetic mine water, SO_4^{2-} was completely removed, likely by conversion to sulfide by sulfate-reducing bacteria. In the wetland operating on synthetic smelter effluent, only approximately 25% of 6 g/L influent sulfate was removed, and a breakthrough period of 4 days for Na^+ was observed. Whole effluent toxicity assays on undiluted wetland effluent from wetlands treating mine and smelter water had 100% survival of fathead minnows and *Daphnia magnia*. Survival of *Ceriodaphnia dubia* was zero in undiluted effluent, but 75 to 100% survival was observed when the effluent was diluted to one-half strength. *Water Environ. Res.*, **73,** 37 (2001).

KEYWORDS: metal removal, lead, zinc, mine wastewater, constructed wetlands, toxicity.

Introduction

Heavy metal contamination of water bodies is a significant concern in mining operations. The primary contaminants in mine drainage are sulfate, iron, and heavy metals such as copper (Cu), lead (Pb), and zinc (Zn). The pH of mine water ranges from a low of 1.8 to a high of 8 (Toler, 1982, and Wakao et al., 1985). Many methods are being explored to remove metals from mining wastewater.

Recently, constructed wetlands have been proposed and implemented as some of the most cost-effective and low-maintenance processes to treat mine drainage (Butterworth et al., 1997, and Eger, 1994). Numerous researchers have chosen constructed wetlands as a technology for the remediation of acid mine drainage (AMD) in the past 10 to 15 years (Brodie et al., 1993; Hedin et al., 1989; Skousen et al., 1994; Wieder, 1989; and Wildeman and Laudon, 1989). Constructed wetlands are natural wastewater treatment systems that combine biological, chemical, and physical treatment mechanisms for water quality improvement (Kadlec and Knight, 1996). The mechanisms for metal removal in wetlands may include adsorption, complexation, precipitation, and plant uptake (Crites et al., 1997, and Machemer and Wildeman, 1992). A large number of constructed wetlands are currently used to treat various forms of mine drainage.

However, wetlands are complex systems, and the effectiveness of water treatment has proved highly variable at different sites (Fennessy, 1989). A survey conducted by the U.S. Office of Surface Mining, Reclamation and Enforcement (Washington, D.C.) to assess the status of constructed wetland treatment of AMD in the eastern United States showed that treatment efficiency was not typically correlated with design criteria (i.e., area of wetlands, depth of the organic substrate in the wetlands, AMD flow rate, and metal loading rates) (Wieder, 1989). It was also reported that the effectiveness of wetland treatment of AMD is not only extremely variable, but also unpredictable. Treatment efficiency was typically not affected by either the type of organic substrate used in wetland construction or the addition of lime or fertilizer to the constructed wetlands.

Nonetheless, effective management of wetlands for water treatment can be facilitated by understanding the variability and intricacies of the system (Hawkins et al., 1997, and Witsch et al., 1998). Controlled laboratory experiments are needed to more fully understand wetlands' functions and the factors affecting these functions for metal removal (Batal et al., 1989; Goodrich, 1996; and Mungur et al., 1997). Data collected through more detailed research should be useful for developing better design criteria for the effective use of this technology to reduce or eliminate the risk of inefficient wetland treatment.

To date, most of the research on constructed wetlands has focused on the treatment of AMD, whereas wetlands that treat nonacid mine drainage have not been significantly explored (Wildeman et al., 1997). In this paper, the ability of constructed wetlands to treat neutral synthetic lead mine drainage and synthetic lead smelter wastewater was studied at laboratory scale. The effect of several factors on wetland treatment efficiency was evaluated, and whole effluent toxicity (WET) assays with *Ceriodaphnia dubia, Daphnia magna*, and fathead minnows were performed to determine the quality of the effluent.

Materials and Methods

Laboratory-Scale Constructed Wetlands. Eight laboratory-scale constructed wetlands were set up in the Environmental Research Center at the University of Missouri–Rolla. Each wetlands was created in a glass aquarium 0.9 × 0.3 × 0.5 m. A schematic of the wetlands is shown in Figure 1. A 76-mm (3-in.) vertical gravel bed was installed to promote vertical distribution of water entering the wetlands. At the effluent end of the wetlands, a perforated Plexiglas wall was installed to maintain vertical distribution of flow. A fine mesh screen to contain sediment from the wetlands immediately preceded this Plexiglas wall. The wetlands were created by filling the volume between the gravel and Plexiglas wall with substrate to a depth of 0.3 m. The eight wetlands were operated with differing flow rates, substrate composition, and temperature, as shown in Tables 1 and 2.

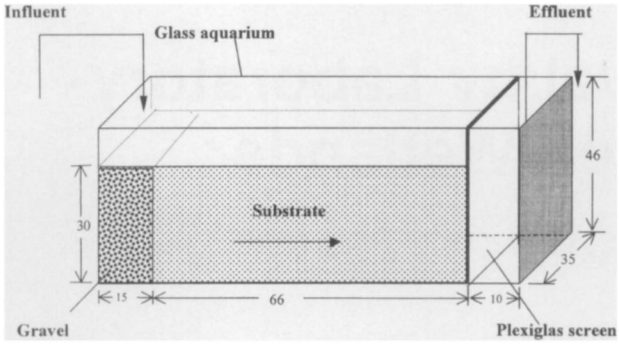


Figure 1—Schematic of laboratory-scale constructed wetlands (measurements in centimeters).

Substrate Composition. One set of four constructed wetlands (No. 1 through 4) was maintained at room temperature, 23 ± 2 °C. These room-temperature wetlands contained one substrate mixture (primary) that consisted of aged manure, alfalfa hay, chip bark, gravel, peat moss, sand, and aged sludge from the Southeast Wastewater Treatment Plant in Rolla, Missouri (Table 2). These inexpensive materials are common to the area, and they were chosen for their hydraulic properties, nutritional value for bacteria, and ease of procurement. The sludge and aged manure were added to provide an initial bacterial population. Chip bark and hay are low-cost, locally available organic materials. Sand and gravel were selected to improve the hydraulic conductivity of the mixed substrate. Flow rates ranged from 5 to 17 mL/min. These flow rates were selected to give approximate hydraulic residence times of 2 to 7 days.

Another set of four constructed wetlands (No. 5 through 8), maintained at 15.3 ± 0.5 °C, was constructed with four different substrate mixtures. Wetlands 5 contained the primary substrate. Limestone was used instead of chert gravel in wetlands 6 to determine possible pH effects from the addition of carbonate-containing gravel. Wetlands 7 contained more peat and hay to examine the effect of increasing the proportion of these materials, which are known for high adsorption capacities. Wetlands 8 contained more sand to determine the effects of decreased organic content and increased hydraulic conductivity (presumably) and also to determine the effect of limestone. These four wetlands had a flow rate of approximately 5.0 mL/min, corresponding to a hydraulic residence time of approximately 7 days.

Table 1—Wetlands variations.

Label	Substrate[a]	Flow rate, mL/min	Temperature, °C
Wetlands 1	Primary	5.0	23[b]
Wetlands 2	Primary	8.5	23
Wetlands 3/ smelter wetland[c]	Primary	7.0/5.0	23
Wetlands 4	Primary	17.0	23
Wetlands 5	Primary	5.0	15
Wetlands 6	Limestone	5.0	15
Wetlands 7	Peat and hay	5.0	15
Wetlands 8	Limestone and sand	5.0	15

[a] Substrate composition is in Table 2.
[b] Room temperature, typically 23 °C.
[c] Wetlands 3 was switched to receiving synthetic smelter water on day 45 of operation.

Table 2—Substrate composition as percent volume.

Component	Primary	Limestone	Peat and hay	Limestone and sand
Peat moss	5	5	20	5
Alfalfa hay	5	5	20	5
Chip bark	50	50	20	30
Limestone gravel	—	20	—	20
Chert gravel	20	—	20	—
Aged manure	3	3	3	3
Wastewater treatment plant sludge	2	2	2	2
Sand	15	15	15	35

The hydraulic conductivity of the primary substrate was determined using a falling head method in a rigid permeameter (Bolis et al., 1994). The device used was a polyvinyl chloride (PVC) pipe with an inside diameter of 137 mm. The length of the sample was approximately 230 mm. A 1000-mL graduated cylinder was used to deliver the water, which flowed up through the sample. Upflow was used to help remove any air bubbles or gas produced in the substrate that would cause flow short circuiting.

Whole Effluent Toxicity. Whole effluent toxicity tests were performed to determine the toxicity of the influent and effluent of the wetlands. Cultures of *C. dubia* were obtained from Aquatic Bio Systems, Inc. (Colorado Springs, Colorado). Fathead minnows (*Pimephales promelas*) that were younger than 24 hours old were delivered by overnight express mail on the test day. Toxicity tests were conducted under conditions similar to those stipulated by current National Pollutant Discharge Elimination System (NPDES) permitting procedures.

When making test solutions, dilution water should be made using natural receiving stream water or local spring water unaffected by industrial discharge, with similar chemical characteristics for growing test organisms and diluting toxicants (Gale and Wood, 1995). The water used for growing the culture and preparing the controls and dilution water were obtained from Lane Springs in the Mark Twain National Forest, which is located approximately 20 km south of Rolla.

The WET test was performed within 2 hours of influent and effluent sampling. Controls were run with every assay. Typically, the water to be assayed was diluted as appropriate and split into four samples. Each sample of water was inoculated with five *C. dubia* neonates, five *D. magna*, or 10 to 11 fathead minnows. At various times (24, 48, 72, or 96 hours, depending on the assay species), counts of viable organisms were performed (Gale and Wood, 1995; Gubbi, 1997; and U.S. EPA, 1994).

Water Composition. Initially, all wetlands received synthetic mine water. One wetlands (wetlands 3) was switched after 45 days of operation to an influent that approximated the effluent discharged by a resource recovery smelter. The composition of each of these waters is given in Table 3.

Water was prepared by adding salts in either a concentrated aqueous solution or a powder form to Rolla tap water (groundwater) that was aerated for 24 hours to remove chlorine. Tap water

Table 3—Water compositions (only substantially differing components shown).

Component	Rolla tap water[a]	Synthetic mine water	Synthetic smelter water
Sulfate, mg/L	37.3	34.2	3700
Nitrate, mg/L	< 0.05	2.2	2.8
Sodium, mg/L	2.9	16.1	1800
Manganese, mg/L	0.002	0.045	0.018
Nickel, mg/L	< 0.003	0.045	< 0.003
Iron, mg/L	0.07	0.23	0.07
Potassium, mg/L	1.00	3.15	52
Chlorine, mg/L	2.2	12.5	225
Lead, μg/L	< 0.004	235 ± 90	290 ± 120
Zinc, μg/L	0.017	180 ± 30	140 ± 35
Arsenic, mg/L	< 0.002	< 0.002	0.1
Cadmium, mg/L	< 0.001	< 0.001	0.05
Calcium, mg/L	60	60	160
pH	7.6	8.0	8.5

[a] Data on tap water provided by Rolla Municipal Utilities.

was found to cause mortality to *C. dubia,* apparently because of the presence of the chlorine added for disinfection, with survival noted only when tap water was diluted 16- to 32-fold.

To remove bias from WET tests on the constructed wetlands influent and effluent prepared from tap water, removal of the disinfectant by aeration was deemed necessary. The aeration time was determined by assaying free chlorine at differing aeration periods and confirming survival of test organisms by WET assay. Free chlorine was assayed by a colorimetric method using a Hach (Loveland, Colorado) standard assay (*n,n*-diethyl-*p*-phenylenediamine [DPD] method, catalog #20603-00).

Sample Collection and Preparation. Influent and effluent water was periodically assayed for lead, zinc, sodium (smelter water), sulfate, sulfide, turbidity, volatile and total suspended solids (VSS and TSS), and pH. Composite samples (200 mL) were collected and immediately assayed for turbidity and pH; 100-mL composite samples were used to assay TSS and VSS; and 50-mL composite samples were filtered through 1.2-μm glass fiber filters to remove any suspended solids, which can interfere with atomic absorption (AA) spectrometers. After filtration, 9-mL samples for AA analysis were taken from the composite sample and placed in vials to which 100 μL of concentrated nitric acid were added. Acidified samples were stored at 4 °C until assayed.

Analytical Procedures. Methods 2540D and 2540E from *Standard Methods* (APHA et al., 1989) were used to determine TSS and VSS gravimetrically. A PerkinElmer (Oak Ridge, Tennessee) 3110 Atomic Absorption Spectrometer was used to analyze zinc, with a lower detection limit of 0.19 μg/L. Sodium was also assayed by flame atomic adsorption, with a lower detection limit of 20 μg/L. For flame atomic adsorption, the instrument was calibrated before each use, calibration standards were used as a check with every assay, and 20 readings were automatically averaged to give a single assay result. Lead samples were analyzed by electrothermal atomic absorption using a graphite furnace, a PerkinElmer 5100 Z with Zeeman background correction, and a detection limit of 0.6 μg/L. Twenty similar replicate readings were performed on each assayed sample.

Sulfate and sulfite analyses were performed on influent and effluent samples using a Hach DR 2000 Spectrophotometer. Sulfide analysis was performed according to Procedure 8051, Sulfa Ver 4 Method (Hach, 1997). A methylene blue method (Hach Procedure 8131) was used for sulfide analysis. In some cases, it was necessary to pretreat sulfite samples to remove turbidity, which was accomplished using a Hach pretreatment set (#24387-00). Turbidity was determined by nephelometry calibrated with known standards. The pH was measured using a combination pH electrode. Except for AA assays, duplicate samples were assayed.

Results

Synthetic Mine Water. The laboratory-scale constructed wetlands produced an effluent with concentrations of lead lower than 25 μg/L and zinc lower than 73 μg/L, as shown in Table 4. However, during the initial weeks of operation, the turbidity and suspended solids content were extremely high (1200 mg/L for suspended solids). Suspended solids levels quickly declined to approximately 200 mg/L and remained steady (Figure 2). The lead and zinc concentrations in the effluent from any of the laboratory-scale wetlands were statistically indistinguishable from any other. Typically, any of the effluents contained lead at 10 ± 3 μg/L, zinc at 50 ± 15 μg/L, suspended solids on the order of 200 ± 50 mg/L, and trace amounts of sulfate (6 μg/L) and sulfide (0.1 μg/L), at a pH of 6.8 ± 0.1 with a turbidity of 6 ± 1 nephelometric turbidity units (NTU).

Table 4—Effluent quality.[a]

Wetlands	1	2	3[b]	4	5	6	7	8
Months operational	10	9.5	1.5	9	7	7	7	7
Flow rate, mL/min	5.0	8.5	7.0/5.0	17.0	5.0	5.0	5.0	5.0
Temperature, °C	23	23	23	23	15	15	15	15
Lead, μg/L	9.6 ± 7.8	4.6 ± 2.0	25 ± 3.3	11 ± 1.1	7.8 ± 3.6	6.6 ± 2.5	7.4 ± 2.7	4.9 ± 2.2
Zinc, μg/L	53 ± 20	53 ± 11	73 ± 19	58 ± 19	42 ± 12	42 ± 13	54 ± 19	40 ± 12
pH	6.7 ± 0.1	6.8 ± 0.1	5.6 ± 1.3	6.8 ± 0.1	6.3 ± 0.2	6.9 ± 0.1	6.5 ± 0.1	6.7 ± 0.1
Turbidity, NTU	6 ± 1	7 ± 1	6 ± 1	6 ± 1	6 ± 2	5 ± 2	6 ± 1	4 ± 1
TSS, mg/L	183 ± 64	130 ± 58	138 ± 52	81 ± 34	378 ± 105	221 ± 94	620 ± 353	485 ± 264
Sulfate, mg/L	6 ± 9	3 ± 6	ND[c]	5 ± 7	5 ± 7	11 ± 7	9 ± 10	6 ± 9
Sulfide, μg/L	130 ± 70	100 ± 70	ND	290 ± 240	20 ± 20	10 ± 10	40 ± 50	40 ± 50

[a] 95% confidence interval reported.
[b] Wetlands 3 operated with mine water for 45 days, then switched to smelter water.
[c] ND = no data.

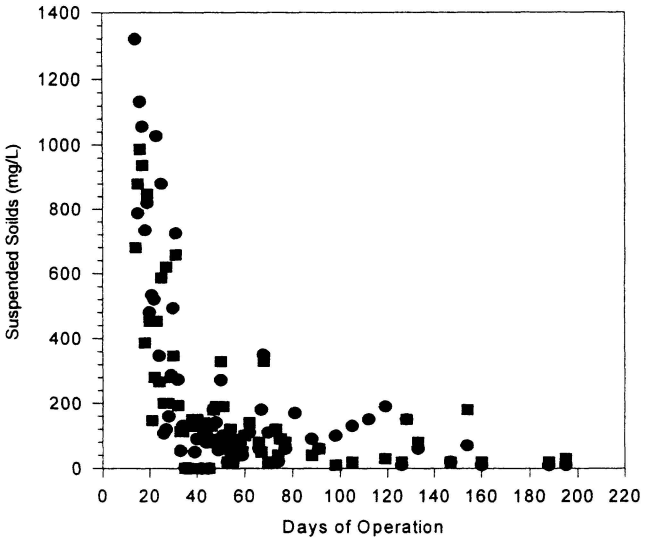


Figure 2—Typical effluent suspended solids from wetlands. Data from wetlands 1 shown. ■ = TSS, and ● = VSS.

The results of WET tests of effluent and influent samples are shown in Table 5. The influent was completely lethal to at least a 16-fold dilution. However, survival in raw effluent was equal to or better than the observed survival of the test organisms in the control water. Although the source of decreased toxicity cannot be easily determined, average removals of 90% lead and 72% zinc were observed in all eight wetlands, bringing the concentrations to lower than the normal 50% lethal dose (LC_{50}) values, which are 35 μg/L for zinc and >244 μg/L for lead when the test organism is *C. dubia* (Gale et al., 1999).

The removal is reflected in Figures 3 and 4, which show that the performance of the wetlands was variable. However, there was little variation in the percent removal among the different operational conditions and substrates of each wetlands.

As shown in Figure 5, sulfate was substantially removed. The influent averaged 40 mg/L sulfate, with a concentration of approximately 11 mg/L in the effluent. The removed sulfate was most likely converted to sulfide by sulfate-reducing bacteria, as indicated by the odor of hydrogen sulfide near the wetlands, gas bubbles on the surface of wetlands, and the detection of sulfide in the effluent from the wetlands (shown in Table 4 and Figure 5).

Table 5—Whole effluent toxicity results for mine water using *C. dubia*.

	Percent survival	
Water	**Undiluted**	**Diluted 1:1**
Lane Springs	85	—
Influent	0	0
Wetlands 1	90	100
Wetlands 2	100	100
Wetlands 4	100	100
Wetlands 5	100	100
Wetlands 6	80	100
Wetlands 7	95	100
Wetlands 8	100	80

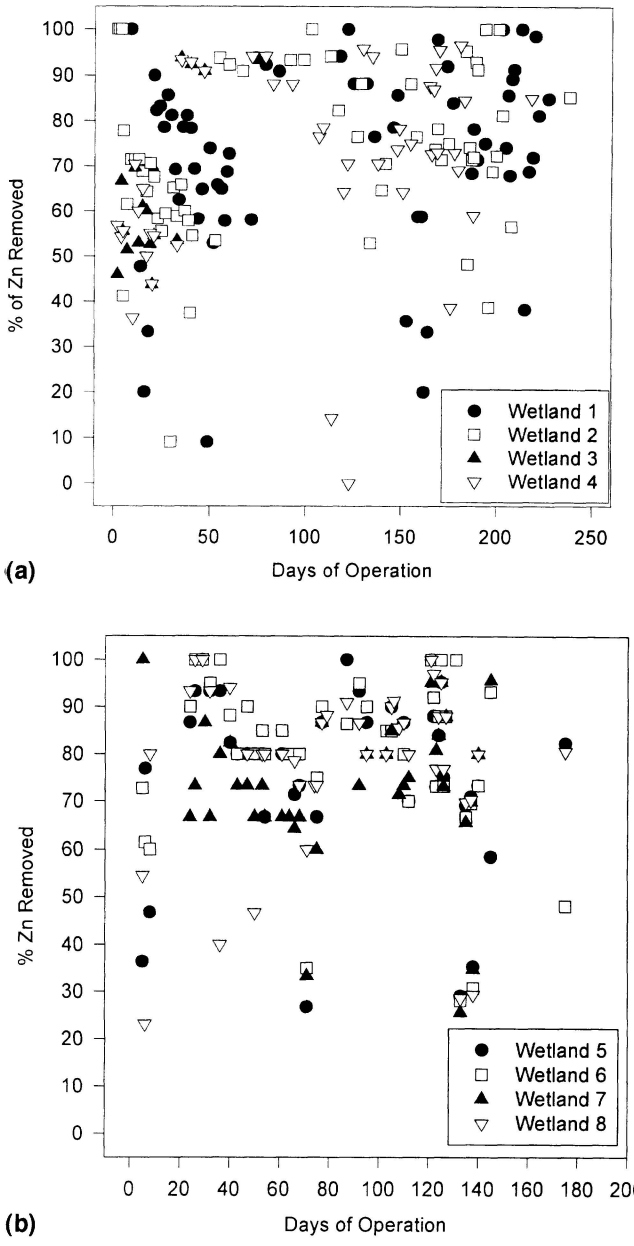
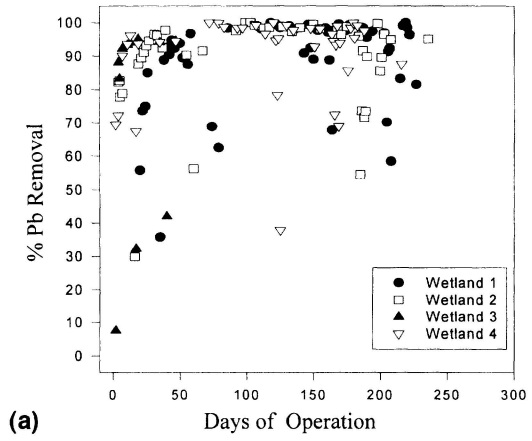


Figure 3—Zinc removal from (a) room-temperature wetlands (wetlands 1 through 4), 180 ± 30 μg Zn/L influent, and (b) low-temperature wetlands (wetlands 5 through 8), 235 ± 90 μg Zn/L influent. ● = wetlands 1, □ = wetlands 2, ▲ = wetlands 3, and ▽ = wetlands 4.

Temperature. The effects of temperature were studied by operating wetlands (1 and 5) having the same composition and flow rate at room temperature (23 °C) and at 15 °C. Operation at the lower temperature apparently improved the repeatability of results slightly as reflected in Figure 4, which seems to show a lower variability in results at 15 °C (lower temperature) than at room temperature. However, none of the variances was found to be statistically different. No significant change in lead and zinc removal rates was observed.

Substrate Composition. Although the four wetlands at 15 °C were filled with differing substrates, as shown in Table 4, no significant differences in performance were observed. Wetlands 6,



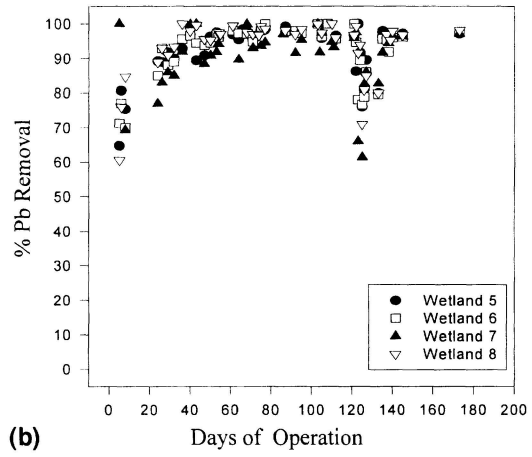


Figure 4—Lead removal from (a) room-temperature wetlands (wetlands 1 through 4), 65 ± 30 μg Pb/L influent, and (b) low-temperature wetlands (wetlands 5 through 8), 110 ± 70 μg Pb/L influent. ● = wetlands 1, □ = wetlands 2, ▲ = wetlands 3, and ▽ = wetlands 4.

which contained a limestone gravel rather than chert, apparently had a lower sulfide concentration in the effluent and a slightly higher than average effluent pH (6.9). Wetlands 8 also contained limestone, but sulfide concentrations and pH were near the average for other wetlands. Thus, the slightly differing effluent values of wetlands 6 might not be caused by the presence of limestone.

Hydraulic Loading and Hydraulic Conductivity. The three room-temperature wetlands with differing hydraulic loadings (29 to 106 L/m^2·d) showed no significant performance differences. There is a maximum hydraulic loading that may be applied to a wetlands. It is a function of the pressure differential and hydraulic conductivity of the wetlands. If the hydraulic loading of a wetlands is greater than the maximum flow rate, surface flow will occur.

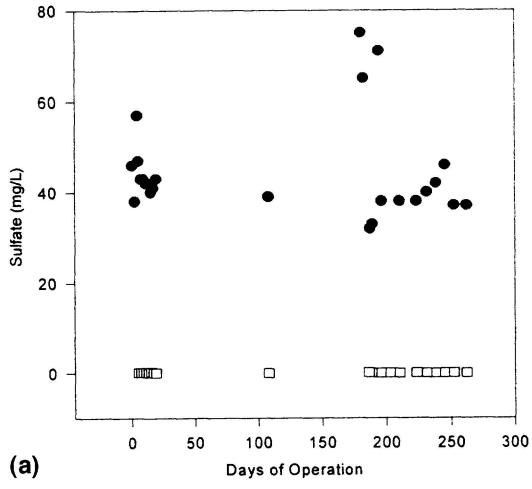
The hydraulic conductivity of the primary substrate was examined. Because wetland materials tend to consolidate over time, one column of substrate was studied over the course of 2 months. Hydraulic conductivity was initially high, approximately 4×10^{-4} cm/s, but declined to values in the range of 3×10^{-6} to 3×10^{-5} cm/s within 30 hours. This range of values is consistent with that reported in the literature (Bolis et al., 1994).

Smelter Water Results

One wetlands was operated with an influent that approximated the effluent from a resource recovery smelter. This wetlands was started with mine water (results labeled wetlands 3 above) and, after 45 days of operation, was switched to a synthetic smelter water, which contained greater concentrations of sodium and sulfate (1800 mg/L and 6 ± 3 g/L, respectively) and a two-fold greater lead concentration.

Although this wetlands developed significant salt deposits and demonstrated a 4-day breakthrough of sodium as shown in Figure 6, lead and zinc removals averaged 95 ± 8% for lead and 61 ± 15% for zinc. The difference between sodium removal efficiency and the removal efficiencies for lead and zinc might show that different metal removal mechanisms are occurring in the wetlands. Lead and zinc could be sequestered as lead sulfide and zinc sulfide that were formed by combining with the sulfide generated by sulfate-reducing bacteria in wetland soil. Sodium removal may be caused by the ion exchange that happens on the sites of sediment surfaces. The effluent detailed in Table 6 had acceptable concentrations of lead and zinc, but the removals of sodium and sulfate averaged only 15 and 30%, respectively.

Lead and zinc play a significant role in the toxicity of lead mine



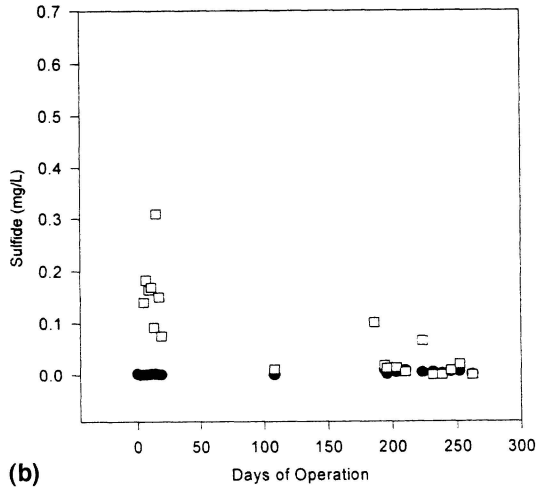


Figure 5—Typical (a) sulfate removal and (b) sulfide generation (wetlands 2). □ = effluent, and ● = influent.

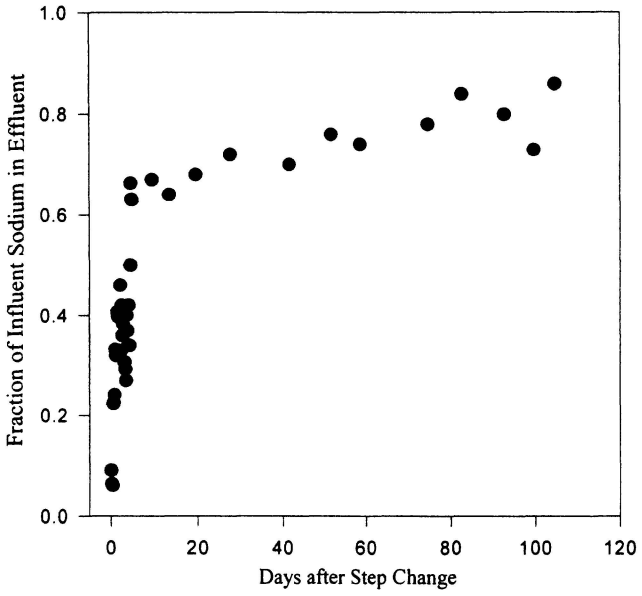


Figure 6—Sodium breakthrough in wetlands 3.

wastewater; so wetlands offered significant promise in decreasing the toxicity of the wastewater. Whole effluent toxicity tests with fathead minnows, *D. magna*, and *C. dubia* were performed on wastewater samples obtained from a lead smelter and selected wetland influent and effluent samples. Minnows displayed high survival rates in the synthetic smelter wastewater (wetland influent) as shown in Figure 7, with death seen only at dilutions of less than four-fold. The effluent from the constructed wetlands had an approximately 100% survival rate at all dilutions, including undiluted effluent.

Although only a single assay was performed with *D. magna* on the effluent from the wetlands treating synthetic smelter wastewater, survival in the undiluted and diluted sample was 100% as shown in Figure 8. The *C. dubia* demonstrated a lower survival than that of either fathead minnows or *D. magna*. The smelter wastewater and synthetic smelter water had similar toxicity to *C. dubia*, as shown in Figure 9. The effluent from the wetlands was assayed twice with *C. dubia*, with no survival in the undiluted effluent but 75 to 100% survival in influent diluted two-fold. Therefore, treatment in the wetlands significantly decreased effluent toxicity for all organisms studied.

Table 6—Influent and effluent quality for treated smelter water.

Parameter	Influent[a]	Effluent
Lead, μg/L	290 ± 120	5.3 ± 5.0
Zinc, μg/L	140 ± 35	43 ± 15
Turbidity, NTU	ND[b]	6 ± 3
TSS, mg/L	ND	104 ± 69
Sodium, mg/L	1800	1550
Sulfate, g/L	6 ± 3	4 ± 1
Sulfide, μg/L	2.4 ± 4.1	22 ± 8
pH	8.5 ± 0.4	7.1 ± 0.2

[a] 95% confidence interval reported as ±.
[b] ND = no data.

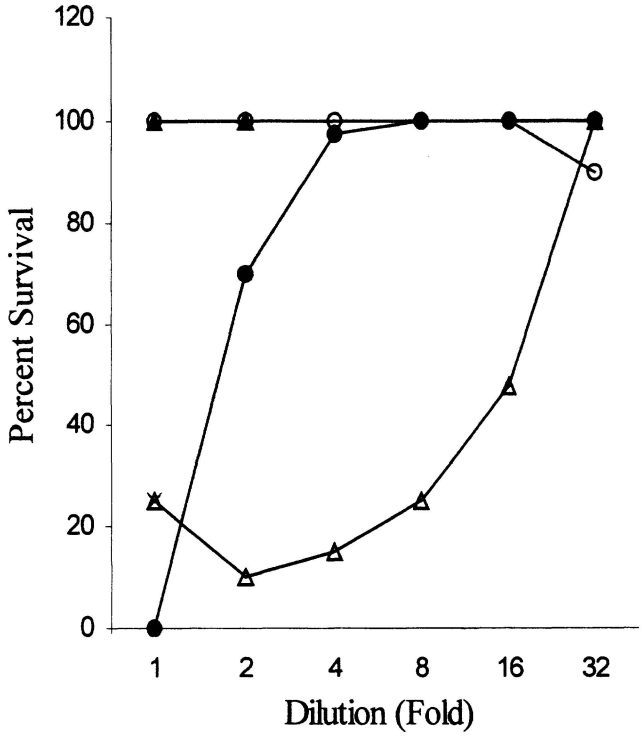


Figure 7—Survival of minnows (*P. promelas*) in WET assays. △ = authentic smelter water, ● = synthetic smelter wastewater, ○ = wetland effluent of smelter wastewater, and ▲ = November 12, 1997, wetland effluent of synthetic mine water.

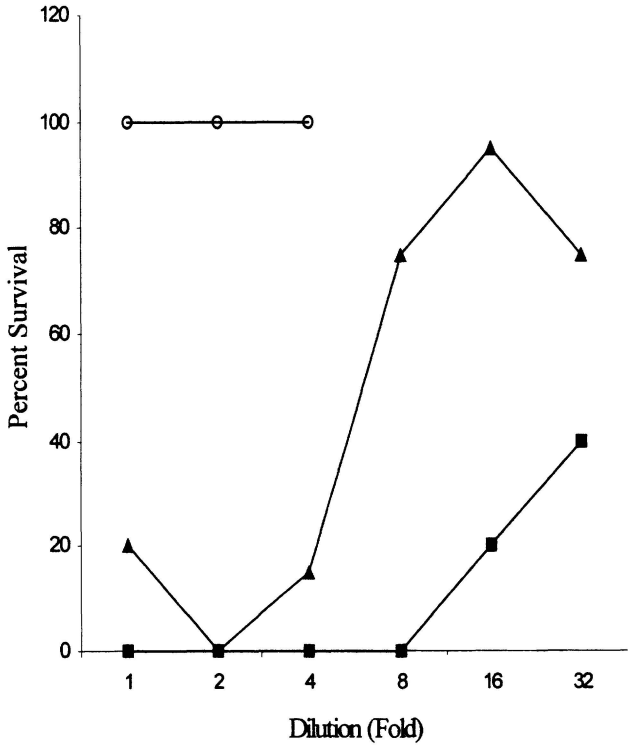


Figure 8—Survival of *D. magna* in WET assays. ■ = authentic smelter water (influent), ▲ = synthetic smelter water, and ○ = wetlands effluent of synthetic and authentic smelter wastewater.

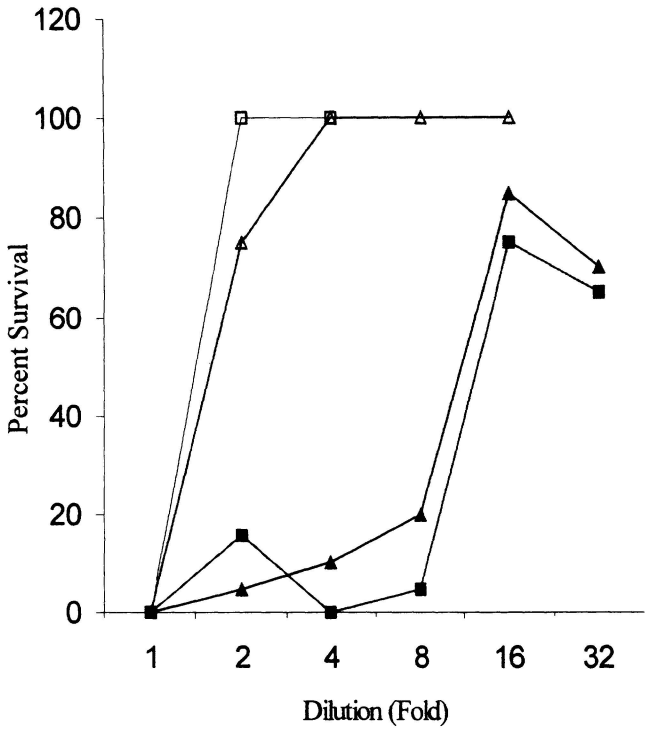


Figure 9—Survival of *C. dubia* in WET assays. ■ = authentic smelter waste water (influent), ▲ = synthetic smelter wastewater, □ = wetland effluent of authentic smelter water, and △ = wetland effluent of synthetic smelter wastewater.

As shown in Table 6, approximately only 30% of influent sulfate was removed by the wetlands, with the maximum removal rate of 10 g/m^3 wetland·h. The removed sulfate seemed to be converted to sulfide, as evidenced by the significant odor of hydrogen sulfide coming from the wetlands and by the 10- to 45-mg/L sulfide concentrations in the effluent from the wetlands. The measured sulfate concentrations were 500-fold greater than those observed in wetlands operating on synthetic mine water.

The change from synthetic mine water to synthetic smelter water was a unique opportunity to perform a tracer test on the wetlands. The step change in influent sodium concentration, from 16 to 1800 mg/L, resulted in the effluent response shown in Figure 6. A breakthrough period of approximately 4 days was observed. Little sodium removal was anticipated, and this breakthrough probably represents the combination of hydraulic residence time and saturation of ionic sites in the wetlands. The concentration of sodium in the effluent continued to increase during more than 120 days of operation in a manner consistent with a mixed reactor. This non-plug-flow behavior might represent a hydraulic flow pattern in which dispersive (diffusional) flow is as high in rate as the advective (pressure-driven) flow, the saturation of sites on soil by sodium, or the slow exchange of some chemicals for sodium.

Conclusions

Over the course of almost 300 days of operation, eight laboratory-scale wetlands removed lead and zinc from a synthetic lead mine effluent with high efficiency. An average 90% removal of lead and 72% removal of zinc were observed, and wetland effluents had little or no toxicity in WET assays. The wetlands also removed 70% of sulfate from the influent, producing sulfide apparently through the metabolism of sulfate-reducing bacteria. Sulfate was completely removed from the synthetic mine water, but it was apparent from the smelter wetland data that there is a maximum rate of sulfate removal, 10 g/m^3 wetland·h. Differing substrate composition and hydraulic loading did not show a significant effect on performance under the conditions studied.

For the constructed wetlands studied here, three primary metal removal mechanisms seem likely. First is adsorption or exchange onto sediments in wetlands. Second is sulfide precipitation of metals in reducing zones catalyzed by bacterial metabolism, which has been claimed to dominate in the treatment of acid mine drainage (Machemer and Wildeman, 1992). The third likely removal mechanism is co-precipitation with (or adsorption onto) iron and manganese oxides. Based on the results noted here, any of the three mechanisms might be occurring.

There was ample evidence of sulfate reduction, the substrates should be able to adsorb substantial amounts of metals, and large quantities of iron oxides were visible in the gravel lens at the front of each wetlands. The observed lack of influence of temperature and hydraulic residence time on removal does not favor any of these mechanisms. Further research is needed to identify the specific mechanisms occurring in the wetlands studied here.

This is the first carefully controlled study on the treatment of neutral mine drainage by constructed wetlands. This laboratory-scale study shows that constructed wetlands are tremendously effective in treating heavy-metal-containing wastewater of neutral pH. This technology should be effective not just for mine waste but for many types of metal-containing wastewater.

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Authors. Ying Song, Mark Fitch, Joel Burken, Linda Nass, Somnath Chilukiri, and Chad Ross are with the Department of Civil Engineering and Nord Gale is with the Department of Biological Sciences at the University of Missouri–Rolla. Correspondence should be addressed to Mark Fitch, Department of Civil Engineering, University of Missouri–Rolla, Rolla MO 65401.

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