Lead and Zinc Removal by Lab-Scale Constructed Wetlands

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Abstract

Thirteen lab-scale constructed wetlands treated a synthetic, slightly basic mine water containing 34.2 mg/L SO₄²⁻, 50 μ g/L Pb and 300 μ g/L Zn. Data from over two years operation showed an average removal of 90% for lead and 72% for zinc, respectively. The pH of the effluent was reduced from 8.0-8.5 to near neutrality. Temperature, hydraulic loading, and substrate composition generally did not affect treatment efficiency. Sulfate was completely removed, likely by sulfate-reducing bacteria. A study of the adsorption capacity of various wetland substrates showed a substantial adsorption capacity for lead and zinc. Measurements on sediments indicated substantial co-precipitation of lead and zinc with iron oxyhydroxides at the gravel lens in the front of the wetlands. Sequential extraction of wetland sediments showed that lead was mostly in the exchangeable and Fe/Mn oxide fractions while zinc was mostly in the Fe/Mn oxide and organic Therefore the major removal mechanisms of these metals in fractions. constructed wetlands seems to be by co-precipitation with Fe/Mn oxide and adsorption on organic matter.

Introduction

Metals-contaminated waters, such as metal industry wastewater, mine drainage, and tailings leachate are a problem of national importance. Constructed wetlands have a demonstrated ability to remove metals from contaminated waters, having been applied to industrial facilities as well as mine drainage (Butterworth *et al.*, 1999). However, the effectiveness of wetlands has proved highly variable at different sites (Fennessy, 1989). On some occasions wetlands have been known to fail for no explainable reason (Wieder, 1989).

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The removal mechanism determines the capacity for a wetland to function and the possibility the removed metal will leach or be bioavailable. Several biogeochemical processes may be responsible for transformation and retention of metals in constructed wetlands, such as adsorption onto organic matter, formation of insoluble sulfides, oxides, or carbonates, and co-precipitation with iron or manganese oxides and hydroxides. Machemer *et al.* (1992) reported that sulfide is the dominant removal mechanism for one wetland receiving acid mine drainage, but this report was based on somewhat contradictory evidence. With better knowledge of removal mechanisms constructed wetlands would be designed to maximize the activity of those processes and to retain metals in forms that are biologically inert.

To date most of the research on metals removal by constructed wetlands has focused on the treatment of acid mine drainage (AMD), while wetlands for the treatment of neutral metals-contaminate waters have not been significantly explored (Wildeman *et al.*, 1997). Lead mines, which produce a slightly alkaline effluent, are of significant interest in Missouri, the nation's leading lead producer. The goal of the research reported here is to evaluate the capacity for constructed wetlands to treat lead mine drainage and to study the fate of lead and zinc in wetland substrates. The effect of several factors on the wetland treatment efficiency was evaluated and whole effluent toxicity assays were performed on the effluents. The adsorption capacity of various wetland substrates and the form and distribution of lead and zinc in wetland sediments were also studied.

Methods and Materials

Twelve lab-scale horizontal flow constructed wetlands and one down-flow wetland were created in glass aquariums three feet by one foot by one-and-a-half foot deep. A six-inch gravel lens in the front for flow distribution was separated by a perforated Plexiglas wall from two foot of substrate with a depth of one foot. This substrate was followed by another perforated Plexiglas wall and a six-inch free water space for effluent collection. The downflow wetland differed from this design, having been installed in a Nalgene barrel with six-inch substrate layers separated by three-inch sand layers to allow for inter-layer sampling. The wetlands received a groundwater supplemented with salts to approximate lead mine effluent concentrations. The wetlands were operated with differing flow rates, substrate composition, and temperature, as shown in Tables 1 and 2.

Influent and effluent water was periodically sampled and assayed for lead, zinc, sulfate, sulfide, turbidity, volatile and total suspended solids, and pH. Standard Methods 2540D and 2540E were used to determine total and volatile

suspended solids gravimetrically. A Perkin-Elmer 3110 Atomic Absorption Spectrometer was used for analysis of zinc and lead, except that lead samples from the effluent were analyzed by electrothermal atomic absorption using a graphite furnace, a Perkin-Elmer 5100 Z with Zeeman background correction and a detection limit of 0.6 ppb. Sulfate and sulfite analyses were performed on influent and effluent samples using a Hach colorimetric technique. Sulfide analysis used Hach Procedure 8131. Turbidity was determined by nephelometry calibrated with known standards. pH was measured using a combination pH electrode.

Component	Primary	Limestone	Peat & Hay	L-stone & 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	
WWTP Sludge	2	2	2	2	
Sand	15	15	15	35	

Table 1. Substrate Composition as Percent Volume

Label	Substrate	Flow	Volume	Temp.
	(see Table 1)	(mL/min)	(L)	(°C)
Wetland 1	Primary	5	85	23
Wetland 2	Primary	50	85	23
Wetland 3	Primary	7	85	23
Wetland 4	Primary	25	85	23
Wetland 5	Primary	5	85	15
Wetland 6	Limestone	50	85	15
Wetland 7	Peat & Hay	5	85	15
Wetland 8	L-stone & Sand	25	85	15
Wetland 9	Primary	5	85	23
Wetland 10	Primary	5	85	23
Wetland 11	Primary	25	28	23
Wetland 12	Primary	50	28	23
Wetland 13	Primary	50	85	23

Tumbler tests were performed to study the adsorption characteristics of the wetland substrates. Peat moss, hay, sand, and chip bark were mixed in glass bottles with solutions of various concentration of lead and zinc (pH 7.5). After five days of tumbling, the concentration in solution, assumed to be at equilibrium, was assayed by AA.

A sequential extraction procedure developed by Tessier *et al.* (1979) was modified and performed on various samples from the wetlands to determine the forms of the lead and zinc in the wetland sediment. The procedure was calibrated against a NIST reference sediment, and acid-washed sand and fresh wetland substrates were used as blank controls.

Acid volatile sulfide (AVS) was determined by adding 5 ml of 6 M HCl to sediment samples. Nitrogen gas was bubbled into the resulting solution and a 1M NaOH solution was used to trap the H_2S extracted from the sediment. The sulfide concentration in the NaOH solution, and sulfide concentrations in sediment pore water were measured by a silver/sulfide selective electrode.

Results and Discussion

The thirteen lab-scale constructed wetlands produced an effluent with concentrations of lead below 25 μ g/L and zinc below 73 μ g/L, with average removal efficiencies of 90% for lead and 72 % for zinc (Figure 2). During the initial weeks of operation the turbidity and suspended solids content was extremely high (1200mg/L for suspended solid) but then quickly declined to about 200 mg/L and remained steady. In general, the effluents from every wetland contained lead at $10 \pm 3 \mu$ g/L, zinc at $50 \pm 15 \mu$ g/L, a pH of 6.8 ± 0.1 , a turbidity of 6 ± 1 NTU, suspended solids on the order of 200 ± 50 mg/L, a small amount of sulfate (6μ g/L) and sulfide (0.1μ g/L). The Lead and Zinc concentration in the effluent from any of the lab-scale wetlands was statistically indistinguishable from any other. Temperature and substrate composition didn't have statistically significant effect on the performance of the wetlands.

The adsorption assays showed that lead and zinc adsorption on wetland substrates could be best describe by the Langmuir model, q=ABC/(1+BC). The adsorption values given in Table 3 indicate adsorption by organics could be a substantive removal mechanism. Based on the measured values for adsorption, breakthrough time for lead and zinc saturation (at influent concentrations) of adsorptive sites in the Wetland 1 will be 145 and 41 years, respectively. Unfortunately, adsorption is not a desirable removal mechanism. The reason is two-fold, first that wetland failure is guaranteed after some time period, and second that the metals are only loosely bound to the wetland sediment. Metal

adsorbed could be easily mobilized and released if competitive ions were introduced, resulting in a significant potential risk to the receiving water body.



Figure 1. Typical Lead and Zinc Removal, Wetland 1 Data Shown

	Zii	nc	Le	Lead		
Component	А	В	А	В		
Peat Moss	0.013	0.69	0.71	0.001		
Hay	0.69	0.69	0.0025	0.15		
Chip Bark	0.023	0.69	10	0.0016		
Gravel			0.013	0.0018		
Sand	0.00082	0.69	0.0014	0.18		

Table 3 Langmuir Parameters for Wetland Substrates.

Sediment extractions were performed on sediment samples from Wetlands 3 and 7 to determine the forms of lead and zinc removal in the wetlands. The

sequential extraction gives metals speciation forms as exchangeable, carbonate, Fe/Mn oxide, organic, and residual. The results for Wetland 7 are shown in Figure 2. In both wetlands, the Fe/Mn oxide fraction is the dominant form of lead and zinc in the sediment.



Figure 2. Forms and Distribution of Lead and Zinc in Wetland 7 Sediment. Samples from centerline (i.e. 6" below surface and 6" from walls).

More lead was apparently present in an exchangeable form, while zinc was more likely to be found in the organic fraction. A large amount of lead and zinc was found to have deposited in the gravel lens rather than in the wetland substrate. A rusty precipitate in the gravel lens yielded very high concentrations of lead and zinc in the Fe/Mn oxide phase, as shown in Tables 4 and 5.

·	Wetland							
	2	4	5	6	8	9	10	13
Exchangable	59	97	11	39	53	10	10	33
Carbonate	130	139	2	58	84	2	.4	512
Fe/Mn oxide	13,190	7620	603	7747	13,483	764	1077	1026
Organic	561	347	46	371	1019	30	27	37
Residual	468	1405	167	661	1803	73	123	14

Table 4. Lead concentrations in $\mu g/g$ 'rust' for each gravel lens.

	Wetland							
	2	4	5	6	8	9	10	13
Exchangable	150	111	5	87	101	1	3	35
Carbonate	1510	1219	7	1433	1512	1	11	799
Fe/Mn oxide	24,533	13,213	152	13,473	18,707	148	153	1819
Organic	681	320	83	263	326	48	152	18
Residual	114	165	30	122	246	29	16	3

Table 5. Zinc concentrations in $\mu g/g$ 'rust' for each gravel lens.

It is an interesting point to note that the amount of lead and zinc associated with the Fe/Mn oxide fraction increases as the water moves through the wetland (Figure 2). Further investigation of the Fe/Mn oxide fraction showed that as the amount of lead and zinc associated with the fraction increases, the mass of iron deposited in the wetland decreases; more iron was found in the front than in the rear of the wetland. The reason for this relationship is unknown and further analysis of the wetland and the Fe/Mn oxide fraction will be necessary to determine why this occurs.

Probably the best form of metals removal would be as metal sulfides. The advantages of this form of removal are the insoluble nature of metal sulfides, and more importantly that the source of the sulfide is continuing biological activity, possibly making wetlands an inexhaustible treatment system. To the nose, sulfide generation was occurring in these systems, and sulfate was removed. However, little lead or zinc was associated with the residual (sulfide) phase in sediments. An examination of acid volatile sulfide in the sediment of Tank 5 showed a range of 0-11 μ g/g (Figure 5), although as much as 3.7 mg/L dissolved sulfide was detected in wetland substrate pore water. This indicates that sulfide precipitation, previously reported in some literature as the most important mechanism in wetlands, is not the predominant process in the wetlands studied here.



Figure 5. Acid Volatile Sulfide in Sediment of Tank 5, Duplicate Assays.

Since the metals associated with the exchangeable, carbonate and Fe/Mn oxide fractions are more likely to be mobilized in a given environment, some concern may be appropriate for wetlands currently in use.

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Comparison of Gravity-Flow and Reciprocating Constructed Wetland Performance

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Abstract

Non-point source pollution to the nation's waterways continues to be a major issue in this new millennium. One of the major sources of this pollution is poorly operating on-site and centralized treatment systems. Clearly there is a necessity for alternative on-site systems to meet the needs of the public where conventional systems cannot. From an environmental standpoint it is also advisable to treat waste on site in order to return treated waters to their point of origin and maintain the natural hydrological balance. The traditional approach to designing constructed wetlands has been to use gravity-flow subsurface systems. Both Environmental Protection Agency [U.S. EPA, 1988] and the Tennessee Valley Authority [TVA, 1993] have published design literature on gravity flow systems. Recently TVA has developed a new technology that relies on a reciprocating reactor system to enhance nitrogen transformations within the wetlands. The reciprocating technology was recently granted a patent [Behrends, 1999] and these systems are currently being used in four states. This paper presents an analysis of operating data from both types of systems operating in North Alabama to determine if there are any significant differences in performance.

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Introduction

It is often difficult to site conventional septic tank/leach field systems in North Alabama (as well as many areas of our country) due to the heavy clay soils, limestone geology and high water tables. This is especially a significant problem for small communities and rural areas that do not have access to sewer lines. Therefore, innovative decentralized and on-site systems are of major interest to health departments and land developers in the region. As a result, several experimental SF constructed wetlands were permitted and installed three to five years ago in suburban neighborhoods in North Alabama.

Gravity flow systems designed using both TVA and EPA methodologies are dependent on Darcy's equation, as well as and hydraulic and organic loading [TVA, 1993]. The dimensions of length, width, and depth are obtained geometrically in both design approaches. However, the most significant difference is in the surface area calculation. The TVA approach determines surface area by a hydraulic loading criterion, which is a constant value, expected to maintain subsurface flow conditions. The EPA model determines surface area by the organic loading of the system and calculates BOD_5 described by plug flow kinetics. The primary assumption for this model is that the wetland behaves similarly to other attached-growth treatment systems [Sauter and Leonard, 1997].

Reciprocating constructed wetlands (RCW) are a patented design consisting of two or more adjacent subsurface flow cells that utilize the concept of reciprocation, that is alternately draining and filling on a defined and recurrent basis. According to the patent description, this flow pattern achieves significant enhancement of both the biological and physical processes by exposing the biofilm directly to atmospheric oxygen [Behrends, 1999]. Obviously this oxygenation should enhance the nitrification process, which is aerobic. However the cells are not drained completely thus anoxic conditions required for denitrification are maintained in the lower regions. A major advantage of the RCW design is the smaller surface area required which may offset the power expense for pumping.

To verify performance efficiency, six constructed wetland (CWs) systems were sampled for a variety of water quality parameters, including BOD, nitrates, ammonia, total bacterial count, turbidity, and solids over a range of water temperatures. Monthly water samples were taken at the influent to the cells (at hydraulic control structures), at the midpoint of two-cell systems and treated effluent at the end of the cell. All of the systems studied had a settling tank upstream from the wetland and were designed for subsurface, non-discharge flow within a gravel medium.