MEASURED AND MODELED REMOVAL MECHANISMS FOR BENCH-SCALE CONSTRUCTED WETLANDS RECEIVING LEAD MINE WATER[1]

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Abstract. Based on a period of 505-2595 days of operating lab-scale wetlands (bioreactors) treating simulated lead mine drainage containing Pb, Zn, and sulfate, a model of flow and metals removal, both equilibria and kinetics, was developed using PHREEQC, a freely-available aqueous geochemistry model. To develop parameters for the model, the fundamental question: "Where does the metal go?" had to be answered. Although the model predicts sulfide formation, we observed limited metal sulfides based on extractive assays. Despite the presence of sulfide in pore water, our wetlands display significant uptake of metals from the water via adsorption instead of via sulfide precipitation. Our operating results have shown that plants do not have a noticeable impact on removal of metals in these wetlands beyond perhaps recharge of organic matter by decaying plants. We speculate that beyond know inaccuracies in extractive assays; the metals undergo very slow reactions in-situ which cause changes in the form of the metals from adsorbed to less soluble forms, presumably due to sulfides present from the biological sulfate reduction. Overall, metals removal in our wetlands appears to follow a two-step process: first adsorption to the sediment, then sulfide formation.

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Introduction

Water pollution associated with lead mining is a substantial concern in Missouri, which produces 90% of lead mined in the United States (Benn and Cornell, 1993). Passive treatment schemes such as constructed wetlands, which are increasingly being referred to as biocells, take advantage of naturally occurring geochemical and biological processes to improve the water quality with minimal operation and maintenance requirements (Gazea and Kontopoulos, 1996). In the past two decades, constructed wetlands have been used with varying success to treat acid mine drainage as well as urban runoff and industrial outfalls (Neculita et al., 2007). However, until recently, most of the studies on the constructed wetland focused on qualitative description of removal mechanisms only. Reports on quantification and modeling of constructed wetland processes are rarely available, resulting in the situation that constructed wetland designs for mine drainage treatment are usually based on rules-of-thumb, therefore the treatment systems may be under- or over-designed and effectiveness is variable (Gerth et al., 2000; Fennesy, 1989). To better understand what happens in such wetlands, research at the Missouri University of Science and Technology (formerly the University of Missouri-Rolla) has focused on quantifying removal mechanisms.

This research builds on our past study of the removal of lead and zinc from neutral mine drainage by lab-scale constructed wetlands. Fourteen lab-scale constructed wetlands were set up treating synthetic mine effluent for up to seven yeas, with more than 90% removal of Pb and 65% removal of Zn observed at hydraulic residence times of 0.45 to 4.5 days (Song et al., 2001). Adsorption by organic matter, Fe/Mn hydr(oxide) association, and bacterially-mediated sulfide precipitation were identified as the primary removal mechanisms responsible for Pb and Zn removal in constructed wetlands (Song, 2003), while plant uptake of these metals is low (Selman, 2006). Each removal mechanism could be dominant under specific conditions and removal mechanisms are usually intertwined in wetlands. Based on the various results, this paper summarizes the effort to develop a comprehensive model to simulate the dynamic process of lead and zinc removal by constructed wetlands treating neutral waters.

The objectives of this work were to determine removal mechanisms in wetlands receiving neutral mine water. This effort focused on the examination of various bench-scale wetlands for metals breakthrough, redox potential, and concentrations in pore waters, and application of a model populated with parameters from independent experiments and literature values.

Methods

Biocells

Three vertical flow lab-scale constructed wetlands and four horizontal flow lab-scale constructed wetland with various configurations were operated for 2 - 7 years. The basic setup and operation conditions of the lab-scale wetlands are listed in Table 1. Composition and properties of the substrate used in those constructed wetlands are listed in Table 2. It should be noted that the initial components were not directly assayed for metals content. The layer of chert gravel was present to aid in distribution of the influent. These wetlands had a porosity of 47.6 ± 3.8%, measured based on mass loss on drying (Song, 2003). The composition of synthetic Pb mine water prepared with tap water and supplied to each wetland is listed in Table 3.

Table 1. Setup and operation conditions of lab-scale wetlands

Wetland	Flow pattern	Flow rate	Dimension [a]	Gravel layer thickness[b]	HRT[c]	Average Dispersitivity[d]	Running time
		(mL/min)	(cm)	(cm)	(min)	(cm)	(day)
V1	Upflow	Varied	14 x 51	9.0	80	15.3	505
V2	Downflow	Varied	14 x 55.5	0	12.5-900	9.2	1022
V3	Upflow	Varied	14 x 51	9.0	31-314	19.3	517
H1	Horizontal	25	20 x 28.5 x 29.5	9.5	157	10.6	2352
H2	Horizontal	50	20 x 28.5 x 28	9.5	294	3.3	2352
H3	Horizontal	5	76 x 28.5 x 28	7.5	5580	18.1	2593
H4	Horizontal	5	76 x 28.5 x 29.5	7.5	5879	10.3	2595
		5					
		5					

[a] Vertical flow wetlands were columns with the reported diameter x height; horizontal-flow wetlands were rectangular with reported length x width x height.

[b] Chert gravel layer was added to the inlet to aid distribution of influent.

[c] Hydraulic residence time, HRT, was calculated based on porous bed volume.

[d] Dispersivity was determined with tracer tests.

Table 2. Composition and properties of the substrate used in lab-scale wetland

Substrates	Weight (%)	Organic (%)[a]	CEC (mol/kg)[b]	Density (g/ml)
Peat moss	0.55	96.5	$7.61x\ 10^{-1}$	0.098
Chip bark	15	95.8	5.86×10^{-1}	0.27
Manure	0.96	97.8	N/A[c]	0.28
Hay	0.59	92.6	$.33 \times 10^{-1}$	0.10
Sand	23	N/A[c]	1.05×10^{-3}	1.4
Gravel	57	N/A[c]	N/A[c]	2.5
Sludge	2.3	N/A[c]	N/A[c]	1.0

[a] The percentage of organic matter in individual substrates was obtained by measuring the weight loss after heating the substrates in a 550 °C oven for four hours.

[b] Cation Exchange Capacity (CEC) in individual substrates was determined by the $BaCl_2$ Compulsive Exchange Method (Gillman and Sumpter, 1986).

[c] N/A = not measured or assumed to be zero.

Table 3. Synthetic mine water composition

Component	Pb	Zn	SO_4^{2-}	Fe	Mn	Ca	Mg	Na
Conc. (µmol/L)	0.217	4.68	356	4.17	0.819	1500	1650	700

Component	K	Cl	Ni	As	Cd	pH	Alkalinity
Conc. (µmol/L)	80.6	352	0.630	< 2 µg/L	< 1 µg/L	7.5 – 8.0	2000

Assays

The pH, flow rate and concentrations of Pb, Zn, and SO_4^{2-} of influent, effluent and pore water samples from various locations of each wetland were measured periodically (somewhat at random) to monitor the metal removal efficiency. The pH of water samples was measured with an IQ150 pH probe and meter (IQ Scientific Instruments). Redox potentials in various locations of wetlands were monitored using in-situ probes (Ahn et al., 1992), by connecting a voltage meter and an Ag-AgCl reference electrode to Pt electrodes embedded in those locations, calibrated with a 234-mV standard solution. The SO_4^{2-} was measured using Hach's Sulfa Ver 4

Method with a reported detection limit of 5 mg/L (Hach, 1998). Water samples for Pb and Zn assays were immediately filtered through 0.2 µm membranes to exclude solids, acidified by adding 0.5% (v/v) of trace metal-grade concentrated nitric acid and were stored in new polypropylene tubes.

Lead concentration in the liquid samples (including extractants) were measured with a Perkin-Elmer AAnalyst 800 Graphic Furnace Atomic Absorption Spectroscope (GFAA) using $NH_4H_2PO_4$ as a matrix modifier and $Pb(NO_3)_2$ in 0.2% HNO_3 standard solution for calibration and quality control. The method detection limit for Pb was about 1.5 µg/L. Zinc concentrations were measured with a Perkin-Elmer 3110 Flame Atomic Absorption Spectroscope (FAA) using $Zn(NO_3)_2$ in 0.2% HNO_3 as a standard solution. The method detection limit for Zn was about 31 µg/L. The spike method was used for some extraction samples in order to minimize the interference from the high concentrations of extractant chemicals (Tessier et al., 1979).

Sequential Extraction

Substrate samples were taken from wetlands using a stainless steel scoop. Samples were obtained from various spatial and locations in the wetlands (discussed further in Chang, 2006). The samples were dried in a nitrogen-filled anaerobic chamber to minimize oxidation. Gravel in the samples was removed by hand because they could not be ground and some were limestone; thereafter the samples were ground and homogenized for a modified Tessier's sequential extraction (Tessier et al., 1979). The modified Tessier's procedure extracted Pb and Zn in five operationally defined fractions (named F1 to F5 in this text). The modification to Tessier's protocol was in the F5 extraction step, using 8 mL of trace metal-grade concentrated HNO_3 at 100 °C for 5 h instead of the $HF\text{-}HClO_4$ reported in Tessier's work.

Dispersion

Dispersion in the wetlands was determined using a step input of 3 g Br/L. Samples at various distances and times after injection of the tracer were taken with plastic syringes using glass tubing emplaced in advance in horizontal-flow wetlands and from pre-placed ports at sand lenses placed within the vertical flow wetlands. Conductivity was used to measure Br concentration; conductivity correlated very well with concentration results from a Dionex DX -120 Ion Chromatograph System during an initial experiment. The breakthrough curves at various distances were analyzed with software CXTFIT v 2.2 (University of California, Riverside) to obtain hydraulic parameters.

Organic Decomposition

The decomposition rate of organic matter in the substrate was determined by comparing the volatile solids of gravel-free substrate in the wetlands at different time periods under submerged conditions. The samples were collected at various distances and depths from the wetlands during operational periods of up to seven years. The collected samples were dried at 105 ºC overnight. The decomposition rate was calculated based on the mass loss per volume of wetland sample, and for convenience of comparison, was converted to the unit of g/(g original substrate day). Original substrate mass was found assuming that the fixed solids content of the substrate was constant.

Model

The geochemical transport model PHREEQC was used as modeling tool; extensive explanation of the model used is provided by Chang (2006). The conceptual model started with the Advection-Reaction-Dispersion (ARD) equation, including adsorption by organic matter, association with hydrous ferric oxide (HFO), and sulfide precipitation as removal mechanisms. The numerical approach used by the software follows the ARD equation in a split-operator scheme. The discretization of the simulated system used a limited grid size, but convergence was checked by doubling the finer grid and producing the same overall results.

Some further simplifying rules were imposed in the model: HFO association can occur everywhere in the wetland including the gravel layer as long as amorphous HFO exists (such existence calculated from PHREEQC's equilibrium database as part of the model); hydrous manganese oxide was not considered as an adsorbent; adsorption by organic matter does not occur in the gravel layer; and sulfide precipitation occurs as soon as sulfide exists.

Adsorption. Adsorption by organic matter was described by the Langmuir equation, with the rate of adsorption described by a pseudo-second order rate equation:

$$dq_t/dt = k_2(q_t-q_e)^2 \text{..} (1)$$

Where q is the amount absorbed at time t or at equilibrium (q_e), t is time and k2 is the rate parameter. Parameters used in the model were measured in batch experiments reported elsewhere (Chang, 2006) and are shown in Table 4.

The model assumed that the organic adsorption capacity was proportional to the organic content of the substrate. Hence the adsorption capacity was decreased with time according to the organic matter decomposition rate.

Adsorption by HFO was modeled using the parameters and diffuse double-layer approach of Dzombek and Morel (1990). The kinetic calculation was the first-order model of Appelo and Postma (2005), based on the diffuse layer model.

Table 4. Parameters for Pb and Zn adsorption by organic matter in batch assays

Pb		Zn	
q_{max} (μmol/g)	b (L/μmol)	q_{max}(μmol/g)	b(L/μmol)
1.15×10^{2}	8.38×10^{-2}	1.30×10^{2}	9.70×10^{-2}
$k_2 = 0.0012\ (\text{sorbate/sorbent})^{-1.2}$ *		$k_2 = 1.05 \times 10^{-4}\ (\text{sorbate/sorbent})^{-1.55}$	

* Sorbate/sorbent is the ratio of moles of sorbate in the initial solution to the moles of adsorption sites in the adsorbent.

Sulfide. Sulfide formation was modeled as following Monod kinetics, using a half-saturation sulfate concentration of 1.62 mmol L^{-1} or 155 mg/L, as determined by Boudreau and Westrich (1984); and the maximum specific rate of sulfate utilization as equal to the rate of organic matter degradation (as COD, assuming the organic to be $C_5H_7O_2N$). To allow this process in PHREEQC, disequilibrium between S(6) (S in SO_4^{2-} form) and S(-2) (S in sulfide forms) was necessary. A switch was also set in the model to restrict sulfate reduction to occur only when Eh was less than -180 mV.

Results

This work focused on quantifying removal mechanisms in bench-scale constructed wetlands. Adsorption to organic matter, adsorption to HFO, and sulfide precipitation had previously been identified as significant mechanisms in lab-scale wetlands receiving synthetic Pb mine drainage, so the work reported below focused on quantifying that removal. As organic matter decomposes, adsorption sites are lost and the liberated electron donors may result in sulfide formation. Therefore, the rate of organic decomposition was determined to provide rate parameters for both of these processes. This data, along with literature values and parameters previously determined in our work, were used in the model run in PHREEQC to predict concentrations and chemistry of Pb and Zn.

Organic Decomposition

Figure 1 shows the time profiles of organic contents of substrate in different wetlands. A part of the VS appears to be refractory, likely because the primary component, chip bark, contains compounds such as lignin that degrade only very slowly. Thus, a modified Monod equation having the following form was used:

$$R = [R_{max} (C_{org} - C_{refrac})]/[K_{org} - (C_{org}-C_{refrac})] \tag{2}$$

where the R is the rate of the organic matter decomposition rate (g/g original substrate day), R_{max} is the maximum rate of organic matter decomposition , C_{org} is the organic content (or volatile solids (VS)) of substrate (g/g original substrate), C_{refrac} represents non-degradable organic content (g/g original substrate), and K_{org} is the half-saturation constant. The parameter values found by least squares fitting of equation (2) to the VS data are listed in Table 5.

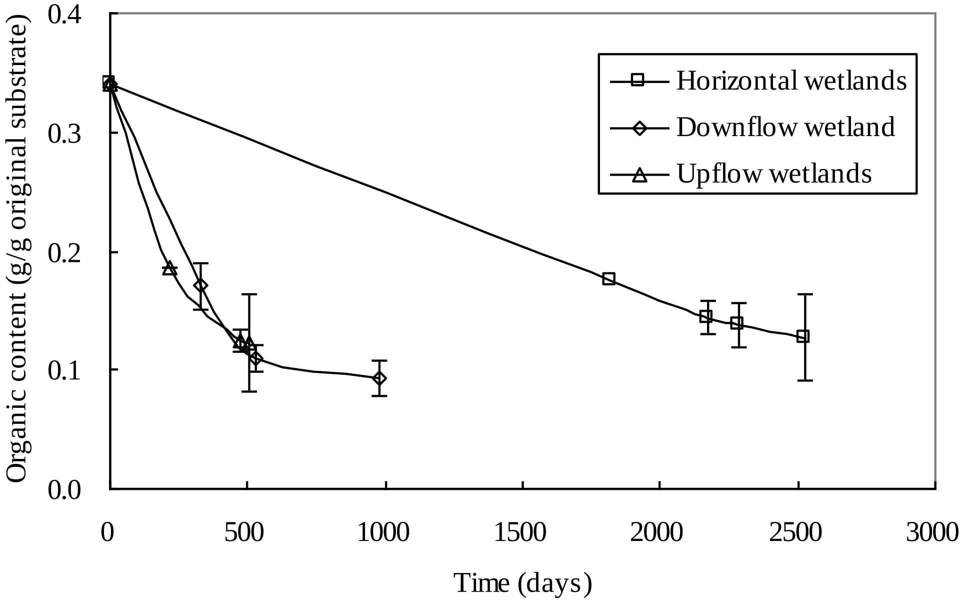

Figure 1. Time profiles of wetland substrate organic content. Error bars represent 95% confidence intervals

The maximum decomposition rate varied significantly among horizontal, downflow and upflow wetlands, possibly due to the various conditions of electron acceptor supply. Upflow wetlands had the highest flow rate and resulting highest dissolved oxygen delivery rate, while the downflow wetland had a lower electron acceptor supply rate due to flow, and the horizontal wetlands had the least oxygen supply. All wetlands had similar C_{nondeg} values indicating the substrate may have around 10% of organic content that cannot be easily degraded.

Table 5. Monod equation parameters for organic decomposition rates

Wetland	R_{max} (mg/g orig. sub. day)	C_{refrac} (g/g orig. sub.)	K_{org} (g/g orig. sub.)
Horizontal	0.098	0.13	0.0068
Downflow	0.71	0.1	0.052
Upflow	1.8	0.12	0.21

Model Simulations

The model, with parameters measured independently of the operating wetlands aside from dispersion, predicted operating results well, as R^2 values were generally better than 0.7. Examples of the model output compared to measured values are shown in Fig. 2 and 3.

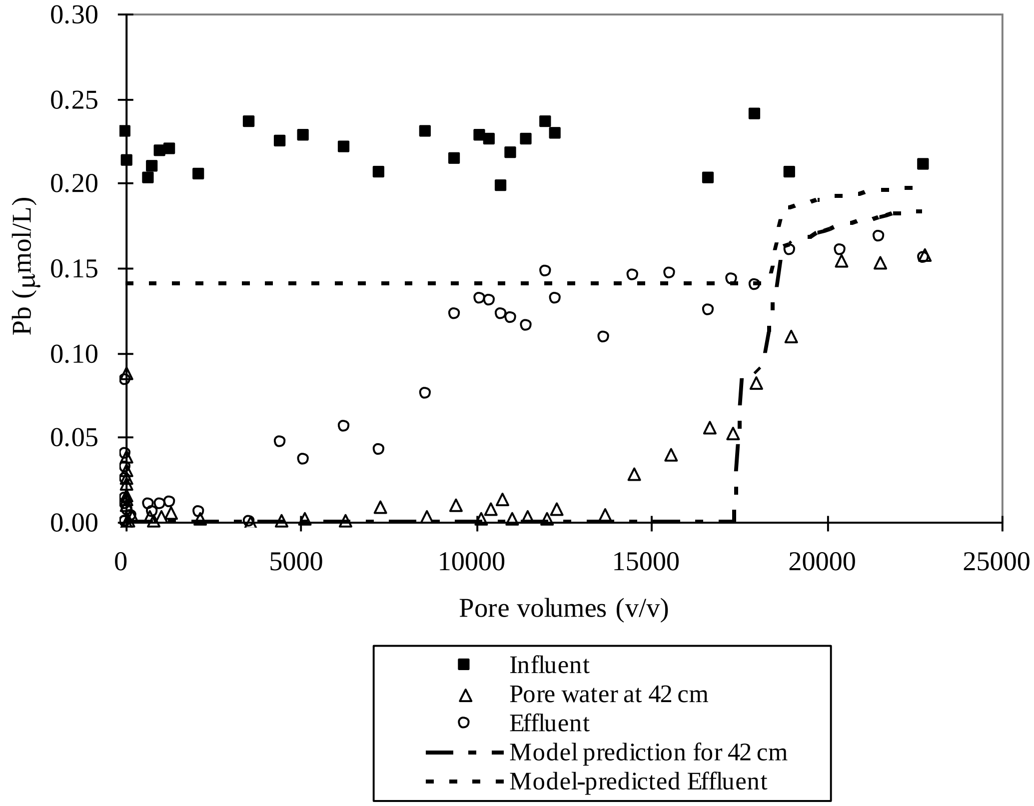

Figure 2. Time profiles of lead concentration in the pore water and effluent of upflow wetland V1. Model results shown as dashed lines.

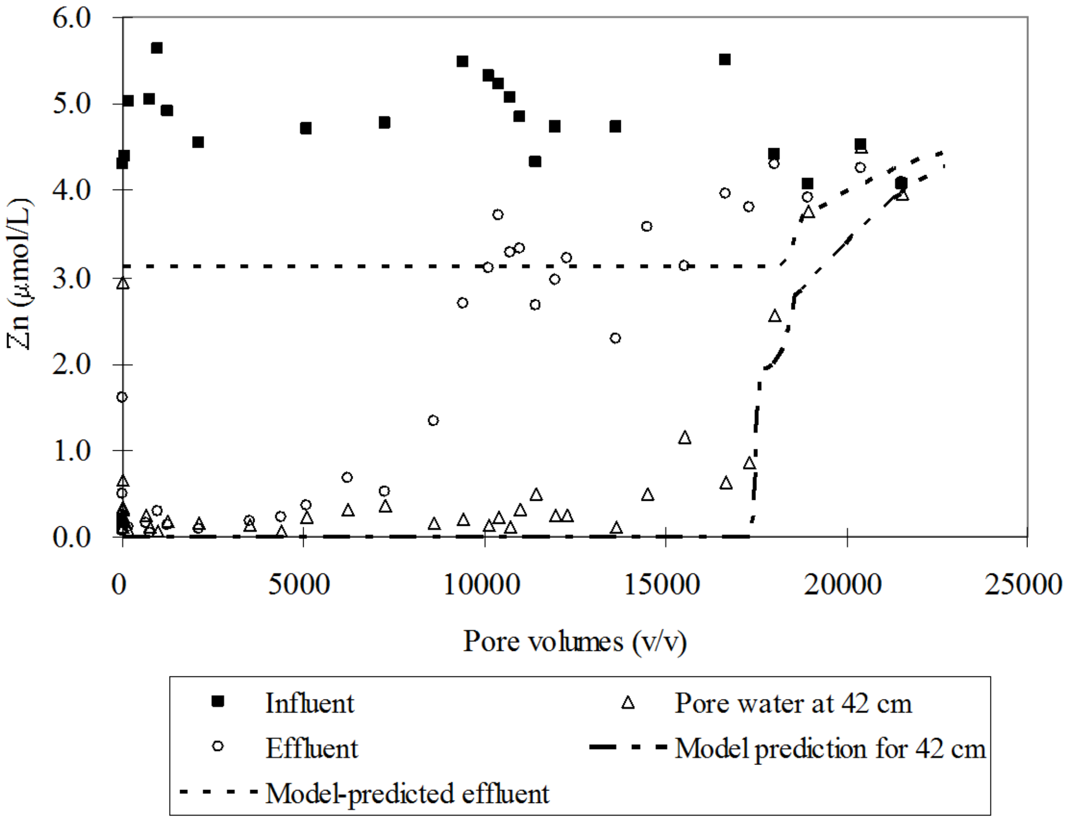

Figure 3. Time profiles of zinc concentration in the pore water and effluent of upflow wetland V1. Model results shown as dashed lines.

The wetland modeled in Fig. 2 and 3 was operated in vertical flow mode for 505 days with an average flow rate 180 mL/min (theoretical hydraulic residence time (HRT) of 80 min), with about 22,790 pore volumes (v/v) of synthetic mine water passing through this wetland. The wetland was characterized with a significant short circuit, a common issue in wetland systems (Hagedorn and Bundt, 2002; Breen and Chick, 1995; Weaver et al., 2003). According to the tracer test conducted on day 450, it was estimated 68% of the influent flowed through a short circuit path and only 32% was actually treated by the substrate. This in part explains the unusual result at 42 cm distance where the pore water has a lower concentration than the effluent, as the short circuit is bypassing the location where pore water was sampled. To simulate short circuiting, the model assumed 32% of the flow rate passed through the substrate and was treated and the resulting effluent mixed with the remaining 68% of untreated influent solution. This simulation of short circuiting caused the deviation between the model and the measured effluent concentration seen during early operation in Fig. 2 and 3.

There is no record of when the short circuit developed in the wetland, so it seems likely that the initial operation had a lesser degree of short circuiting and thus low but non-zero concentrations in the effluent, with increased short-circuiting with continued operation.

The model-predicted values agreed with measured values well for pore water samples (with R^2 = 0.852 for lead and 0.813 for Zn, effluent data not included). The values show a sharp increase of both Pb and Zn concentration at 13,250 pore volumes at the distance 21.5 cm. This was attributable to the model predicting a sharp change of Eh from negative to positive (Fig. 4) due to exhaustion of organic matter, resulting in the dissolution of metal sulfide. The actual change of Eh in the wetland was not drastic as the model predicted; this difference is due to 1) oxygen diffusion from the surface; 2) organic degradation rates differing from the modeled values; or 3) oxygen or other electron acceptors in the influent. The wetland did trend towards aerobic after about 17,000 pore volumes of flow.

Figure 5 illustrates the model prediction of Pb concentrations in the effluent of another wetland, H1. This horizontal-flow wetland was operated for 6.5 years at a much greater residence time than V1 (Table 1), with around 14,673 pore volumes of mine drainage, about 175 m^3, passing through the wetland. However, operation was sometimes unstable during the first two-and-a-half years due to overflow and tubing blockage problems.

Measured lead concentration in the effluent from H1 gradually increased, with considerable fluctuation, as operation continued. The model-predicted lead concentration was slightly higher than the measured values and showed minimal fluctuation.

For other vertical-flow wetlands, the model predicted breakthrough by Pb and Zn with R^2 from 0.562 to 0.807. Simulation of horizontal-flow wetlands resulted in agreement that both model-predicted values and most of measured values were below detection limits. In addition to prediction of metals concentrations, the model was moderately effective at predicting pH changes and agreed well with measured Eh values.

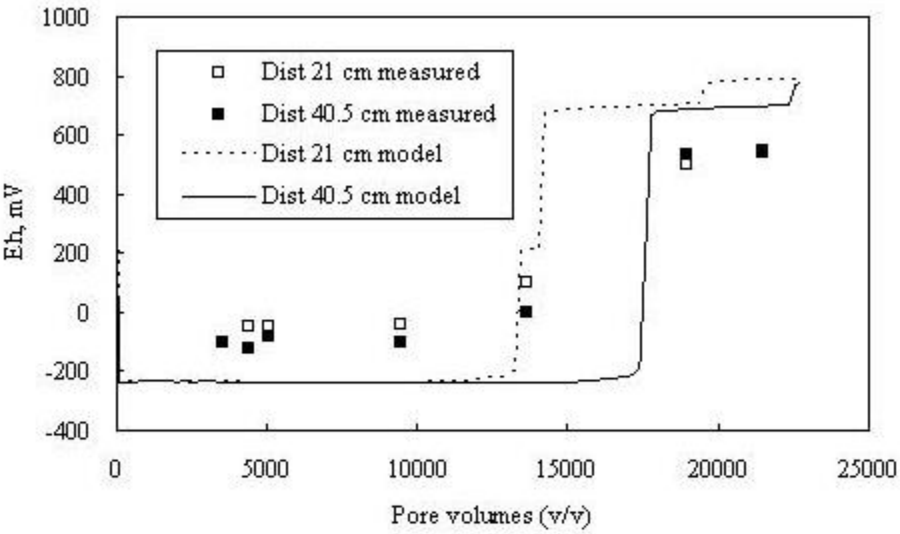

Figure 4. Time profiles of Eh upflow wetland V1. Dist is the distance along the wetland, not including 9.5 cm gravel layer.

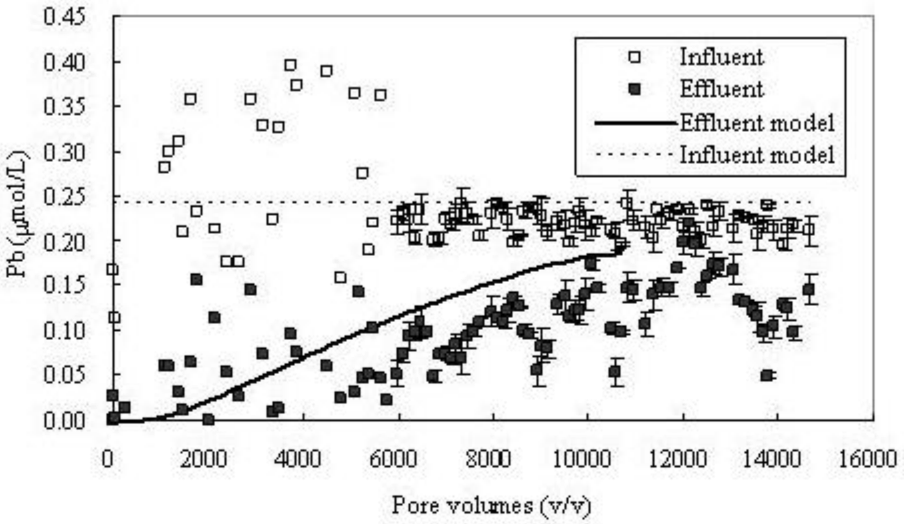

Figure 5. Time profiles of lead concentrations in effluent of horizontal wetland H1. Error bars indicate 95% confidence intervals.

Removal Mechanisms

The kinetic parameters and equilibrium values used in the model greatly favor the formation of metal sulfide if sulfide is present, and when hydrous ferric oxide (HFO) is present that adsorption to HFO is dominant. The reported Eh for sulfide formation is well below that at which HFO will dissolve. Thus the model predicted three cases: first, at high Eh, Pb and Zn are associated with HFO; second, in anaerobic sections of the wetland with Eh above -180 mV, organic adsorption is dominant (~100% of removed metal is adsorbed); and third, if Eh is sufficiently low, essentially all removed metal is present as metal sulfide. An interesting trend is shown in Fig. 6 for horizontal-flow wetland H2. In this case, the model predicts that HFO-associated Pb builds up consistently in the gravel lens as Fe and O_2 are in the influent along with Pb, but in the anaerobic zone removal is first dominated by adsorption as the organic utilization starts to drive the Eh below -180 mV, after which removal switches to exclusively sulfide dominated, around 3800 pore volumes. At 6500 pore volumes, the organic utilization rate falls below the rate of electron acceptor supply, and the Eh was modeled as rising, resulting in dissolution of metal sulfide and a large increase in the metal adsorbed by organic material.

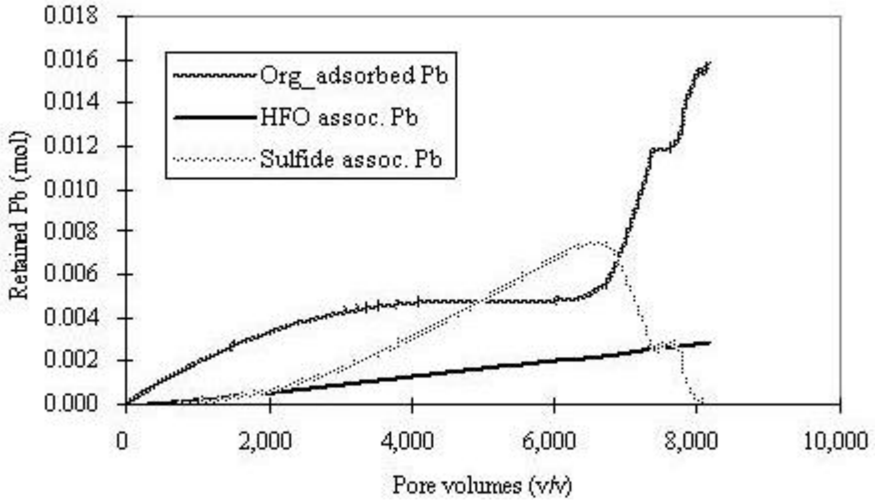

Figure 6. Model-predicted time profile of fractions of retained lead for horizontal wetland H2

The results shown in Fig. 6 can also be compared to extractive assays. Samples of substrate from wetland V1 were subjected to extractive assay after 505 days of operation, with results compared in Fig. 7 for Zn to the model-predicted composition at the same location. Results for Pb speciation were quite similar amongst the various wetlands.

Tessier's extraction was developed to use various reagents in a sequential extraction process to show chemistry of the extracted metals. Table 6 shows Tessier's extractants and the expected chemistry of extracted metals. As previously noted, the actual chemistry of the extracted metals may not be that shown in Table 6 and thus here we preferentially refer to the fractions by the labels F1-F5.

Table 6. Tessier's sequential extraction method (Tessier, 1979)

Fraction	Reagent
Exchangeable	1 M $MgCl_2$ at pH = 7 for 1 hr at 20 ^oC
Carbonates -bound	1 M NaAc at pH = 5 for 5 hr at 20 ^oC
Oxides-bound	0.04 M $NH_2OH{\cdot}HCl$ in 25% HAc for 6 hr at 96 ^oC
Organic-bound	0.02 M HNO_3 + 30% H_2O_2, pH = 2 for 2 hr at 85 ^oC + 30% H_2O_2, pH = 2 for 3 hr at 85 ^oC + 3.2 M NH_4OAc in 20% HNO_3 for 30 min at 20 ^oC
Residual	$HF\text{-}HClO_4$

The general agreement of total mass of Pb or Zn between the measured values and predicted values was quite good. However, the fractions observed by means of extraction had no significant relationship with those of the model-predicted fractions, for example as shown in Fig. 7. It is well-known that sequential extraction procedures are not completely accurate as assays of metals chemistry, but they are also not unrelated to metals chemistry (Sobolewski, 1999; Kheboian and Bauer, 1987). The model indicated the primary portions of retained Pb and Zn were by organic adsorption, while in the results of sequential extraction, organic-associated Pb only had limited percentage of total Pb, organic-associated Zn was minor, and carbonate-associated and FeO associated Pb and Zn were significant. This difference might be due to various issues including: 1) the retained Pb or Zn experienced changes in chemistry as substrate aged; 2) application of empirical equations instead of detailed description of removal mechanisms; 3) known weakness of Tessier's protocol, notably non-selectiveness and redistribution problems.

Although sequential extraction results are known to be of limited accuracy, changes in phase are unlikely to be so large that a metal sulfide would be extracted in the fraction designed to mobilize organic-adsorbed metal. For cases in which the model predicted sulfide formation, metal distributions were similar to those shown in Fig. 8. The extractive assay would indicate metal present as HFO associated and covalently bound to organic, while the model predicted 100% sulfide.

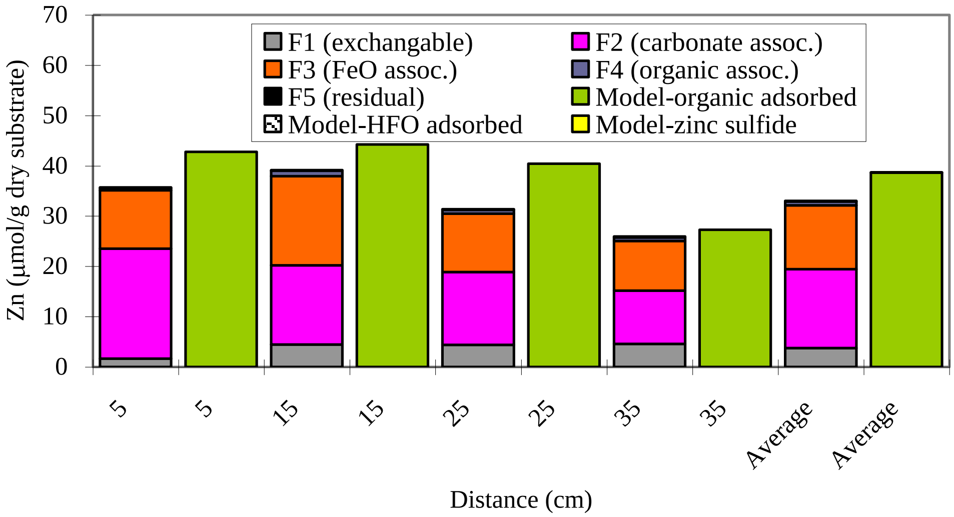

Figure 7. Zinc fractions in the substrate in upflow wetland V1 at the end of operation on day 505. Distance measured from gravel layer.

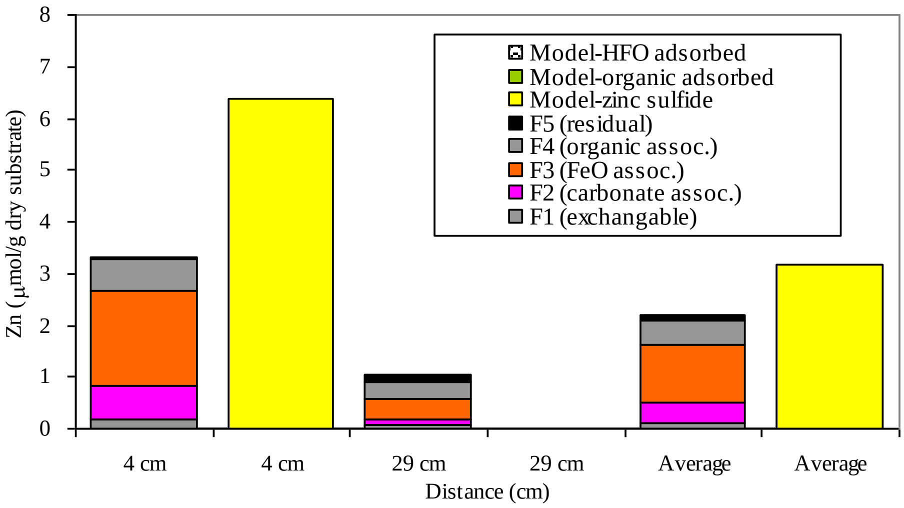

Figure 8. Lead fractions in the substrate in Wetland H3 at 464 pore volumes. No bar shown at 29 cm reflects that no removal was predicted by the model this far into the wetland.

To explain the discrepancy in the anaerobic substrate, we speculate that adsorption is a significant removal mechanism: metal may contact an organic site before encountering sulfide.

If the organic site largely isolates the metal from sulfide, then only slowly will the expected equilibrium form, metal sulfide, be formed. Metals thus might undergo very slow reactions in-situ which cause changes in the form of the metals from adsorbed to less soluble forms. Overall, metals removal in our wetlands appears to follow a two-step process: first adsorption to the sediment, then sulfide formation. This speculation is supported by our data reported elsewhere (Chang, 2006) in which extractive assays with 1 M NaCl extracted a large fraction of metals from young wetlands, but much less metal was extracted from older wetlands.

Conclusions

The PHREEQC model was able to simulate Pb and Zn breakthroughs in four wetlands with modest precision (R^2 of 0.56 to 0.87), and accurately predicted effluent concentrations below the detection limit in three other wetlands, which agreed with observations. The success of the modeling was also supported by the spatial distribution of total retained Pb and Zn, but the predicted metal species were different from the results of sequential extraction. These results indicate that competition amongst removal mechanisms may occur. Further, the success of the model at predicting operation is encouraging: with increased information on removal mechanisms, more precise measurements of organic utilization, and better description of dispersion and short circuiting; models may be developed which can be applied to the design of biocells.

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