VALIDITY OF MANGANESE AS A SURROGATE OF HEAVY METALS REMOVAL IN CONSTRUCTED WETLANDS TREATING ACIDIC MINE WATER

by

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Abstract: The evaluation of manganese as a surrogate for heavy metal behavior in two wetland treatment systems receiving acidic coal mine drainage in central Pennsylvania was investigated. The use of manganese as an indicator is based on physical/chemical treatment processes quite different from wetland treatment. The treatment systems represented one anoxic, subsurface flow system and one oxic surface flow system. Water quality parameters measured included pH, alkalinity, acidity, and a suite of metals. Correlation and linear regression analysis were used to evaluate the ability of a candidate predictor variable (indicator) to predict heavy metal concentrations and removal. The use of manganese as a predictor of effluent quality proved to be poor in both wetland treatment systems, as evidenced by low linear R^2 values and negative correlations. Zinc emerged as the best predictor of the detectable heavy metals at the anoxic wetland. Zinc exhibited positive strong linear correlations with copper, cobalt, and nickel (R^2 values of 0.843, 0.881, and 0.970, respectively). Effluent pH was a slightly better predictor of effluent copper levels in the anoxic wetland. Iron and cobalt effluent concentrations showed the only strong relationship (R^2 value = 0.778) in the oxic system. The lack of good correlations with manganese strongly challenges its appropriateness as a surrogate for heavy metals in these systems.

Additional Keywords: cobalt, copper, iron, nickel, zinc.

Introduction

Point-source discharges, which include runoff from mineral mining sites, are regulated by the Federal Clean Water Act (1972) to meet certain water quality standards. Major water quality parameters pertinent to acidic coal mine drainage are pH (between 6 and 9), iron (less than 7 mg/l daily and less than 3.5 mg/l on a monthly average), and manganese (less than 4 mg/l daily and less than 2 mg/l on a monthly average; Weider 1989).

Various methods may be employed to meet the effluent water quality criteria specified by the U.S. EPA. Bringing treated acidic mine water into compliance often involves the utilization of chemical treatments to raise pH to sufficiently alkaline values to precipitate metals. As a passive alternative to chemical treatment for AMD containing relatively low concentrations of iron and manganese (usually less than 100 mg of metal/l), natural or constructed wetlands have been utilized to provide long-term treatment.

A problem associated with the use of a wetland for treatment of AMD is meeting effluent

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quality standards for manganese. Owing to its ability to remain soluble in reduced form at low to circumneutral pH, particularly in the absence of an oxidant, manganese often limits acceptable wetland treatment performance.

Kleinmann and Watzlaf (1988) reviewed the history of the development of mine water effluent standards from the perspective of the inclusion of manganese among water quality parameters. Initially, manganese was included by the U.S. EPA in the mining industry standards as a representative of priority pollutants, owing to suspected adverse physiologic and economic properties of the metal. Subsequently, toxicity of manganese was de-emphasized with attention directed to the role of manganese as a surrogate (indicator) of the possible presence of heavy metals in the effluent of treated AMD.

The current manganese standard originated with the observation made by the U.S. Environmental Protection Agency that during chemical neutralization/oxidation treatment of AMD, the removal of any of eight heavy metals (arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc) from solution was accompanied by a reduction in soluble manganese to 2 mg/l (Watzlaf 1988). To achieve transformation of soluble manganese to an insoluble hydroxide form at a rate commensurate with reasonable reactor residence time in treatment of the drainage, alkaline additions to the flow must be sufficient to raise the pH to approximately pH 11; a pH value well in excess of that required to achieve the formation of insoluble oxides/hydroxides of pertinent heavy metals.

Because the excessive alkaline conditions imposed in chemical treatment of AMD are not reflective of the biogeochemical events occurring in wetland systems serving in the capacity of AMD renovation, relevance of the manganese standard applied to effluents from these systems has been called into question (Kleinmann and Watzlaf 1988). The objective of the present study was to assess the relationship between manganese removal and heavy metals from four wetland systems receiving AMD for treatment.

Materials and methods

Sample collection and analysis

Water samples were obtained from two constructed wetland sites located in central and western Pennsylvania. Samples were collected in duplicate in 250 ml polypropylene bottles that had been rinsed with about 50 ml of water from the site. Care was taken during sampling to prevent debris from entering the sampling container. All bottles were filled to overflowing to minimize headspace. The bottles were labeled and placed in a cooler with ice, then transported to a laboratory at The Pennsylvania State University.

One set of the samples was analyzed in the laboratory for alkalinity (method 2310 B, hot peroxide treatment), acidity (method 2320 B, potentiometric titration to a specific pH), and pH (method 4500-H^+) (Standard Methods for the Examination of Water and Wastewater 1995). The duplicate set of samples was acidified to a pH of <2 with high purity concentrated nitric acid (Fisher's Optima®). Acidified samples were packed in coolers with ice and delivered to the water laboratory at the Environmental Resource Research Institute at The Pennsylvania State University. Samples were analyzed for manganese, zinc, arsenic, chromium, lead, nickel, cadmium, iron, aluminum, copper, silver, cobalt, magnesium, and calcium by atomic adsorption spectroscopy (method 31111, Standard Methods for the Examination of Water and Wastewater 1995).

Wetland Sites

Bark Camp Run. The Bark Camp Run is a subsurface loaded, demonstration constructed wetland site located south of Pennfield, Clearfield County, Pennsylvania. The wetland system consists of six lined, individual cells, each 52 m long and 8 m wide at the water surface (Hellier 1996. A series of baffles or deflectors placed perpendicular to the long axis of each wetland 2 m on center promotes uniform flow. The initial 2 m x 8 m stage of the wetland consisted entirely of river gravel and the final 2 m x 8 m stage consisted entirely of crushed limestone of approximately 1.5 cm diameter. The organic substrate consisted of 50% by volume horse manure, which had a measured alkalinity of 15000 mg of $CaCO_3$ equivalent per kg dry weight prior to placement, and 50% river gravel (ca. 5 cm diameter) composed mainly of SiO_2. The substrate was placed 55 cm deep and covered with a 5 cm of topsoil. The design water depth above the topsoil layer or rock is 5 cm. The dominant macrophyte was cattails (*Typha latifolia*) which were planted 0.5 m apart and grew to nearly 100% cover prior to the experimental period.

Median values of influent mine water constituents for the period 1992-1995 are as follows (Hellier,1996): pH = 3.0; acidity = 202 mg/l as $CaCO_3$ equivalent; alkalinity = 0 mg/l as $CaCO_3$ equivalent; $[Fe^{3+}]$ = 22.9 mg/l; $[Fe^{2+}]$ = 0.8 mg/l; $[Al^{3+}]$ = 10.9 mg/l; $[Mn^{2+}]$ = 2.0 mg/l; and $[SO_4^{2-}]$ = 592 mg/l.

Mancuso wetland. The Mancuso wetland site is located at the edge of a former strip-mine location in a reclaimed field outside of Luthersburg, Pennsylvania and receives its influent from an underground seep. Four rectangular cells precede a former treatment pond which was used initially for chemical treatment. The influent to each cell flowed diagonally to the effluent end in order to encourage water flow through the entire wetland. Samples for this project were collected at the influent to the first cell and the effluents from the second and fourth cells. Water depth in the cells ranged from 6 to 73 inches; three of the four cells contained less than 20 inches of water. The substrate ranged in depth from 12 to 33 inches. All of the cells have an area of 1756 m^2. Cattails existed throughout the wetland, and flow occurred primarily across the surface.

Data analysis

All data were entered into spreadsheets in Microsoft Excel for statistical analysis. Because there are three sampling locations at the Mancuso wetland, percent removal was calculated both from the influent of the first cell to the effluent of the second cell, and from the effluent of the second cell (i.e. the influent to the third cell) to the effluent of the fourth cell.

Correlation coefficients were determined for the effluent values of each wetland for acidity, alkalinity, pH, manganese, nickel, copper, aluminum, cobalt, and zinc. The values were calculated by Microsoft Excel according to the following equation:

$$\rho_{X,Y} = \frac{\operatorname{cov}(X,Y)}{\sigma_X \bullet \sigma_Y} \qquad (1)$$

where: $\rho_{x,y}$ = correlation coefficient, σ_X = standard deviation of X, σ_Y, = standard deviation of Y, cov = covariance

A value of $\rho_{x,y}$ close to 1 indicates a strong correlation between the two sets of data. Individual plots of data versus linear models allowed for the evaluation of residuals (the difference between predicted and observed values) for randomness, an important characteristic of an accurate linear model.

Results

Bark Camp Run

Influent water quality data was consistent spatially (between wetlands 3 and 5) and temporally (Figure 1 and Table 1). Effluent values for wetlands 3 and 5 were not significantly different for a specific sample date as determined by two-tailed pair-wise t-test comparisons in which $p > 0.05$ for effluent values tested.

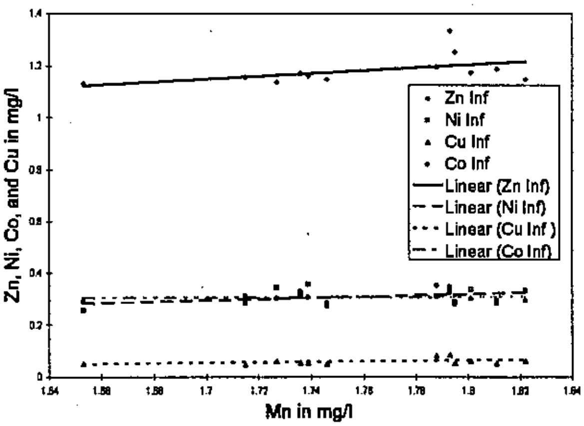

Figure 1. Influent values of Zn, Ni, Cu, and Co as a function of Mn at Bark Camp

Correlation values for Bark Camp effluent concentration levels are shown in Table 2. Correlation values for manganese with other metals were generally poor, and in most cases negative. Although manganese is observed to be a poor predictor variable for zinc, nickel, copper, and cobalt, these metals tended to have a reasonably strong positive correlation value ($\rho \geq 0.90$) with each other, indicating that they tend to behave in similar fashion. Copper was also highly inversely correlated with pH (ρ = -0.940). Aluminum and iron showed no strong correlations with any other variables. Further statistical analyses were performed to resolve the relationships between manganese, zinc, nickel, copper, and cobalt.

Table 1. pH and Percent Removal Values for Bark Camp and Mancuso Wetlands

Date	Location	pH in	pH eff	Mn	Percent Removal Zn	Ni	Fe	Al	Cu	Co
3/30/95	Bark Camp #	3.05	7.1	-183.45	70.12	89.52	74.46	-279.58	99.97	46.13
3/30/95	Bark Camp #	3	6.12	-126.57	27.56	19.24	87.98	70.85	58.82	7.86
6/21/95	Bark Camp #	3.07	5.79	-103.29	46.17	39.16	17.40	64.72	72.13	12.54
6/21/95	Bark Camp #	3.06	6.16	-201.67	89.36	84.57	34.97	85.53	99.98	62.91
7/3/95	Bark Camp #	3.03	5.33	-76.92	44.16	46.83	33.54	66.78	63.27	19.58
7/3/95	Bark Camp #	3.01	6.34	-186.99	94.43	100.00	54.79	62.24	99.97	82.76
7/19/95	Bark Camp #	2.99	5.86	-135.60	73.34	66.29	-107.29	75.91	87.27	26.62
7/19/95	Bark Camp #	3.13	6.31	-209.50	91.73	90.99	14.44	85.13	99.97	57.76
8/2/95	Bark Camp #	3	6.24	-172.87	97.61	94.23	-167.02	96.06	99.97	50.30
8/2/95	Bark Camp #	3.06	6.27	-193.94	70.65	84.91	30.07	55.91	99.97	38.76
6/5/96	Bark Camp #	3	4.39	-123.37	20.09	9.76	34.73	34.90	46.43	6.34
6/5/96	Bark Camp #	2.96	3.64	-94.97	2.51	-4.47	61.97	25.34	20.99	-0.28

Date	Location	pH In	pH eff	Mn	Percent Removal* Zn	Ni	Fe	Al	Co
7/3/95	Mancuso M2	5.86	6.19	7.00	-6.45	40.43	82.13	80.49	9.92
7/3/95	Mancuso M3	6.19	6.49	7.90	12.12	35.71	84.17	-37.50	22.02
7/18/95	Mancuso M2	6.05	6.31	3.23	37.14	36.36	72.70	46.15	10.00
7/18/95	Mancuso M3	6.31	6.65	3.77	65.91	42.86	87.23	-100.00	19.66
8/2/95	Mancuso M2	6.25	6.38	-1.55	69.07	25.81	73.73	-68.75	14.59
8/2/95	Mancuso M3	6.38	6.83	9.02	26.87	2.90	91.70	70.37	24.17

* Percent Removal of M2 = (M2-M1)/[(M2+M1)/2] x 100

*Percent Removal of M3 = (M3-M2)/[(M3+M2)/2] x 100

Table 2: Effluent Water Quality Values Correlations for Data Obtained at Bark Camp[1]

	pH	Mn	Zn	Ni	Cu	Fe	Al	Co	Acidity	Alkalinity
pH	1.00									
Mn	0.65	1.00								
Zn	-0.78	-0.74	1.00							
Ni	-0.80	-0.72	0.99	1.00						
Cu	-0.94	-0.56	0.91	0.92	1.00					
Fe	0.04	0.07	-0.39	-0.41	-0.40	1.00				
Al	0.24	0.04	0.11	0.02	-0.19	-0.36	1.00			
Co	-0.84	-0.79	0.94	0.96	0.95	-0.06	-0.02	1.00		
Acidity	-0.78	-0.68	0.62	0.64	0.69	0.30	-0.04	0.80	1.00	
Alkalinity	0.56	0.89	-0.74	-0.70	-0.73	-0.13	-0.14	-0.83	-0.75	1.00

[1] Correlation values calculated from metals, alkalinity, and, acidity concentrations in mg/l and pH.

Percent removal of manganese, zinc, nickel, copper and cobalt is presented in Table 1. The export of manganese is represented by a negative percent removal, in contrast to the positive values seen for other metals at almost all times.

Linear correlations for zinc, nickel, cobalt, and copper against manganese with correlation coefficients (R^2) and linear models appear in Figure 2. Manganese exhibits low R^2 values and negative slopes for each of the models indicating very poor predictive capability for heavy metal behavior and opposite (negative) of the predictor variable (manganese).

Effluent zinc demonstrated a strong correlation with effluent nickel, cobalt, and copper with R^2 values of 0.970, 0.881, and 0.843 respectively (Figure 3). However, zinc had a R^2 value of 0.544 and a negative slope when used as a predictor of manganese.

Comparative analysis of paired relationships of each heavy metal to manganese demonstrated poor agreement between actual metal effluent values and those predicted by a linear model based on manganese. However, examination of the relationship of zinc to nickel, copper, and cobalt, respectively, revealed that the data appeared to fit a linear trend with residuals randomly distributed.

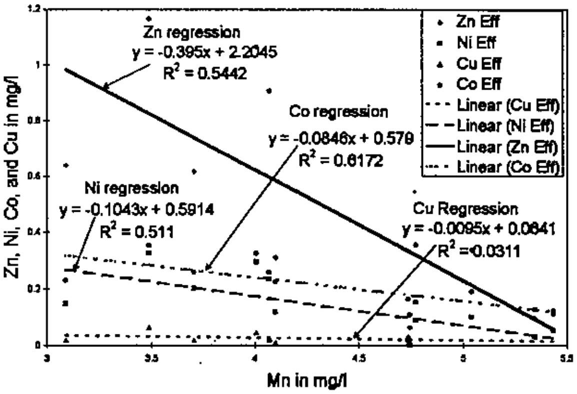

Figure 2. Effluent Co, Ni, Zn, and Cu as a function of effluent Mn at Bark Camp

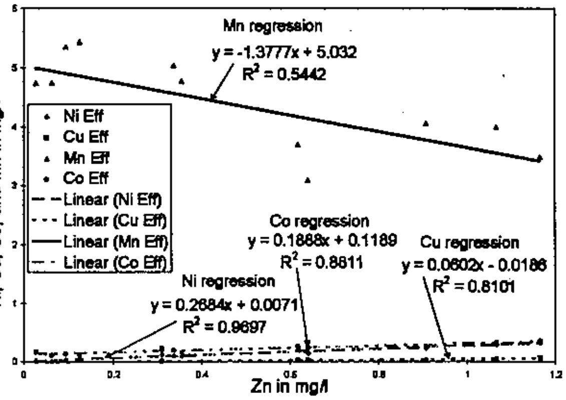

Figure 3. Effluent Co, Ni, Cu and Mn for Bark Camp as a function of effluent Zn at Bark Camp

Effluent pH was a weak indicator of metals behavior in all cases except copper. Effluent values for copper correlated more strongly with pH than they did with zinc (R^2 values of 0.883 and 0.810 respectively). Cobalt and nickel were not well predicted (R^2 values of 0.702 and 0.644 respectively) relative to their correlation with zinc.

Mancuso wetland

Influent water quality for the study period was consistent across the sampling dates, which permitted effluent values to be analyzed as one data set (Table 1).

Correlation values for Mancuso effluent metals concentration levels and percent removal are given in Table 3. The correlation values for manganese with other metals were poor. The only notably strong correlation was between iron and cobalt percent removal ($\rho = 0.93$). Iron proved to be a poor predictor variable of all of the metals in the Mancuso effluents with the exception of cobalt. The cobalt iron relationship was, however, moderately strong ($R^2 = 0.778$).

Table 3: Effluent Water Quality Values Correlations for Data Obtained at Mancuso[1]

	Mn	Zn	Ni	Co	Al	Fe	pH	Acidity	Alkalinity
Mn	1.00								
Zn	0.13	1.00							
Ni	0.47	0.27	1.00						
Co	0.75	0.64	0.49	1.00					
Al	0.54	-0.20	0.27	0.38	1.00				
Fe	0.36	0.74	0.42	0.88	0.15	1.00			
pH	-0.05	-0.75	-0.07	-0.69	-0.06	-0.91	1.00		
Acidity	0.61	0.55	0.19	0.93	0.26	0.88	-0.77	1.00	
Alkalinity	0.57	0.26	-0.28	0.62	0.08	0.45	-0.42	0.80	1.00

[1] Correlation values calculated from metals, alkalinity, and, acidity concentrations in mg/l and pH.

Effluent manganese as a predictor of zinc, nickel, cobalt, copper, and aluminum and plotted linear correlations for these metals against manganese together with correlation coefficients (R^2) are presented in Fig. 4. Manganese exhibits low R^2 values for each of the models, indicating very poor predictive capability of the predictor variable (manganese). Specific linear models with zinc as a predictor variable of nickel, aluminum, and cobalt are presented in Figure 5. Zinc is a poor predictor of the effluent values of all of these metals.

Discussion

The origin of manganese as a surrogate for heavy metal removal in treatment of acidic mine drainage is grounded in the application of alkaline chemicals to elevate the pH of the water in order to facilitate oxidation/hydroxylation and ultimate precipitation of the metals (Kleinman and Watzlaf 1988). The alkaline pH requirements for manganese removal exceed those for heavy metals, hence, if sufficient alkalinity was provided to convert soluble manganese to precipitable form, it could be assumed that heavy metals would be precipitated as well.

The environment of wetlands employed in mine water treatment does not generate sufficient natural alkalinity to achieve the high pH values possible with alkali feed systems, hence, major mechanisms involved in metal removal, particularly in anoxic wetlands, are potentially different. Anoxic manganese removal in the organic matrix of wetlands is largely fostered by cation exchange and adsorption whereas iron is retained by precipitation as a mineral sulfide(s) under sulfate reducing conditions. Although no sulfide data was obtained on the two wetland systems during this study, evidence exists for sulfate reduction over a two year period at Bark Camp Run, both by odor and influent/effluent chemical analysis (Hellier 1996).

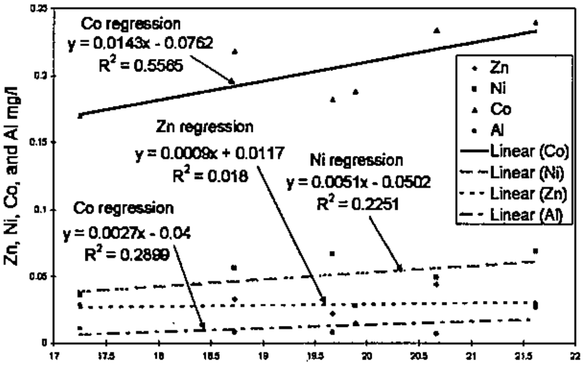

Figure 4. Effluent Zn, Ni, Co, and Al as a function of effluent Mn at Mancuso

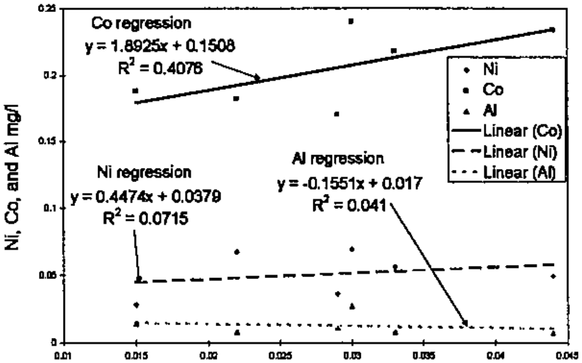

Figure 5. Effluent Ni, Co, and Al as a function of effluent Zn at Mancuso

Although selection of a single metal as a surrogate of treatment performance for removal of a suite of heavy metals in acidic mine drainage is a practical alternative to the routine monitoring of individual heavy metals, such a practice is not justified unless the factors which affect the fate of the surrogate metal and the target metals for elimination are similar. The present study was undertaken to examine the reliability of manganese as an indicator of heavy metals found in acidic mine drainage. Due to difficult logistic and technical problems, only a limited sampling of wetland systems was possible and the bulk of the data presented was obtained in work with the Bark Camp facility.

Bark Camp is a wetland designed to employ subsurface flow and anoxic processes to accomplish metals removal and pH abatement. Statistical methods for the analysis of metals, such as linear regression and correlation procedures, were used satisfactorily to demonstrate firm suggestive reasoning that manganese is not a universally suitable indicator of the effect of acidic mine water wetland treatment on heavy metals. All correlations between manganese and the heavy metals (zinc, nickel, copper and cobalt) were found to be very poor and negative. The chemical instability of manganese under reducing conditions typical of anoxic environments (Burdige and Nealson 1986) and the likelihood that sulfide precipitation of manganese is nil probably contributed to the unparalleled trends in manganese and heavy metal removal. The negative correlation and slope of the linear models indicates net export of manganese but not the heavy metals. Such a pattern is compatible with the chemistry of manganese and the other elements. The export of manganese at above influent levels during periods of sampling suggest desorption or perhaps reduction of bound manganese occurred in the sediments (Weider 1988; Burdige & Nealson 1986).

Data contained in Tables 1 and 2 and Figures 2 and 3 make clear that the behavior of manganese did not mirror that of zinc, copper, cobalt and nickel at this site. The principal heavy metals in Bark Camp drainage have similar theoretical capacities for sulfide complexation and displayed fairly strong correlations in relation to each other (Table 2). Stable sulfides of heavy metals, if formed in the Bark Camp wetland sediments, could be well immobilized (Singh 1992). Although manganese is theoretically precipitable as a carbonate (rhodochrosite) in an anoxic environment under a high carbon dioxide tension (Wildeman et. al. 1994), in the presence of iron, competition by manganese for carbon dioxide would not be favorable.

Zinc was always present in the effluent at Bark Camp and proved to better profile the behavior of the heavy metals in the mine waters than did manganese. Zinc exhibited high, positive linear correlations with nickel, cobalt, and copper (R^2 values of 0.970, 0.881, and 0.810, respectively; Figure 3).

Copper exhibited a better linear correlation with pH than did Zinc. Copper is a very strongly adsorbed metal, generally displacing other metals when adsorption sites are limited (Weider 1988). A combination of removal mechanisms may be controlling copper removal at Bark Camp. Copper is a relatively minor constituent in Eastern US coal mine drainages, however, it is prevalent in many Western drainages.

The Mancuso wetland is designed for surface hydraulic loading of mine water and relies on oxic processes to remove metals. The influent is characterized by a net alkalinity and a pH near 6. However, metal removal did not exhibit the trends which existed at the Bark Camp site (Tables 1 and 3). Manganese behavior did not correlate with that of any of the other metals (Table 3 and Figure 4). In addition, zinc, which presented high correlations with the other heavy metals at Bark Camp, displayed no statistical relationships to nickel, cobalt, and aluminum (Figure 5).

Conclusions and Recommendations

Based primarily on data obtained from treated mine waters analyzed from an anoxic (Bark Camp) and oxic (Mancuso) wetland treatment system, little justification exists for using manganese as a surrogate for the removal of heavy metals which may be present in acidic mine water effluents. Removal mechanisms for heavy metals differ with respect to the characteristics of the wetland environment, however, evidence obtained in the present study suggests that different heavy metals may behave more similarly in their removal in an anoxic than an oxic wetland and that manganese is not a reliable indicator of the removal of heavy metals regardless of the oxygen profile of the wetland system. Zinc was highly correlated with the presence of the heavy metals copper, cobalt, and nickel in the subsurface loaded wetland (Bark Camp), although insufficient data exists to arrive at an explanation of the phenomenon. Manganese is a poor indicator of heavy metal removal performance of wetland cells receiving subsurface influent loading. No parameter was found to be a good indicator of heavy metal performance in the oxic (Mancuso) wetland.

Controlled laboratory studies are needed to further resolve the issue of manganese as a surrogate of heavy metal removal in passive acidic mine water treatment. It is apparent that very different biogeochemical events occur in surficial and subsurface loaded wetlands such that a single chemical mechanisms of heavy metal transformation does universally prevail. In particular, known mechanisms of heavy metal and manganese immobilization need to be comparatively tested on anoxic (operated in sulfate-reducing and nonsulfate reducing modes) and oxic systems. The future of passive mine water treatment as an economically feasible process requires that equitable regulatory standards be in place with which to judge the performance of these units.

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