IRON AND MANGANESE REMOVAL IN A TYPHA-DOMINATED WETLAND DURING TEN MONTHS FOLLOWING ITS CONSTRUCTION[1]

Lisa L. Stillings, Jeffrey J. Gryta, Tedd A. Ronning[2]

Abstract. A _Typha_-dominated wetland was constructed in September 1986 to remove iron and manganese from a surface mine seep characterized by an average flow of 10 gpm, pH of 5.5, and maximum concentrations of 40, 50, and 2700 ppm Fe, Mn, and SO_4^{2-}, respectively. _Typha_ were planted at 1-ft centers in a 110 by 20 ft basin containing a basal 6-inch layer of agricultural-grade limestone and an upper 10-inch layer of an equally proportioned mixture of peat, compost, and sandy soil. Surface waterflow volume was recorded with inlet and outlet weirs, and rainfall was measured by a continuous recording rain gauge. Water samples were collected at the inlet and outlet of the wetland, and at 33 surface locations within the basin. Substrate interstitial water was sampled from six, two-level piezometer nests. All samples were analyzed for Ca, Fe, K, Mg, Na, Mn, P, and SO_4^{2-}, on a biweekly basis from October 1986 to July 1987. Seventy-four percent of the 186 kg of iron introduced to the system was removed during this period. Manganese removal was less successful; only 8% of the 368 kg influx was removed. Periods of increased waterflows corresponded with the smallest percent reduction of influent mass concentrations. The greatest reduction of influent mass occurred during the June 1 sample period, when 26.4 kg of iron, and 14.2 kg of manganese, were removed from solution. The wetland's ability to remove iron and manganese varied with time and location within the basin. Inlet flow volume, basin length, and water flow through the substrate were important factors affecting the retention of influent iron and manganese.

INTRODUCTION

Wetlands have been used since the 1970's for the treatment of acid mine drainage (AMD) and municipal wastes. Studies conducted by Huntsman et al. (1978) and Wieder and Lang (1982) have compared influent and effluent concentrations of AMD passing through wetlands. Wieder et al. (1985) and Girts and Kleinmann (1986) have examined the wetland flow conditions which surround AMD amelioration. Recommendations regarding the most effective flow rates, basin size, and vegetation types have

been made by Kleinmann et al. (1986) Girts and Kleinmann (1986) and Girts et al. (1987). Research has also been conducted with wetlands for the treatment of municipal waste (Wile et al. 1985, Kadlec 1987), and while AMD and municipal waste influent possess inherently different qualities, criteria such as length and retention time are found to be important in the successful treatment of these two types of contamination. Detail is lacking, however, pertaining to where metal removal takes place within wetlands, what chemical conditions surround removal, and how removal rates vary with time. In this study, an instrumented wetland was constructed to quantify iron and manganese removal over a 10-month period following wetland construction. The wetland received flow from an AMD seep emerging from spoil reclaimed following mining of the Middle Kittanning (#6) and Lower Kittanning (#5) Coals of the Allegheny Formation in Tuscarawas County, OH.

METHODS

Wetland Construction and Instrumentation

Based upon an average flow estimate of 10 gpm, a 110 by 20 ft basin was constructed (fig. 1) following the recommended size of 200 ft^2. of wetland/1 gpm of flow (Kleinmann et al. 1986). The basin was leveled and filled with six inches of agricultural-grade limestone which, in turn, was covered with a 10-inch humic layer consisting of an equally proportioned mixture of peat, compost, and sandy soil. The limestone was placed as a distinct layer and not mixed with the humic soil to avoid coating the limestone with a ferric hydroxide precipitate (Kleinmann et al., 1986). Cattails (_Typha_) were collected from the surrounding area and planted in the basin at 1-ft centers. Cores taken one month later showed that these layers had compacted to approximately 5.5 inches of limestone, and 7 inches of humic material.

The water budget is recognized as a key factor affecting water quality and wetland functions (Kadlec 1987). Therefore, 40° V-notch weirs with continuous water level recorders were installed at the inlet and outlet to measure surface waterflow into and from the wetland. Flow volumes were calculated from the following equation for sharp-edged, V-shaped weirs (Brakersiek et al. 1979):

$$Q = C \times 8/15 \times \sqrt{2g} \times \tan(\theta/2) \times H^{2.5} \quad (1)$$

where,
Q = discharge (ft^3/sec)
C = weir coefficient (0.582 for a 40° V-notch weir)
θ = total angle of notch (degrees)
H = head above the lowest point of the notch (ft), and
g = gravitational acceleration (32.17 ft^2/sec).

A weighing-bucket continuous recording rain gauge was placed at the site to measure rainfall; potential evapotranspiration was estimated from evaporation pan data collected during the spring/summer months. Additionally, six, two-level piezometer nests were placed within the basin: the lower level sampled subsurface water within the bottom 3 inches of the humic substrate, and the upper level sampled the top 3 inches of the substrate.

Sampling Procedure and Chemical Analysis

Wetland water samples were collected on a biweekly basis from October 11, 1986 through July 3, 1987 from the piezometers, the inlet and outlet weir pools, and from 33 surface sites defined by an 11-column by 3-row sample grid (fig. 1). Nineteen separate collections were made. Frozen wetland surface conditions, and site inaccessibility due to excessive rainfall precluded the collection of some samples. Chemical analysis included Ca, Fe, K, Mg, Na, Mn, SO_4^{2-} and orthophosphorus. Inductively Coupled Plasma (ICP) spectrometry was used for all analyses except for SO_4^{2-} and ortho-P. These were determined by colorimetric procedures outlined by Hach (1986), with one modification: rather than reading sample concentration directly from the spectrophotometer, a series of standards was analyzed with each sample batch to establish a regression relation of concentration versus absorbance. Sample concentrations were then determined with this equation.

Water Budget Analysis

Water budget volumes were calculated as described in LaBaugh and Winter, 1984, by dividing the study period into intervals whose midpoints correspond to the date of water sampling. Budget components include inlet flow (If), outlet flow (Of), rainfall (Ppt), potential evapotranspiration (Pet), and change in volume of surface water stored (ΔS) within the basin (volume determined by multiplying wetland area times average surface water depth). All of the above components were calculated for each interval, and the following equation was used to determine the residual (Res) component:

$$If + Ppt - Of - Pet - \Delta S = Res \quad (2)$$

A positive residual value denotes a net water gain or an ungauged loss of water (such as vertical seepage down through the basin), while a negative residual value denotes a net water loss or an ungauged source of water (such as vertical seepage up into the basin). Residual values might also reflect operator and/or instrument error.

Mass Budget Analysis
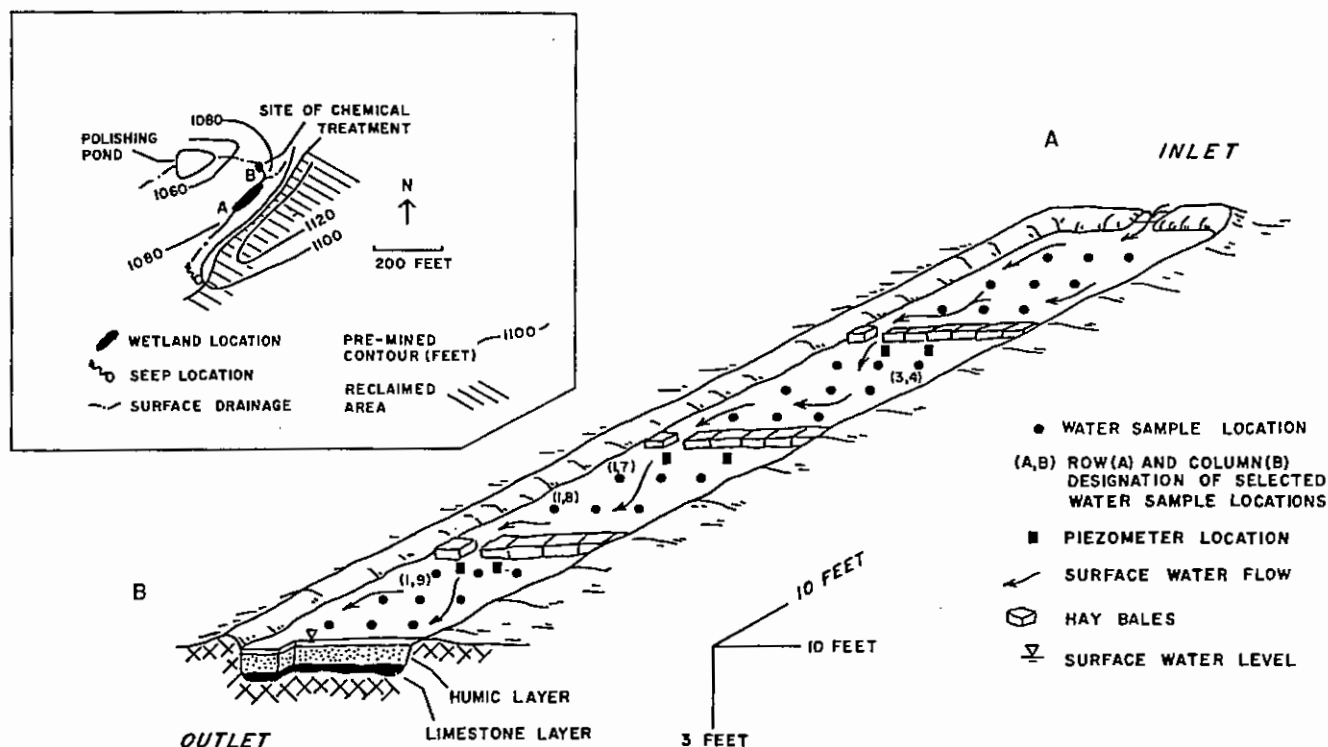
Following water budget analysis, a

Figure 1.--Schematic drawing of the wetland basin with sample locations. The insert locates the wetland with respect to the AMD seep and the site of pre-wetland chemical treatment.

total mass flux for each interval was calculated by multiplying inlet and outlet flow volumes by their respective inlet and outlet concentrations. Assuming that negative residual volumes (equation 2) resulted from an ungauged source, these were multiplied by the inlet concentrations and added to the amount of mass entering the wetland. Positive residuals were attributed to ungauged outflows, and these were multiplied by the outlet mass concentrations and added to the amount leaving the wetland. Total influx was calculated as the sum of the influx values for each interval. Total outflux was determined in a similar manner. Inflow and outflow were the only water budget components used in mass budget calculations because iron and manganese concentrations in rainfall were assumed to be negligible, and because change in surface storage accounted for less than one percent of the total water budget.

RESULTS & DISCUSSION

Concentrations of Fe, Mn, and SO_4^{2-} at the seep varied throughout the study period, and while their maximum concentrations were 44, 50, and 2720 ppm, respectively, they averaged 31 ppm Fe, 34 ppm Mn, and 1130 ppm SO_4^{2-}. Mass concentrations at the inlet to the wetland averaged 13 ppm Fe, 30 ppm Mn, and 990 ppm SO_4^{2-} ; evidently Fe and SO_4^{2-} were removed from solution while the water flowed through a ditch leading

from the seep to the wetland (insert, fig. 1). The following discussion considers only the mass concentrations which actually entered the wetland.

Overall, 74% of the 186.4 kg of iron delivered to the wetland during the study period remained within the basin. Each sample interval within this period consistently displayed a smaller mass outflux than the influx, indicating that iron removal continued through time (fig. 2a). The smallest percentage of iron removal, 43%, occurred on two separate occasions: first, during the December 8 interval, when 2.4 kg of iron were removed from the flow; and second, during the April 15 period, when 6.2 kg were removed (fig. 2a). The largest reduction occurred over the June 1 sample interval, with the removal of 26.4 kg of iron (94% of the inlet mass flux).

Manganese was not as successfully treated by the wetland: only 8.3% of the 368.5 kg of mass which entered the basin during the entire study period was removed from the flow. During most of this period (October 11 through March 18, fig. 2b) inlet and outlet manganese flux values barely differed except for the December 8 and January 5 sample intervals when the outlet flow carried an additional 5 and 2 kg, respectively. Not until mid-May (fig. 2b) did the system begin to consistently remove manganese from solution, and, as with iron, the June 1 period displayed the greatest manganese removal, retaining 14.2 kg (26%
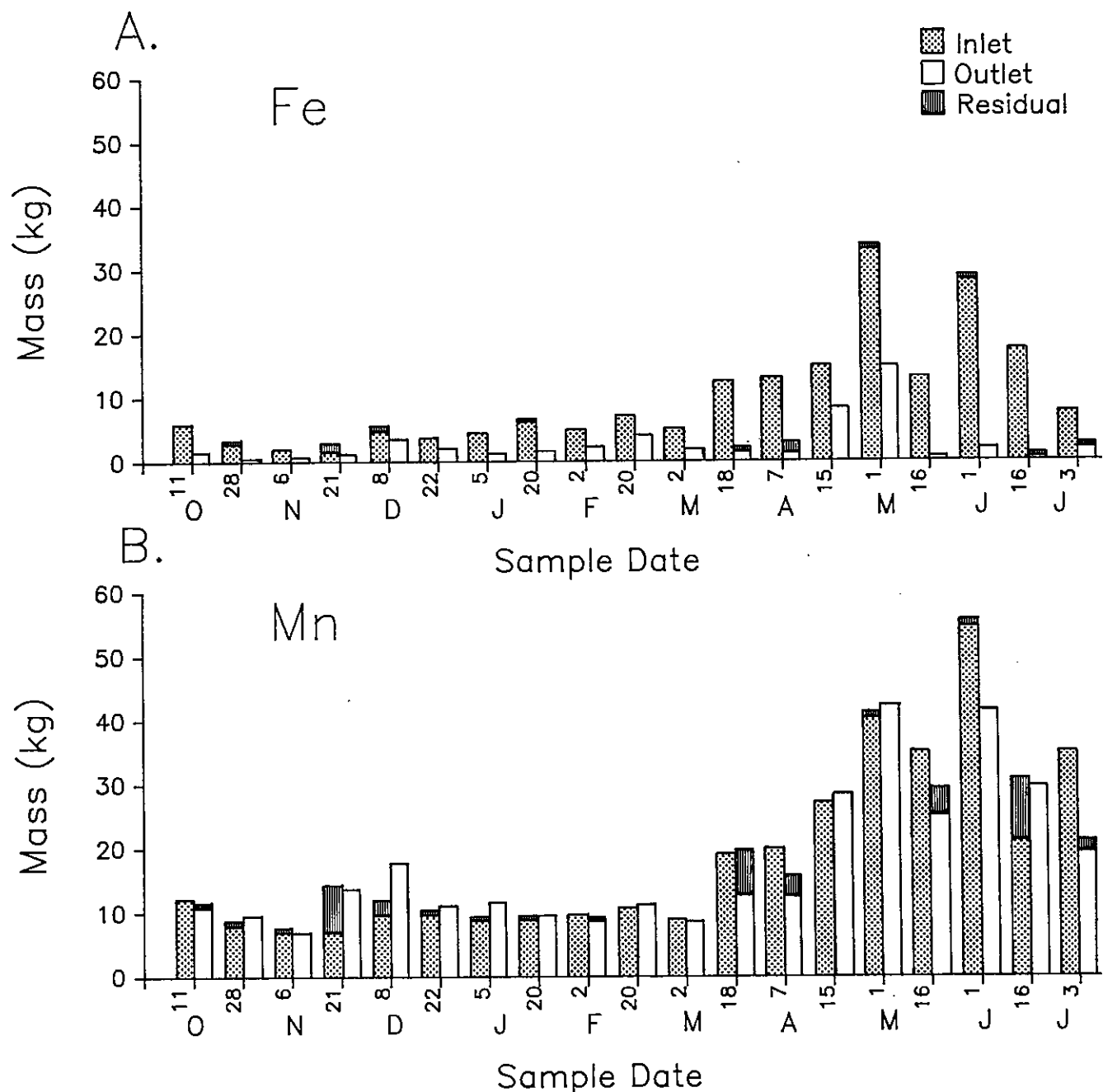
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Figure 2.--Inlet and outlet components of the iron (A) and manganese (B) budgets calculated for each sample period.

of the inlet mass concentration) within the wetland. Later, during the July 3 sample period, inlet manganese concentrations were reduced by 40%, a percentage corresponding to the removal of 13.8 kg.

Flow, as suggested by Kadlec (1987), does appear to influence metal removal in a wetland system. The peak inlet flow volume, 20.1 gpm, occurred over the period of April 15 (figs. 3a,c). Peak inlet mass concentrations followed this springtime hydrograph peak: the maximum iron influx of 23.6 ppm occurred on May 1 (fig. 3a), and the maximum manganese

influx of 53.9 occurred on June 1 (fig. 3c). This sequence-- peak mass concentrations following after peak flow volumes--could result from the springtime "flushing" of metals from the mine spoil.

The wetland responded to the increased flow volumes by decreasing the percentage of iron removed from its inlet water. During the springtime increase of the inlet hydrograph (March 18 to April 15), the amount of mass removed dropped from approximately 10 kg (80-85% of the inlet mass) for each of the March 18 and April 7 periods, to 6.2 kg (43% of the inlet mass) for the April 15 period (fig.
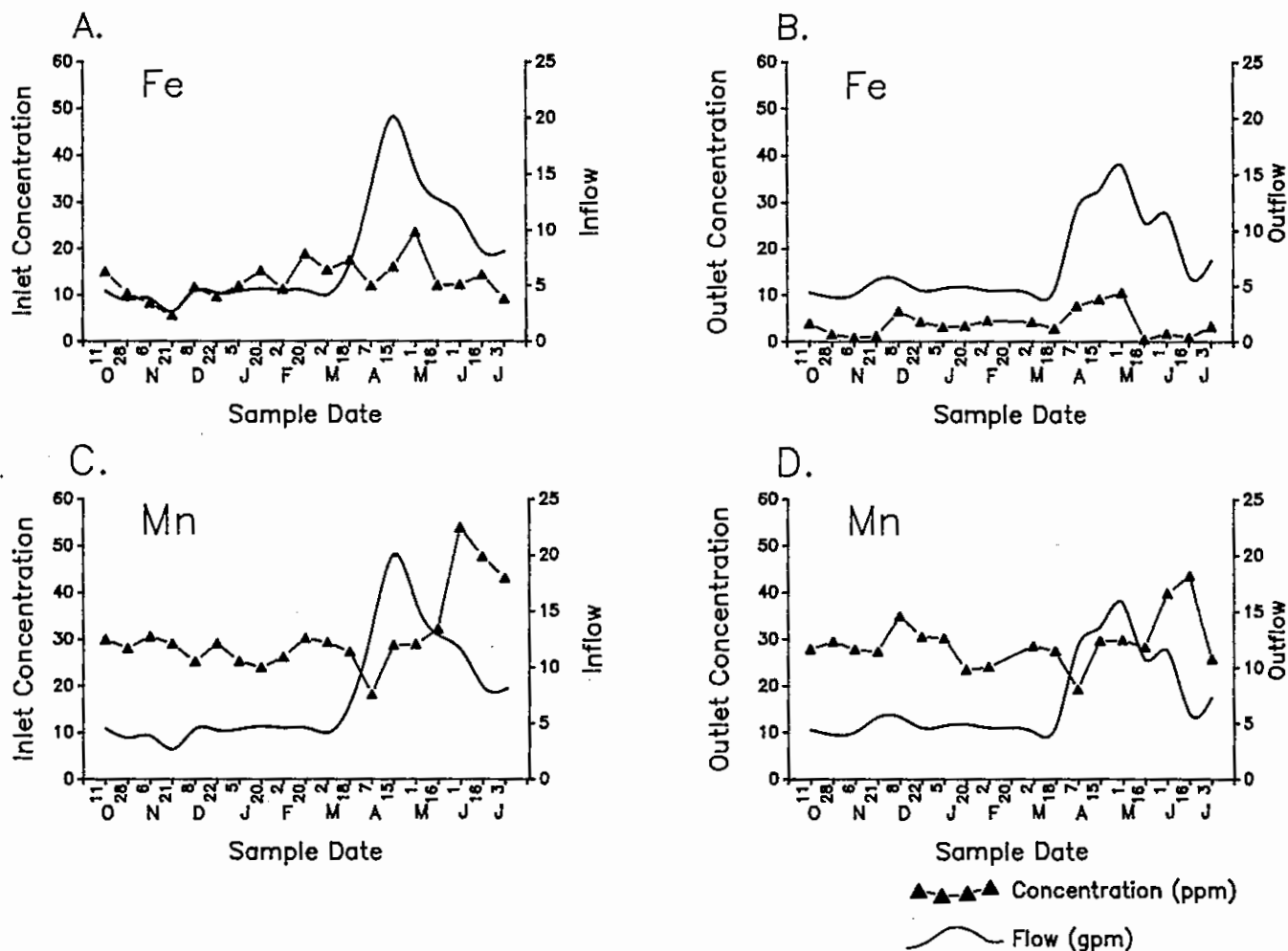
Figure 3.--Inlet and outlet concentrations of iron (A & B), and manganese (C & D), documented for the 10-month study period. Plots of the inlet and outlet hydrographs are included for comparison of flow volumes with mass concentrations.

2a). The amount of iron removed during May 1 increased to 18 kg, but since inlet iron concentrations increased greatly during this period, this removal corresponded to only 55% of the total mass.

The outflow hydrograph exhibited a lower, and more broad springtime peak, suggesting that the increased inlet volume did not immediately flow through the basin, but that a portion of the water was stored within the wetland, and then released at a more constant rate. Iron concentrations at the outlet increased with increasing outflow volume (March 18-May 1, fig. 3b).

During the April 15 period, when the inlet flow was at its highest and percentage iron removal at its lowest, manganese concentrations were slightly higher at the outlet than at the inlet. Mass budget calculations show an extra 0.9 kg of manganese leaving the wetland during the April 15 period, and an extra 1.3 kg leaving over the May 1 period. From May 16 through the end of the study

period manganese was removed from the wetland flow. In fact, the greatest amount of removal (14.2 kg) coincided with the largest manganese influx (54.3 kg) during the June 1 period (fig. 2b).

Outlet manganese concentrations were greatest during the intervals of June 1 and June 16, reflecting the high inlet concentrations of those same periods (fig. 3d). The peak outlet concentration of 43.6 ppm did not occur during the same interval as the peak inlet concentration however, instead the outlet peak appeared during following, June 16, period.

The period from March 18 through April 15 was not the only period of rising inlet flow volumes: a small flow increase also occurred from November 21 to December 8 (fig. 3c). The response of the wetland to this flow increase was similar to its response during the springtime flow increase--iron removal dropped from 78% of the inlet mass during November 21 to 43% during December 8, and an extra 5 kg of manganese left the wetland over the December 8 period.

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The effects of length and width on the removal of iron and manganese from the surface water were examined with an analysis of variance. Removal was calculated by subtracting the concentration at each grid point from the inlet concentration. Time effects were not examined with these tests; instead, all nineteen samples obtained from a particular location were considered to 'replicate' the average chemical conditions at that area. While width was not found to be significant in the removal of either metal, length was significant in both cases, with iron being more affected. Duncan's multiple range test was used to examine the equality of the column means averaged over the three rows. It indicated that while removal did increase with length, the means for columns 7-11 (refer to fig. 1 for sample grid design) were not significantly different from one another, similarly, the means for columns 5 and 6 were also not significantly different.

A second-order regression analysis of iron removal versus length produced a predicted curve (fig. 4), with a 0.962 r-squared value. While a first-order relationship would also describe the data points, the quadratic curve provides a better fit and also suggests that the rate of iron removal slows during the time it takes water to flow from inlet to outlet. This is a likely possibility since reaction rates can slow as the reactants become more dilute.

The importance of length in the removal of manganese cannot be as clearly defined as with iron. Length was found to be a significant factor, but Duncan's test revealed that the greatest removal occurred in columns 7-9, and that columns 10-11 averaged the same amount of removal as columns 5-6. Factors in addition to length must be influencing manganese removal. The first-order regression of
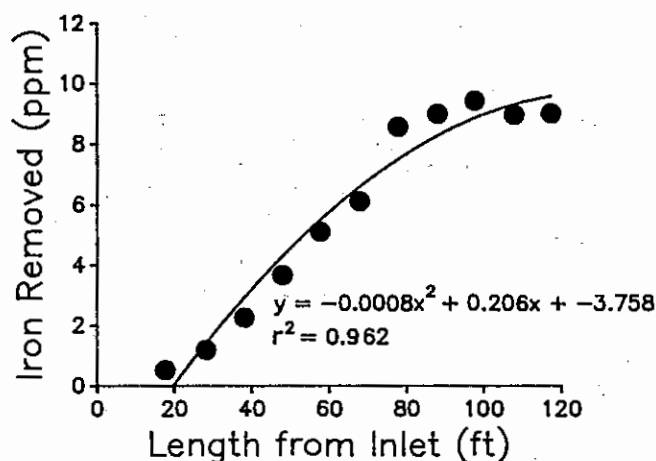
manganese removal versus length (fig. 5) demonstrates this with an r-squared of 0.53; length cannot explain all of the variability in manganese removal. A second-order fit did not significantly improve the r-squared value, and therefore is not presented here.

The two-way interaction of length x width was significant as well, and a plot of the row means per column indicated that three surface locations (designated as [1,7], [1,8], and [1,9] in fig. 1), contained water with less iron and manganese, 37% and 20%, respectively, than water at the outlet. Samples from these areas were also distinguished by an enrichment in K, P, Na, Mg, and Ca. Similar water chemistry, i.e., high nutrient and low dissolved metal concentrations, was also found in the interstitial waters, especially from samples from the lower piezometers located immediately above the limestone layer. Based upon this information, two hypotheses can be made: 1) the high calcium and magnesium values at these three locations were due to the dissolution of limestone, which could have been mixed with the humic layer in these areas during wetland construction, and/or 2) interstitial water, rather than surface water might have been collected at these areas. The second possibility is likely since the wetland surface surrounding these areas can be described physically as a hummocky area where surface water was found in shallow depressions (0.5 to 1.0 inches deep) separated by emergent clumps of cattails, grasses, and saturated soil. Water collected as a surface sample might have actually flowed from the substrate at the time of collection.

SUMMARY AND CONCLUSIONS

An important question concerning this study is, of course: did the wetland

Figure 4.--Plot of the relationship between iron removal and basin length. Each point represents the column average for the 10-month period.
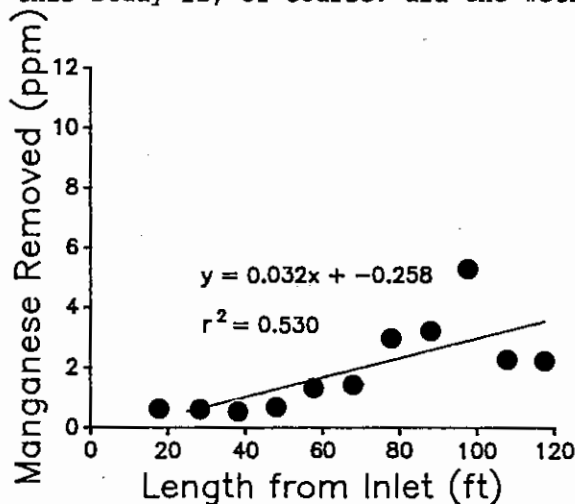
$$y = -0.0008x^2 + 0.206x + -3.758$$
$$r^2 = 0.962$$

Figure 5.--Plot of the relationship between manganese removal and basin length. Each point represents the column average for the 10-month period.

$$y = 0.032x + -0.258$$
$$r^2 = 0.530$$

effectively treat flow from the AMD seep? Effectiveness implies that effluent water quality meets standards set by the Surface Mining Control and Reclamation Act of 1977. Iron concentrations can be no greater than 7 ppm daily, or an average of 3.5 ppm monthly; manganese limits have been set to 4 ppm daily, and 2 ppm for a monthly average (USEPA 1983). Effluent from the wetland met the daily iron requirement at every sampling except for April 7, 15, and May 1, when the inlet flow volumes were higher than average. The monthly standard was met in every month but February, April, and May. Manganese concentrations remained above limitations throughout the entire period. In February, however, the mining company discontinued its downstream chemical treatment of the wetland effluent. Nevertheless, outflow from the polishing pond (fig. 1) still continued to meet iron and manganese requirements for the remainder of the study.

Flow appeared to be an important variable affecting iron and manganese removal: increased flow volumes coincided with drops in in percentage removal of iron and increased outlet manganese concentrations. In addition, peak inlet mass concentrations, and therefore peak outlet concentrations, followed the peak springtime inflow.

The importance of length as a factor which influences wetland treatment abilities agrees with findings from other researchers. A study by Wile et al., (1985) of a municipal waste wetland showed that one system with a length-to-width ratio of 75:1 constantly outperformed another with a 4.5:1 ratio. WAPORA (1983) recommended a ratio of 20:1. Within the present study, the increase of iron effluent concentrations during the spring (fig. 3b) suggests that the system was underdesigned for the maximum mass influx. The relationship between length and iron removal (fig. 4), suggests that a lengthwise extension of the basin would increase iron removal. Although length was not as important in removing manganese, figure 5 suggests that a longer basin would also improve manganese removal.

While outlet concentrations did not always show improvement in water quality, a few surface locations, and the interstitial waters, did exhibit consistently lower iron and manganese concentrations. Interaction with soil, and/or the underlying limestone layer, appears to be a common factor between these spots. A wetland designed with a more permeable substrate might provide greater contact between soil and water, provided water remains shallow.

ACKNOWLEDGMENTS

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