METAL REMOVAL IN WETLAND TREATMENT SYSTEMS[1]

Paul Eger, Jon R. Wagner, Zena Kassa, and Glenn D. Melchert[2]

Abstract: Wetland treatment has successfully removed nickel, copper, cobalt, and zinc from neutral mine drainage in northeastern Minnesota. Pilot and full-scale overland flow wetlands have removed up to 90% of the incoming nickel and 50% to 90% of the other metals. Nickel is the major contaminant in the mine drainage, with average concentrations from 2 to 5 mg/L. The other metals were generally present at concentrations less than 0.1 mg/L. In short-term tests, using drainage that contained around 1 mg/L zinc and 0.4 mg/L of copper and cobalt, concentrations were reduced about 90%. Input and output flow and water quality measurements were collected, and a mass balance was calculated. To determine the fate of the metals and the removal mechanisms, samples of vegetation and peat were collected to examine the distribution, form, and depth of metal removal. Although the overall metal concentrations in the predominant vegetation types (cattail, grass, and sedge) had increased by factors ranging from 3 for above ground vegetation to around 14 for cattail roots, the mass of metal removed by the vegetation was less than 1% of the total mass removed. The remaining metals were associated with the peat substrate. Core samples of the peat were collected and divided into 2 to 4 cm sections. Each section underwent a sequential extraction procedure and was analyzed for total concentration and metal forms. Nickel removal occurred to a depth of 20 cm, with about 60% of the nickel being organically bound.

Additional Key Words: metal sulfides, peat, adsorption, complexation, nickel, copper, cobalt, zinc.

Introduction

Acid mine drainage is a serious environmental problem. Thousands of miles of streams have been affected by acid drainage from both coal and metal mines (U.S. Bureau of Mines 1985). Acid drainage associated with metal mines usually contains elevated concentrations of the metals associated with the ore body. These metals, in addition to the acid, can pose dangers to downstream human and aquatic communities. Although this type of drainage can be chemically treated in an active treatment plant, this is an expensive and long-term commitment, particularly since drainage problems can persist for over a hundred years.

An alternative approach to chemical treatment is the use of wetlands to remove metals from mine drainage. In wetlands, a variety of processes are responsible for metal removal. These include a mixture of chemical, biological, and microbiological reactions that occur in the aerobic and anaerobic zones of wetlands.

Treatment effectiveness in most studies has been measured as the difference between input and output concentrations, and as a result there are often insufficient data to complete an overall mass balance for the system, or to determine the fate of the removed metals. These type of data are important not only because they allow better estimations of performance, but also better prediction of system lifetimes and future availability of the removed metals. In 1989, a joint project between the Minnesota Department of Natural Resources and LTV Steel Mining Company was begun to evaluate the effectiveness of wetland treatment systems to remove metals from mine drainage. Previous reports have described the background of the project, the mine and construction of the wetland cells (Eger et al. 1989, 1991).

---

[1] Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994.

[2] Paul Eger, Principal Engineer, Jon R. Wagner, Research Analyst, Zena Kassa, Research Analyst, and Glenn D. Melchert, Hydrologist, Minnesota Department of Natural Resources, Division of Minerals, St. Paul, Minnesota.

Proceedings America Society of Mining and Reclamation, 1993 pp 80-88
DOI: 10.21000/JASMR94010080

https://doi.org/10.21000/JASMR94010080

Methods

Cell Description

Four test cells, 6 m wide by 30.5 m long, were constructed in northeastern Minnesota. Since design and operating conditions varied between the cells, this paper will focus on the results from only one of the cells (cell 1). This cell contained an undisturbed portion of the original wetland, which contained primarily grasses (*Carex sp.*) and sedges (*Calamograstis sp.*), and to a lesser degree, cattails (*Typha latifolia*). The cell was hydrologically isolated from the surrounding area by a perimeter peat berm which contained a sand-bentonite cut-off wall. The cut-off wall extended from the top of the berm into the silty clay underlying the wetland. Input flow was distributed across one end of the cell with a 5 cm perforated PVC pipe, while the outflow was collected at the other end in a collection trough set to maintain the water in the cell at an average depth of 5 cm. Data for the other cells will be discussed in a future publication which is presently being prepared.

Input and output flows from each cell were measured continuously with Data Industrial electronic flow meters. The flow meters were calibrated in the laboratory prior to initiation of the study, and were periodically checked during the field season.

Water quality samples of the input and output were collected at least once per week and analyzed for pH, specific conductance, alkalinity, calcium, magnesium, sodium, potassium, sulfate, iron, manganese, copper, nickel, cobalt, and zinc. Results reported in this paper are for total metal values; the difference between total and filtered metals was generally less than 5%.

Vegetation

Preoperational vegetation samples were collected in July 1989. Sedge and grass leaves were collected randomly at five sites within the cell. Duckweed samples were collected from approximately 12 open-water sites, and entire cattail plants were collected from the surrounding area.

Cattail samples were rinsed, separated into leaves, roots, and rhizomes, and air dried. Any visible soil was removed from the roots and rhizomes. All samples were oven dried, ground and screened to minus 20 mesh, ashed, digested with concentrated nitric acid, and analyzed for metal content by atomic absorption.

In July 1991, additional vegetation samples were collected. Cattails, grasses and sedges were collected at sites that were 6, 12, 18, and 24 m from the inlet end of the cell (at 1.5 m intervals across the cell) and then composited for each distance from the inlet end of the cell. Duckweed samples were collected randomly from open water sites within the cell and composited. These vegetation samples were handled, processed, and analyzed in a manner similar to that used for the 1989 samples.

In August 1991, percent cover was estimated by inspecting random 0.5-m^2 subplots at ten foot intervals down the length of the cell. Above ground biomass was collected from within a 0.1 -m^2 frame placed within the larger 0.5-m^2 frame. The above ground biomass was then separated into cattails, grasses and sedges, and duckweed, oven dried at 24°C for 24 h, and then weighed. Total above ground biomass was calculated by multiplying the total area of the cell (186 m^2) by the average of the biomass values determined for each vegetation type.

Below ground biomass was not directly measured. Literature values (Zhang et al. 1991, Hill 1987) indicate that the ratio for Typha roots-rhizomes-leaves biomass is approximately 1:18:14. Mass calculations for metal uptake by the underground portion of cattails were based on this ratio.

Peat samples

Baseline peat samples were collected in September 1988. Six core samples were collected using a Macauley sampler. Triplicate samples were collected in the center of the cell at distances of 4.5 and 14 m from the inlet (fig. 1). Samples were collected at depths of 0 to 20 cm, 20 to 50 cm, and then at 50 cm intervals until mineral soil was encountered.

The peat samples were oven dried at 105° C for 24 h, processed with a blender to break up clumps, and sieved to minus 80 mesh. Greater than 70% of all the processed samples were less than 80 mesh. All samples were digested using a total digestion procedure, in which 0.5 g of sample was digested with a concentrated acid solution containing 1 mL HCl, 2 mL HNO_3, and 0.5 mL HF at 90°C for 2 h.

In late May 1991, after 2 yr of operation, additional peat samples were collected from the 0 to 20 cm segment and from the 20 to 50 cm segment, at the sites shown in figure 1. Triplicate samples were collected at several of the sites (for both surface and deep segments) to determine the variability between samples. The deep samples were collected with a Macauley sampler, while the shallow samples were collected with a power soil auger that had been modified to accept a 10-cm-ID stainless steel tube with serrated cutting teeth. Shallow samples that were at first collected with a Macauley sampler were small in volume and difficult to collect due to the loose consistency of the surface peat; in contrast, the power auger samples were larger in volume (and therefore less apt to be influenced by local concentration variations within the peat, and more likely to accurately represent the actual conditions within the cell).

After 3 yr of operation, another set of samples were collected to determine the depth and form of metal removal. These samples were collected with the power soil auger in March 1992 when the wetland was frozen. Three cores were collected at each site, and each core was 20 to 40 cm long. The cores were extracted from the core tube, wrapped in freezer paper, and stored in the freezer. Each core was cut into 2 to 4-cm segments while the core was still frozen. These sections were stored in the freezer until the sequential extraction procedure was performed.

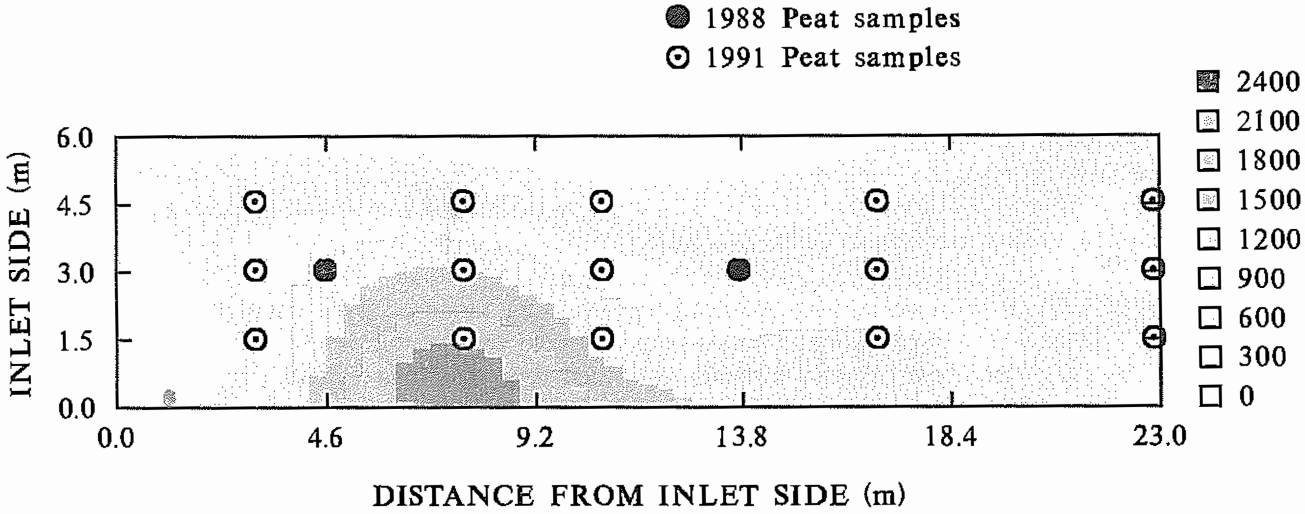

Figure 1. Plan view of cell 1, showing locations of 1988 and 1991 peat samples, and mean nickel concentrations in the surface peat (0 to 20 cm) as of May 25, 1991. (The nickel concentration contour lines were generated by a computer model that performs weighted quadratic multiple regressions of all data points.)

A series of steps was used to differentiate the form of the metal in the core (fig. 2). In general, the procedure was the same as the one developed by Weider (1991, Miller et al. 1983), except that the peat was not rinsed and centrifuged between each step. A comparison of samples run with and without rinsing showed little difference between the results. The only major difference in our extraction procedure was the inclusion of additional pyrophosphate extraction tests. Initial results indicated that a large fraction of metal removal occurred in the carbonate form (EDTA extraction). Since EDTA can also extract metals that are bound to organics, a total of six pyrophosphate extractions were performed to determine if additional metal would be extracted. Based on these results, it was determined that four extraction steps were needed to extract the majority (>90% extraction) of the metals associated with the organics. A 10 g subsample of the substrate was analyzed using a total digestion with HNO_3, HF, and HCl.

Results

Water Quality

The input drainage can be characterized as a high hardness, neutral mine drainage with elevated concentrations of sulfate, nickel, copper, zinc, and cobalt. The major contaminant is nickel, which is typically about 1 to 2 mg/L. Flow rates into the cell were usually around 3.8 L/min (1 gpm) but ranged from around 2 to 8 L/min. Residence time, measured with Rhodamine dye and a potassium iodide tracer, was on the order of 48 hr.

The cell was generally effective in removing nickel from the drainage (table 1), and was effective in removing copper, cobalt, and zinc after concentrations in the input were increased in the fall of 1990. During the first 2 yr of the study, the input concentrations of copper, cobalt, and zinc were all less than 0.03 mg/L, and although there was a statistical difference between the input and output zinc concentrations, there was no difference for cobalt and copper (Eger et al. 1991). Beginning in the fall of 1990, the source of input water was changed, resulting in an increase in influent metal concentrations. In 1991, mass removal ranged from 73% for nickel to 26% for cobalt (table 1). Over the entire 3 yr of the study, nickel removal was 79%.

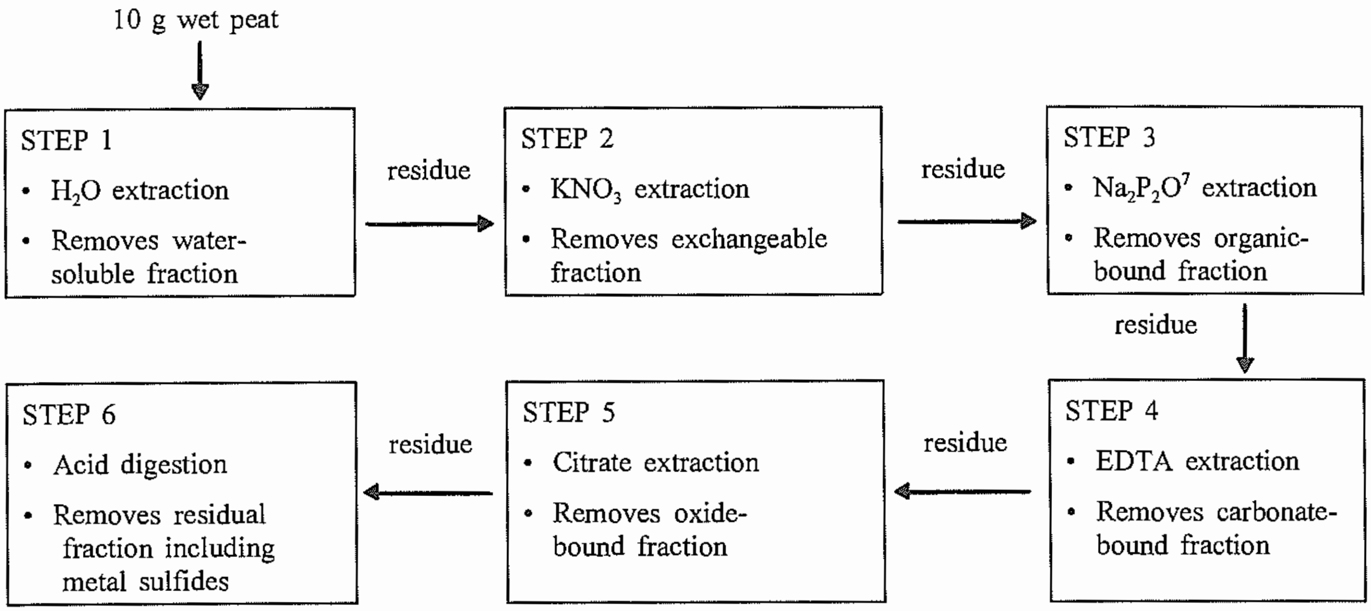

Figure 2. Sequential extraction procedure used to differentiate the metal forms present in 1992 peat samples.

Metal Removal

Metal mass input and output for the cell was determined by multiplying the total daily flow by the measured or the calculated average concentration for the site. Mass balance calculations based on the difference between the inflow and outflow mass indicated that about 3 kg of nickel was retained in the cell over the 3 yr course of the study. Since the input concentrations of other metals were generally lower than nickel, the total removal was also lower. From September 1990 through 1991, the cell removed less than 0.1 kg of copper and cobalt and about 0.3 kg of zinc (table 1). If the overall mass removed is divided by the area of the cell and the total number of days of operation, a daily rate of removal per unit area ($g/m^2/d$) can be determined (table 1). The nickel removal rate in our system was about 0.04 to 0.05 $g/m^2/d$, while removal rates for the other metals were generally about an order of magnitude lower. During the fall of 1990, the zinc removal rate was similar to the nickel rate due to the elevated zinc content of the drainage. The lower rates in 1991 for copper, cobalt, and zinc are the result of the lower input concentrations.

Metal removal was assumed to have occurred in two compartments within the system; the vegetation (i.e., cattails, grasses and sedges, duckweed), and the peat. Over 99% of the metal that was removed was associated with the peat. The mass removal calculated from the peat and vegetation data was in the same general range as that calculated from the input and output water chemistry and flow data.

Over the course of the study, nickel concentrations increased in all parts of the cattails. Average nickel concentration in the roots, rhizomes, and leaves increased from 28.0, 9.8, and 5.5 mg/kg to 72.0, 16.8, and 12.0 mg/kg, respectively. In this cell, mean nickel concentrations in the grasses and sedges did not significantly change during the same time period, while concentrations in the duckweed increased from 175 to 735 mg/kg (though the small biomass of duckweed in the cell makes it a relatively minor agent of nickel removal).

Table 1. Overall mass removal in wetland treatment cell 1.

	Time periods	Average conc. (mg/L)		Mass retained	Percent removal	Areal Rate of removal
		Input	Output	(g)		($g/m^2/day$)
Nickel	1989-1991 1991	1.65 1.98	0.39 0.92	2920 1290	80 73	0.04 0.04
Copper	Fall 1990[1] 1991	0.19 0.04	0.02 0.01	39 50	83 91	0.005 0.002
Cobalt	Fall 1990[1] 1991	0.31 0.02	0.02 0.01	66 4.4	89 26	0.009 0.0001
Zinc	Fall 1990[1] 1991	1.13 0.06	0.01 0.02	271 20	94 51	0.04 0.0006
Sulfate	Fall 1990[1] 1991	2020 2430	2050 2400	--- ---	--- ---	--- ---
pH	Fall 1990[1] 1991	6.89 7.12	6.76 6.84	--- ---	--- ---	--- ---

[1] From short term tests conducted with elevated input metal concentrations (Eger et al. 1991).

Preoperational peat samples contained an average nickel content of 174 mg/kg dry peat in the 0 to 20 cm segment, and 134 mg/kg dry peat in the 20 to 50 cm segment. In general, there was less than 20% variation in the preoperational values. Assuming a bulk density of 0.1 g dry peat per cubic centimeter of wet peat (Minnesota Department of Natural Resources 1987), the total nickel mass present in each portion of the cell was calculated. By late May 1991, the mean nickel concentration of the 0-20 cm samples collected from the cell had increased to 1020 mg/kg. Nickel concentrations in the surface peat were generally highest in the samples collected from sites 25 ft from the inlet side of the cell, and the distribution of concentrations suggest that a preferential flow path exists in the cell (fig. 1). Nickel concentrations in the 20-50 cm samples were similar to the baseline values, indicating little nickel removal in the deeper layers of peat.

Metal Forms; Depth of Removal

Since nickel was the main contaminant in the drainage, this paper concentrates on the results for this metal. Additional data on the other metals (copper, cobalt, and zinc) will be discussed in a report presently in preparation. Nickel concentrations in the upper portion of the peat increased during the study by more than an order of magnitude. Concentrations generally decreased with depth, reaching background concentrations at 20 to 30 cm (fig. 3).

Most of the nickel removal during the sequential extraction procedures occurred in the pyrophosphate step, indicating that most (60%) of the nickel was associated with the organic fraction (fig. 3). The next largest fraction was in the nitric acid extraction, which generally removes metals that are associated with sulfides and primary or secondary mineral forms. In the deeper peat (20 to 30 cm), where little increase in nickel concentration had occurred during the study, the largest amount of nickel was in the precipitated form.

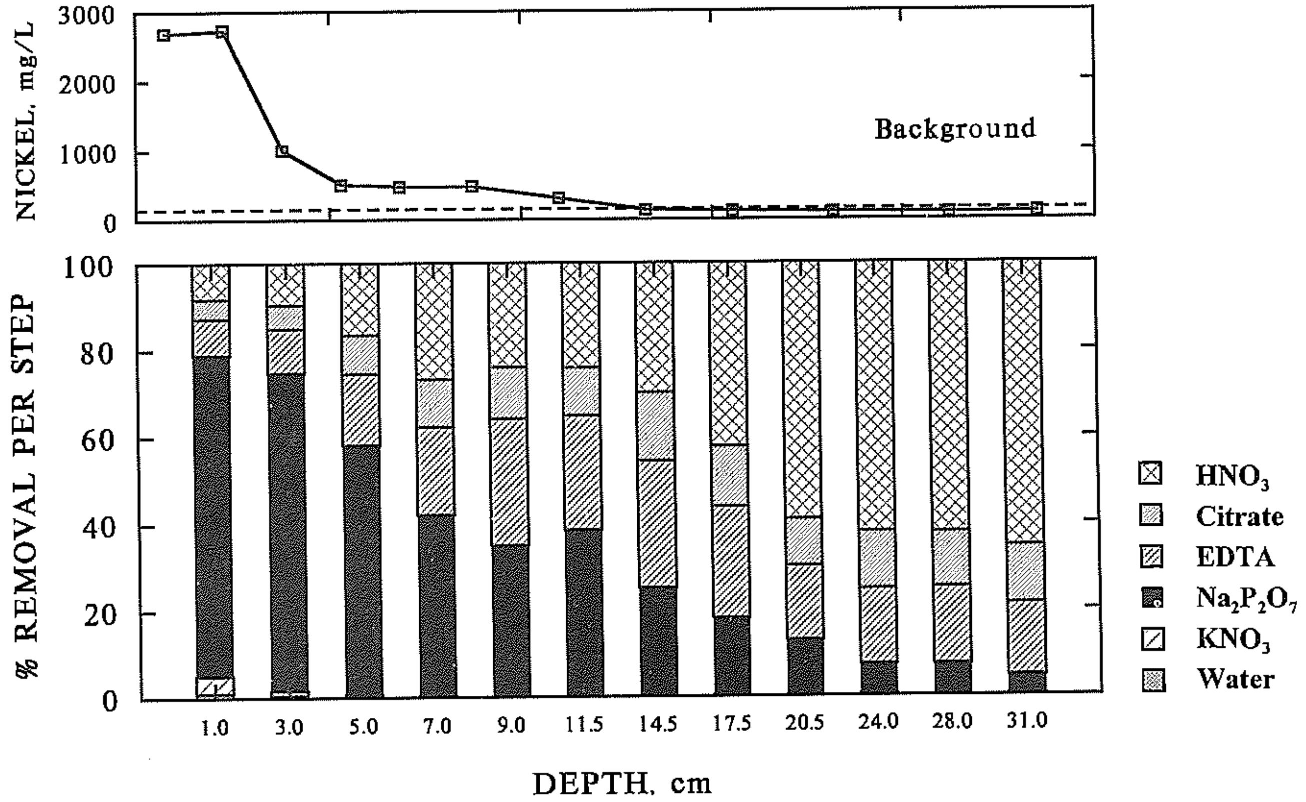

Figure 3. Nickel concentration vs. peat depth (top), and percent nickel removal by each extraction step vs. peat depth (bottom). Data is from 1992 cell 1 peat samples (after 3 yr of operation).

Discussion

In this study, significant amounts of metals were removed from neutral mine drainage in an overland flow wetland. Although metal concentrations increased in the vegetation in the wetland, greater than 99% of the metal removal was associated with the peat substrate. This finding is consistent with our initial work on removal in a white cedar wetland (Eger and Lapakko 1988) and with data reported by others (Skousen 1992, Wildeman et al. 1991).

Vegetation naturally accumulates metals in areas where mineralization occurs. Nickel concentrations in black spruce (*Picea mariana*) and Labrador tea (*Ledum groenlandicum*) overlying a mineralized area in northeastern Minnesota were 5 to 6 times higher than background values (Agrawal 1964). These higher concentrations were in the same general range as those found in the plants in the treatment cell.

The primary removal mechanism in this wetland was the removal of metals by association with the organic fraction of the peat. Peat contains a complex mixture of organic compounds with a series of functional groups. These groups provide a variety of sites for metals to bind. Sulfide precipitation was much less important in the overall removal of nickel. These results are consistent with the changes in water quality observed in the treatment cell. The pH of the drainage decreased as it passed through the cell; the result of the exchange of metal ions in the water for hydrogen ions on the peat. In contrast, there was no statistically significant difference between the input and output sulfate concentration, which implies that the overall rate of sulfate reduction was small (table 1).

The minor amount of removal associated with sulfide precipitation is similar to that reported in studies by Wieder for peat wetlands, in which minimal accumulation of sulfur was found (Wieder and Lang 1986). Wieder suggests that although metal sulfides may form, they are later oxidized and converted to other forms. The oxidation of sulfide precipitates may not be a major concern in a constructed wetland if the water level is maintained so that the substrate remains saturated. In compost based wetlands, however, significant amounts of reduced and elemental sulfur have been measured (Hedin et al. 1989). Compost provides a readily decomposable organic substrate, and sulfate reduction rates up to 1,200 $\text{mmol/m}^3\text{/d}$ have been measured (Reynolds et al. 1991). More typical rates are on the order of several hundred millimoles per cubic meter per day (Eger 1992).

The specific mechanisms of metal removal are important because they affect the overall lifetime of the wetland. Long term treatment of mine drainage is an important regulatory issue, and the ability of wetlands to provide continued treatment has not been demonstrated. As a result, the Office of Surface Mining has required back-up chemical treatment for wetlands built to control coal mine drainage (O.S.M. 1988). If the removal is primarily due to removal by organics, then the system lifetime is limited by the total amount of removal sites that are available in the top portion of the wetland. If the primary removal mechanism was sulfate reduction, the process would continue as long as there was an organic food source and an input of sulfate. Sulfate reduction would be more likely to offer long-term treatment. Although additional adsorption sites will be generated annually as plants die and decompose, the formation of new sites is minimal. To provide a balance between the input of metals and the formation of new removal sites in our test cell, input flow would need to be reduced by about an order of magnitude (table 2).

Another method to increase the treatment life of the wetland is to construct the system so that the surface peat can be replaced. This approach has been used by LTV Steel Mining Company at their Dunka Mine in northeastern Minnesota, where a peat mixture was placed on top of an existing wetland (Frostman et al. 1993). New material can be added when the removal capacity of the mixture is exhausted.

Another factor that limits the removal in natural wetlands is the transport of metals to reaction sites. Although peat depth in our wetland was about 1 m, only the upper 20 cm was effective in removing metals. In natural wetlands, flow occurs primarily across the surface, generally within the upper 30 cm (Romanov 1968).

This occurs as a result of a minimal vertical hydraulic gradient and a decrease in hydraulic conductivity with depth. However, wetlands can be constructed to encourage vertical flow and provide more contact with the substrate. This type of wetland requires additional engineering design, but the increase in treatment per unit area can be significant (Eger and Melchert 1992).

Conclusion

Wetlands can effectively remove metals from neutral mine drainage. Over 99% of the removal in our system was associated with the peat substrate. Although metal concentrations increased in the vegetation, the levels were comparable to levels in areas of natural mineralization. Wetland vegetation is important since it disperses flow, stabilizes the substrate, provides additional organic material, and improves the aesthetics of the wetland. The primary removal mechanism in this system was associated with the organic fraction of the peat, and the bulk of removal occurred in the upper 20 cm of the wetland. As a result, the removal capacity of this wetland is limited, and although new adsorption sites are produced by decomposing vegetation, the metal load into the system would have to be reduced by an order of magnitude to remain in balance. Wetlands can be successful in providing long-term treatment of mine drainage, provided that input flows into the wetland are reduced or that periodic maintenance of the wetland is performed.

Table 2. Comparison of annual production of metal removal sites with current annual metal input.

Annual input of removal sites:	
• Peat accumulation rate	1 mm/yr[1]
• Bulk density	0.1 g/cm^3
• Removal capacity	10 g Ni/kg dry peat[2]
• Area of cell	186 m^2
• Annual removal capacity	0.2 kg Ni/yr
Present loading rate to cell	
• Flow	3.8 L/min
• Concentration	2.0 mg/L
• Average days of flow	225
• Annual metal input	2.5 kg Ni/yr
Flow reduction needed to balance input with annual generation of sites	92%

[1] Craft and Richardson 1993

[2] Eger and Lapakko 1988

Literature Cited

Agrawal, M. U. 1964. Biogeochemical investigation in a swamp environment. M.S. Thesis, University of Minnesota, Minneapolis, MN. 128 p.

Craft, C.B. and C. Richardson. 1993. Peat accretion and N, P, and organic C accumulation in nutrient-enriched and unenriched Everglades peatlands. Ecological Applications 3 (3):446-458.
http://dx.doi.org/10.2307/1941914

Eger, P. 1992. The use of sulfate reduction to remove metals from acid mine drainage. Paper presented at 1992 American Society for Surface Mining and Reclamation Meeting. (Duluth, MN, June 14-18, 1992).
http://dx.doi.org/10.21000/JASMR92010563

Eger, P., and K. Lapakko. 1988. Nickel and copper removal from mine drainage by a natural wetland. In Mine Drainage and Surface Mine Reclamation. Vol. 1. Mine water and mine waste. BuMines IC 9183.
https://doi.org/10.21000/JASMR88010301

Eger, P., and K. Lapakko. 1989. Use of wetlands to remove nickel and copper from mine drainage. In Constructed Wetlands for Wastewater Treatment. (Lewis Publishers, Chelsea, MI).

Eger, P. and G. Melchert. 1992. The design of a wetland treatment system to remove trace metals from mine drainage. Paper presented at 1992 American Society for Surface Mining and Reclamation Meeting. (Duluth, MN, June 14-18, 1992).
http://dx.doi.org/10.21000/JASMR92010098

Eger, P., G. Melchert, D. Antonson, and J. Wagner. 1991. The use of wetland treatment to remove trace metals from mine drainage. Presented at the International Symposium on Constructed Wetland for Water Quality Improvement. (Pensacola, FL, 1991).

Frostman T., S. Gale, and D. Koschak. 1993. Base metal removal from mine drainage. Presented at 1993 10th National Meeting. (Spokane, WA, May 16-19, 1993).

Hedin, R. S., R. Hammack, and D. Hyman. 1989. Potential importance of sulfate reduction processes in wetlands constructed to treat mine drainage. In Constructed Wetlands for Wastewater Treatment. (Lewis Publishers, Chelsea, MI).

Hill, B. B. 1987. Typha productivity in a Texas pond: implications for energy and nutrient dynamics in freshwater wetlands. Aquatic Botany 27. p. 385-394. http://dx.doi.org/10.1016/0304-3770(87)90075-1

Miller, W. P., W. W. McFee, and J. M. Kelly. 1983. Mobility and retention of heavy metals in sandy soils. J. Environ. Qual. 12:579-584. http://dx.doi.org/10.2134/jeq1983.00472425001200040030x

Minnesota Dept. Natural Resources. 1987. Planning of milled peat production systems at two sites in northern Minnesota. (Division of Minerals, St. Paul, MN).

Office of Surface Mining. 1988. Use of wetland treatment systems for coal mine drainage. OSMRE Dir. TSR-10. U.S. OSMRE, Washington, DC.

Reynolds, J. S., T. Wildeman. 1991. Determination of the rate of sulfide production in a constructed wetland receiving acid mine drainage. In Proceedings of the National Conference of the American Society of Surface Mining and Reclamation. (Durango, CO, May 14-17, 1991). http://dx.doi.org/10.21000/JASMR91010175

Romanov, V. V. 1968. Hydrophysics of bogs. Israel Program for Scientific Translations.

Skousen, J., A. Sexstone, K. Garbutt, and J. Sencindiver 1992. Wetlands for treating acid mine drainage. Green Lands 22(4):31-39

U.S. Bureau of Mines. 1985. Control of acid mine drainage. Proceedings of a Technology Transfer Seminar, BuMines IC 9027. p. 2.

Wieder, R. K. 1991. Laboratory procedure manual. Villanova University.

Wieder, R. K. and G. E. Lang. 1986. Fe, Al, Mn and S chemistry of sphagnum in four peatlands with different metal and sulfur input. Water, Air, Soil Pollution 29:309-320. http://dx.doi.org/10.1007/BF00158762

Wildeman, T., J. Gusek, and G. Brodie. 1991. Wetland design for mining operations. Draft handbook presented at the American Society of Surface Mining and Reclamation Conference. (Durango, CO, May 14-17, 1991).

Zhang, T., J. B. Ellis, D. M. Revitt, and R. B. E. Shutes. 1991. Metal uptake and associated pollution control by *Typha latifolia* in urban wetlands. Urban Pollution Research Center, Middlesex Polytechnic, Queensway, Enfield, EN3 4SF, UK.