NICKEL AND COPPER REMOVAL FROM MINE DRAINAGE BY A NATURAL WETLAND[1]

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Abstract.--Recently a considerable amount of attention has been focused on the use of wetlands, both natural and constructed, for the treatment of acid coal mine drainage. Wetlands also may have a significant capacity for removing trace metals from other types of mine drainage. Minnesota has many small and large peatlands near existing and potential mining developments, and the use of peatlands for the control of drainage quality is an attractive alternative to chemical treatment. A study has been conducted on a white cedar peatland receiving stockpile drainage which had an average concentration of 17.9 mg/L nickel and 0.62 mg/L copper. Surface and ground water, vegetation (white cedar (Thuja occidentalis), alder (Alnus rugosa), sedge (Carex spp.)) and peat were all analyzed for trace metal content. Based on mass balance calculations, and water quality data, essentially all of the copper and 80% of the nickel were removed by the peatland. Removal by peat accounted for greater than 90% of the overall metal reduction. Maximum observed concentrations in the peat were 6400 mg/kg nickel and 3600 mg/kg copper; while the maximum values for the vegetation were 239 mg/kg nickel and 10.1 mg/kg copper.

[1]Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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Proceedings America Society of Mining and Reclamation, 1987 pp 301-309
DOI: 10.21000/JASMR88010301

INTRODUCTION

Wetlands, both natural and constructed, have been used successfully in the treatment of acid mine drainage (Kleinman, 1985; Wieder et al., 1982). Wetlands and the peat they contain have a significant trace metal adsorption capacity and offer a potential low maintenance treatment technique for metal laden mine drainage. In laboratory studies, peat has been used successfully to remove trace metals from various types of stockpile drainage (Lapakko and Eger, 1981, Lapakko et al., 1986).

Minnesota has 6 million acres of peatland most of which are located in the northern portion of the state. This area also has the highest mineral potential and exploration for gold and base metals is presently occurring on over 250,000 acres. Wetland treatment systems for mine drainage could be applicable to mining developments in Minnesota.

The objective of this study was to determine both the short-term and long-term effectiveness of a peatland in removing trace metals from stockpile drainage. This paper describes the initial phase of the study; the evaluation of the short-term effectiveness.

SITE DESCRIPTION

The initial phase of the study was conducted from July 1976 to August 1977 at the LTV Steel Mining Company's Dunka Mine in northeastern Minnesota. The Dunka Mine is a large open pit taconite operation, covering approximately 160 ha. The pit is 4 km long, .4 km wide and has a maximum depth of 110 meters. At this location, the Duluth complex, an igneous intrusion overlies the taconite ore and must be removed and stockpiled. The material has been separated based on copper content and has been stockpiled along the east side of the open pit. Drainage from all stockpiles and mine dewatering discharges (011, 012) flow to Unnamed Creek (fig. 1).

Drainage from a stockpile containing Duluth complex material with an average grade of 0.30% copper and 0.09% nickel flowed through a white cedar (Thuja occidentalis) peatland into Unnamed Creek (fig. 2). The stockpile covers 0.12 km^2; flow rates varied from zero during the winter to a maximum of 16 L/sec. Mean trace metal concentrations were 17.9 mg/L nickel, and 0.62 mg/L copper; the mean pH of the drainage was 7.2 (table 1).

The peatland covers 0.04 km^2, the depth of the peat ranges from 1.5 to 1.8 m, and the area is covered by 3-5 cm of standing water. The peat is generally well-decomposed, with decomposition increasing with depth, and is underlain by a layer of silty blue clay. Another white cedar

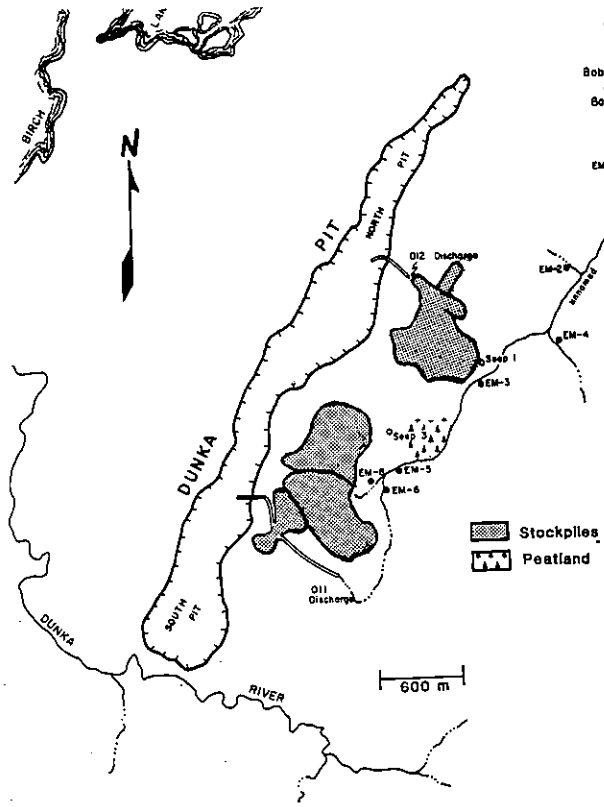

Figure 1.--Dunka Mine, stockpile and sampling locations.

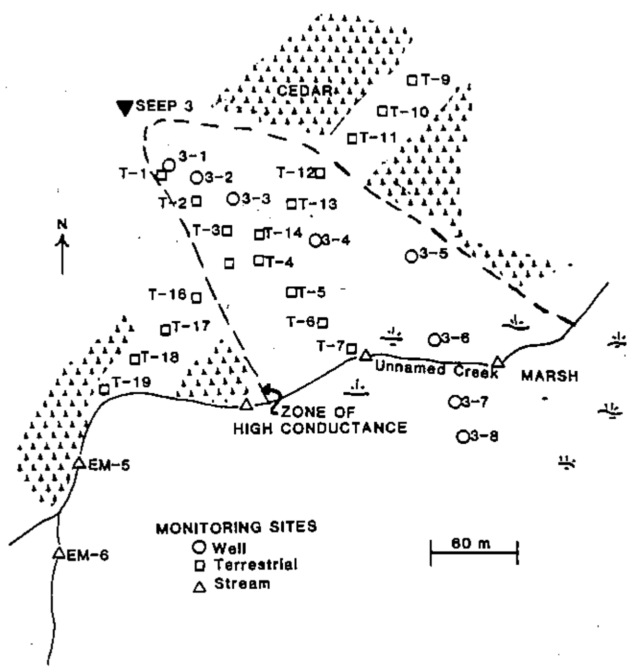

Figure 2.—White cedar peatland.

Table 1.--Stockpile Drainage Water Quality, July 1976 through August 1977.

	Mean	Range	n
pH	7.2	6.68 - 7.79	24
Alkalinity (mg/l as $CaCO_3$)	113	47 - 206	24
Specific conductance (us/cm)	2540	890 - 3550	25
Calcium (mg/l)	285	93 - 388	17
Magnesium (mg/l)	225	52 - 288	12
Sulfate (mg/l)	1300	370 - 2600	17
Copper (mg/l)	.62	.04 - 1.7	24
Nickel (mg/l)	17.9	.4 - 39.8	24
Cobalt (mg/l)	1.16	.4 - 2.4	8
Zinc (mg/l)	.38	.07 - .65	12
Iron (mg/l)	1.44	.4 - 5.4	24

peatland in the same watershed but remote from trace metal sources, was selected as a control.

METHODS

Sampling stations were established at 6 sites along the stream, at each of the major stockpile flows (Em-8, Seep 1, Seep 3), at the two dewatering discharges (011, 012), and at 26 sites in the peatland (figs. 1, 2). Continuous flow data was collected at three sites along the stream (Em-1, Em-3, Em-5) at the largest volume of stockpile seepage (Em-8), and pumping records were available for the mine dewatering discharges. Flow measurements at all other stream and stockpile sites were collected every two weeks.

Water quality samples were collected at each site twice monthly during open water (typically April 1 - November 15) and approximately monthly during the winter. There was no drainage from any of the stockpiles during the winter.

In addition to the twice monthly samples special sampling programs were conducted to better quantify the source of metal input and the amount of metal transport in various parts of the watershed. Automatic samplers were used to collect composite samples along the stream, low flow samples were collected under the ice, and dye studies with Rhodamine WT were conducted to determine the travel times between the different sampling stations on the streams. Water quality samples were collected sequentially (from upstream to downstream) at the specific time intervals measured in the dye study so that the same parcel of water was sampled as it moved downstream.

In the peatland, at 8 of the sites (3-1 to 3-8) shallow wells and piezometers were installed. The shallow wells consisted of a perforated 10 cm diameter, 46 cm long PVC pipe, taped at the top to minimize surface water infiltration. The piezometers (1.5 m depth) were constructed of PVC, with a flange and a bentonite seal to prevent leakage. Specific conductance was sampled in the surface water at all 26 sites, and in the piezometers and wells. Specific conductivity surveys of the surface water were conducted monthly during the summer of 1977 to establish the path of stockpile seepage through the peatland. All 26 sites and additional sites perpendicular to the well line were sampled. In June and August, at sites 3-1 to 3-8, the water at the surface and in the wells and piezometers was filtered, and analyzed for trace metals by atomic absorption.

At the odd numbered T sites and at the control peatland within the same watershed, releves (Mueller-Dombois and Ellenberg, 1974) were used to describe the plant community; and visual estimates of plant damage were made. Samples of leaf tissue were collected at each T site for each of three species; white cedar (Thuja occidentalis), alder (Alnus rugosa), and Carex spp.. These samples were wet ashed using a $HNO_3/HClO_3$ digestion and analyzed for trace metal content using inductively coupled plasmaspectroscopy (ICP). Digestions and analyses were performed by Barringer Laboratories in Toronto, Canada.

At each site a composite of three peat samples was collected from the top 20 cm and analyzed for trace metals by total acid extraction (HF, HCl, HNO_3) (Meineke and Klaysmat, 1976). At four stations (3-1, 3-2, 3-5, 3-8) and the control site, trace metal concentrations were determined at approximately 25 cm depth intervals for the entire depth of the peat.

RESULTS

Stockpile drainage typically began in late March and ended around the middle of November, while mine dewatering and groundwater inputs maintained flow in the stream for the entire year. The mean nickel concentration at the mouth of the stream (site Em-1) was 0.1 mg/L and ranged from 0.03 to 0.22 mg/L. Concentrations throughout the stream exceeded the natural background levels (.001-.005 mg/L) for streams

Table 2.--Water Quality Summary at White Cedar Peatland, August 1977.

parameter	surface samples		shallow wells		piezometers	
	mean	range	mean	range	mean	range
specific conductance (us/cm)	3100	2250 - 3500	2600	2100 - 3000	270	213 - 325
copper (mg/l)	.13	.002 - .46	.001	.001 - .002	.001	.001 - .002
nickel (mg/l)	20	8.4 - 26.0	.6	.18 - .93	.03	.01 - .06

in the area, even during the winter when stockpile input ceased. Copper concentrations ranged from .001 to .006 mg/L and were similar to the values measured in unimpacted streams (.001-.005 mg/L) (Thingvold et al., 1979).

Water quality in the peatland varied with distance from the drainage input, depth in the peatland, and time. The specific conductance values in the surface water were used to define the path of stockpile drainage through the peatland. The boundary on the west side was particularly dramatic; specific conductance decreased from over 2000 to 400 within several meters. Specific conductance decreased as distance from the seep and depth in the peatland increased. Conductivity values decreased from 3000-3500 us/cm at the seep to 600-2000 us/cm near the stream with the majority of the reduction occurring over the final 200 meters (fig. 3). Specific conductance values were highest in the surface water and were an order of magnitude greater than those measured in the piezometers (table 2).

The reduction of copper and nickel concentrations with increasing distance from the seep in surface samples was greater than that of specific conductance (fig. 3). In both June and August the copper concentration was reduced by about two orders of magnitude. The greatest reduction occurred within the initial 100 meters of flow, with concentration remaining relatively constant, essentially at or slightly above background levels ($\leqslant$ .005 mg/l) over the final 200 meters. In June, nickel was reduced by about two thirds within the first 150 meters, but in August little reduction occurred in this portion of the peatland. In August, nickel did decrease by about two thirds over the final 200 meters of the peatland but the concentration near the stream (8.4 mg/L) was still about three orders of magnitude greater than background values. Surface concentrations of both metals were two to three orders of magnitude greater than the values from the wells and the piezometers (table 2).

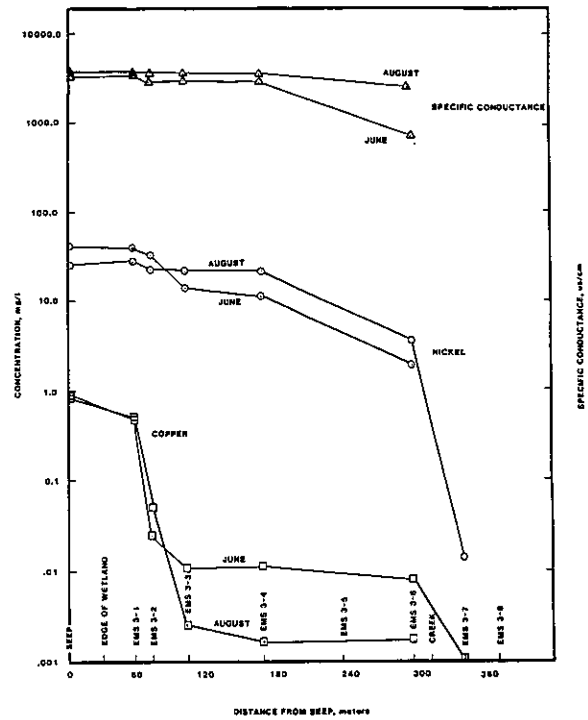

Figure 3.--Copper, nickel, and specific conductance in surface water in white cedar peatland, June and August, 1977.

Vegetation

The predominant vegetation in both the impacted and control peatlands was white cedar, alder and Carex. Damage levels were determined by the presence of chlorosis in the leaves, and gave only a qualitative indication of plant stress. High levels of damage to vegetation were observed at two of the ten T sites (T_1, T_{13}), but no definitive pattern relating damage to distance from the seep was observed.

Leaf tissue nickel concentrations were about one to two orders of magnitude higher in the impacted area than the values measured in the control peatland, where nickel was not detectable ($\leqslant$ 1 mg/kg). The highest nickel concentrations were generally found within the zone of high conductance water and the lowest values were measured outside this zone in the northeast section of the peatland at sites T_9-T_{11} (fig. 4). Elevated nickel values were, however, found at sites T_{16}-T_{19} which were outside the zone of high specific conductivity. Copper concentrations were about an order of magnitude lower than the nickel values even at sites near the seep, and there was no relationship between the

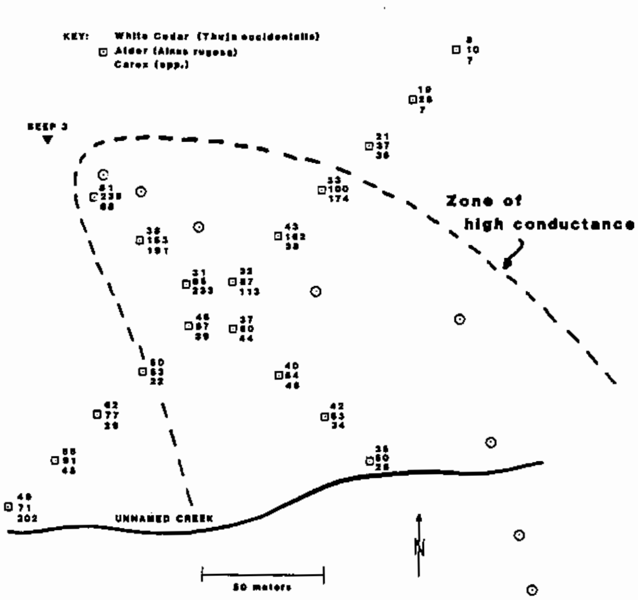

Figure 4.--Nickel concentration in vegetation, mg/kg (August 1977).

copper values and location in the peatland. Concentrations in the leaves of cedar and alder were slightly higher at the control than the values measured at the impacted area (table 3).

Peat

Nickel and copper concentrations in the peat decreased as distance from the seep and depth in the peat column increased. The maximum copper concentration of 3600 mg/kg was found in the top 20 cm sample near the seep (site 3-1). The concentration decreased with depth and the maximum value was about 6 times the value at the base of the peat (fig. 5). Samples collected at sites further from the seep had a more uniform concentration versus depth profile and concentrations near the creek were only 200-400 mg/kg. Surface nickel concentrations ranged from 6400 mg/kg near the seep to 1116 mg/kg near the creek and decreased with depth at all sites in the impacted area (fig. 6). Isopleths of the concentrations in the top 20 cm and the specific conductance in the surface water were used to define the area of drainage impact (fig. 7).

Generally the zone of high specific conductance corresponded to the area with the highest nickel concentrations in the peat. However, concentrations increased along the line from T_{16}-T_{19}, and the nickel values at T_{19} was comparable to the values within the zone of influence. Concentrations of the trace metals at the control peatland (25 mg/kg average copper, 65 mg/kg average nickel) and across the stream (site 3-8) were one to two orders of magnitude lower than the concentrations near the stockpile and were relatively constant with depth at both sites.

Mass Balance

To quantify the overall removal of copper and nickel occurring in the peatland a mass balance was calculated for the period of study. An overall watershed balance and a balance for the peatland alone were computed. Flow and concentration measurements were combined to compute overall mass inputs and outputs. Individual time periods were analyzed and error estimates for the nickel mass were made for Seep 3, Em-8 and Em-1. The overall mass values were estimated to be within ± 15% (Eger and Lapakko, 1980).

For the watershed, the major source of nickel and copper was the stockpile drainage, with seep 3 contributing about 87% of the total nickel input and 78% of the total copper input (table 4). The total input from stockpiles comprised 99.2% and 82% of the nickel and copper inputs, respectively. The total nickel input was 2087 kg and total output, as measured at the mouth of the stream (Em-1), was 340 kg. The overall nickel removal was 84%. Total copper input was 112 kg and the output was 9 kg, resulting in an overall copper removal of 92%.

The only significant input of nickel and

Table 3.—Trace Metal Concentrations in Vegetation.

	Peatland Receiving Stockpile Drainage (sites T1 - T19)				Control Peatland (mean, composite sample)		[1]Regional Values		
Plant Species	Copper (mg/kg) mean	range	Nickel mean	(mg/kg) range	Copper (mg/kg)	Nickel (mg/kg)	Copper (mg/kg)	Nickel (mg/kg)	No. of Sites
White Cedar (Thuja occidentalis)	2.6	2.1 - 3.8	37	8 - 62	4.1	1.0	No Data	No Data	1
Alder (Alnus rugosa)	7.8	4.8 - 10.1	82	10 - 239	12.1	1.0	3.9 - 12.1	1.0	3
Carex spp.	6.1	3.3 - 9.2	76	7 - 233	2.6	1.0	0.9 - 8.6	1.0 - 8.0	10

[1]Minnesota Regional Copper-Nickel Study

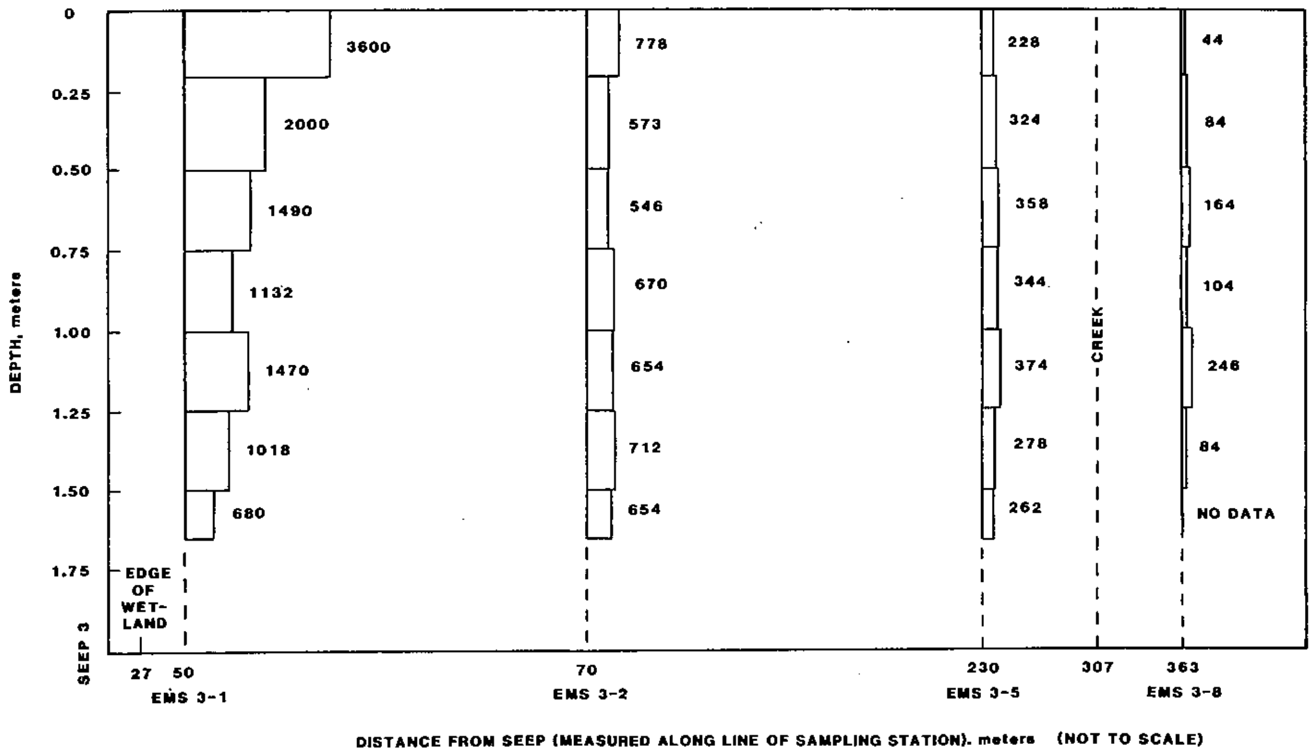

Figure 5.--Copper concentration (mg/kg) vs depth and distance from seep.

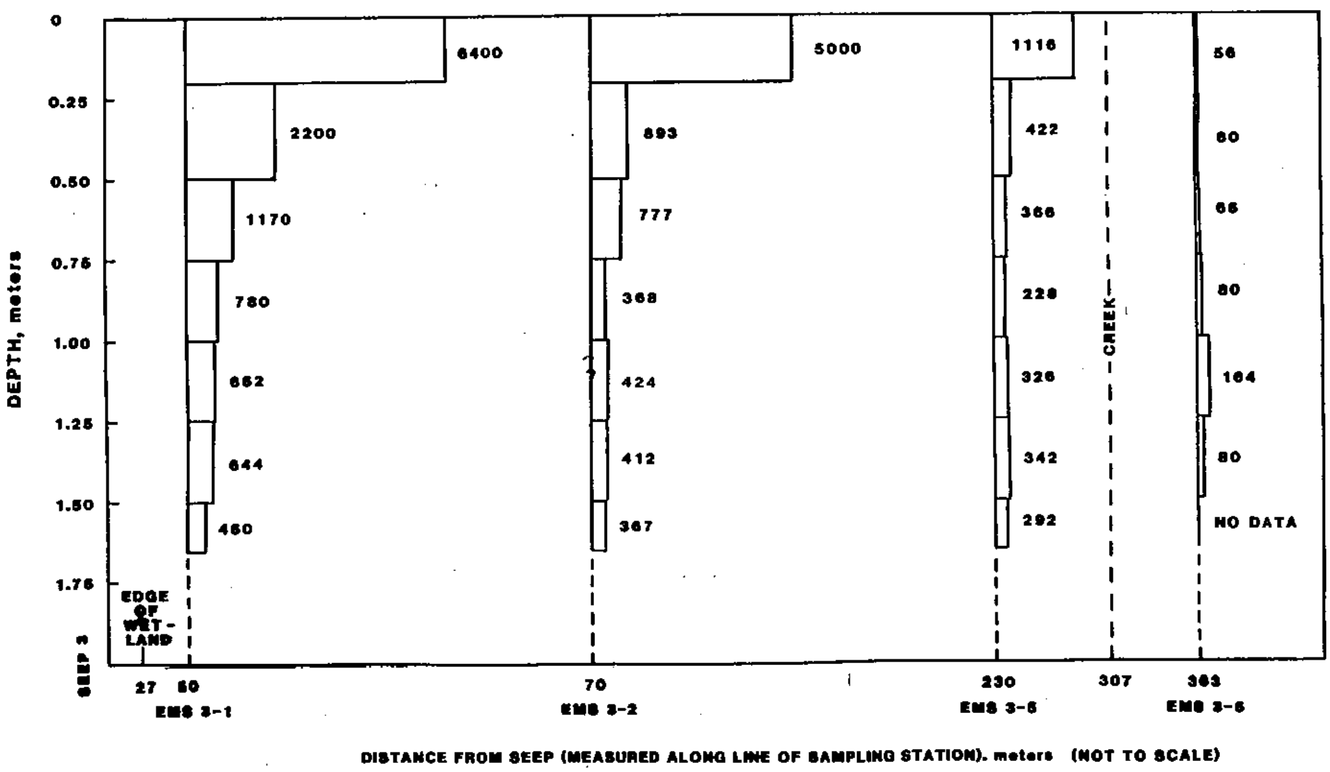

Figure 6.--Nickel concentration (mg/kg) vs depth and distance from seep.

Table 4.—Overall Mass Balance for Watershed.

	Volume ($L \times 10^6$)	Mass (kg) Nickel	Copper	Sulfate
Inputs				
Stockpile Seepage				
Seep 3	90	1810	72	103,000
Em8	184	150	4	128,000
Seep 1	29	110	16	72,000
Mine Dewatering Pumps				
011	2530	14	16	205,000
012	255	0.8	2	78,000
[2]Natural Runoff	426	2	2	13,000
Total Input	3514	2087	112	599,000
Outflow				
Em-1	3514	340	9	563,000
[1]Overall Removal		84	92	6

[1] $\frac{\text{input} - \text{output}}{\text{input}} \times 100\%$

[2]Computed by difference.
Volume at Em-1 minus the sum of all input volumes.

Table 5.—Nickel Mass Input from Stockpile Drainage and Release from the Peatland to Stream.

Time Period	Nickel mass loading: Seep (mg/sec)	Input to Stream from Peatland (mg/sec)
7-15 to 10-25-76	45.4	3.6
12-07 to 12-10-76	0	1.2
5-05 to 5-13-77	1.1	5.4
8-16 to 8-17-77	111.0	28.0

copper to the white cedar peatland was the stockpile drainage from Seep 3. Nickel input during the 13 month study period was 1800 kg, and copper input was about 70 kg (table 4). The output from the peatland was much more difficult to quantify since there was no one single point where the drainage from the peatland entered the creek. The drainage occurred in a diffuse manner along the stream for about 250 meters (determined by specific conductivity measurements). The output of nickel was determined through the overall balance for the watershed, by comparing upstream and downstream nickel loads in the stream, and through low flow sampling along the stream (Eger and Lapakko, 1980). During the study period, discharge rates of nickel from Seep 3 ranged from 0 during the winter to 111 mg/sec, while contributions to the stream ranged from 1.2 to 28 mg/sec during the

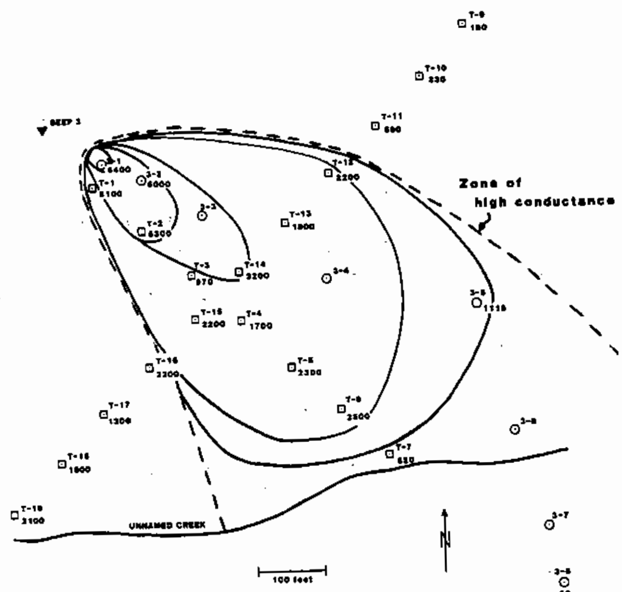

Figure 7.--Nickel concentration (mg/kg) in top 20 cm of peat, August 1977.

same period (table 5). The total estimated load from the peatland to the stream was about 300 kg, or about 80% of the nickel had been removed in the peatland. The copper output was not calculated since water quality data in the peatland and in the stream indicated that 1) copper concentrations were reduced to background levels within 200 meters from the seep and 2) there was no measurable input of copper from the peatland to the stream.

Metal accumulation was estimated in the water, vegetation and peat, using the specific conductance values to determine the boundary of the impacted area. Since the upper portion of the peat is about 90% water and since field observations indicated about 3-5 cm of standing water in the peatland, a substantial amount of metal could be stored in the water. Using the concentrations measured at the well sites and dividing the area between the sites, estimates were made for the mass of metal stored in the water. For nickel the total was 42 kg, with 76% of the metal being stored in the top 20 cm of the peatland.

Biomass estimates were made for cedar, carex, and alder (Ohman and Grigal, 1985; Dyer, 1967) and the average concentrations for each species was used to estimate the mass of nickel in each species. The total mass was less than 6 kg with cedar containing about 70% of the total.

The total mass of nickel contained in the top 20 cm of peat was calculated by using the area between the isopleths and applying the mean metal concentration to that volume of peat. Since a certain percentage of the metals were contained in the peat prior to the stockpile drainage a background correction was applied. The concentration at depths greater than 75 cm at the sites 3-2 and 3-5 was assumed to be representative of natural conditions. Estimates were made for the 20-75 cm depth based on the measured depth profiles and assuming that the isopleths at depth would be similar to those in the top 20 cm. Using these assumptions the nickel mass was estimated to be about 1150 kg in the top 20 cm and 350 kg between 20-75 cm. The mass of copper was calculated in a similar fashion and was estimated to be 77 kg.

DISCUSSION

Significant removal of nickel and copper has occurred in this watershed. The overall watershed balance indicated that about 1750 kg of nickel and 100 kg of copper were being removed. The largest source of metal input was Seep 3, but analyses of upstream and downstream loads in the stream revealed that only a portion of the nickel and none of the copper were transported through the peatland. Most of the metal removal in the watershed was occurring in the white cedar peatland.

Both the input - output calculations and accumulation estimates indicated that about 1500 kg of nickel and about 70 kg of copper were removed and stored in the peatland during the period of study. Based on the overall mass balance and water quality results, essentially 100% of the copper and about 80% of the nickel were removed. Analysis of the individual compartments demonstrated that greater than 90% of the metals were associated with the peat. Although the nickel and copper concentrations in the peat are on the order of several tenths of a percent, laboratory experiments with stockpile drainage have demonstrated that peat can accumulate up to 2% nickel during a continuous column removal experiment (Lapakko et al., 1986) and peat from the Tantramar Swamp in New Brunswick was found to contain as much as 10 percent copper (MacDonald et al., 1976). Typical metal concentrations for peat in Minnesota are about two orders of magnitude less than the values measured in the impacted peatland (Grigal and Nord, 1983). Metal values above background have been found near zones of mineralization, but were generally an order of magnitude less than the concentration in the study area (Meineke et al., 1977).

Specific conductance and peat metal concentrations indicate that the contact zone between the stockpile drainage and the peatland is confined to the upper portion of the peat, a zone referred to as the acrotelm, or the zone of active water movement (Romanov, 1968; Ingram, 1978). Since peat decomposition generally increases and hydraulic conductivity decreases with depth, only a small amount of the stockpile drainage will contact the lower levels of the peat and therefore treatment is restricted to the upper more permeable zone.

Even though the nickel values in the vegetation were elevated the removal of nickel by plant up take accounted for less than 1% of total nickel removal. Increasing the biomass in a wetland might provide greater metal removal, but for the metals in this study the increased removal would not appear to be significant.

CONCLUSIONS

Nickel and copper have been successfully removed from stockpile drainage as it flowed through a natural white cedar wetland. Essentially all of the copper and about 80% of the nickel was removed during the study period. Peat uptake accounted for over 90% of the removal while vegetation uptake provided less than 1% of the overall removal. Wetland treatment appears to offer a low maintenance alternative to seepage collection and treatment of metal contaminated drainage.

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