

FATE AND TRANSPORT OF METALS IN A NATURAL WETLAND RECEIVING MINE DRAINAGE

By

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Abstract. The Forest Queen Wetland, adjacent to the Animas River near Silverton, Colorado receives acid mine drainage from the adit of the Forest Queen Mine. Because the pH of the mine drainage averages between 3 and 5 and the iron concentration averages 18 mg/L, it was thought that the wetland would naturally treat the water. One of the important contaminants to be treated is zinc which averages 0.60 mg/L in the adit water, while the aquatic criterion is 0.50 mg/L. In the study that was undertaken to determine whether metal removal was occurring, considerable effort was made to link the water and soil chemistry with the wetland hydrology. There are at least two water systems influencing the wetland: the mine drainage across the surface and ground water from the adjacent slope that typically flows under the wetland. These two are, for the most part, separated from each other by a layer of peat that is of low hydraulic conductivity and is over 1.8 meters deep in places. Because of the separated hydrologic systems, the Fe and Al is removed from the adit effluent when it flows across the surface. However, because the pH does not exceed 6.5 for the most part, Zn is not removed.

Additional Key Words: Colorado, iron, aluminum, zinc, ground water hydrology

Introduction

The goal of this project is to understand wetland processes in cases where a natural wetland is positioned in the landscape and receives impacts from an abandoned mine. The overall approach of this project is designed to gain an understanding of the hydrological and geochemical processes occurring in a site-specific natural wetland ecosystem. The site is the Forest Queen Wetland located near Silverton, Colorado.

Site-Related Background

Placer gold was discovered in the San Juan Mountains, Colorado in the 1860 near Eureka. However, the gold fever did not take over until 1871 when a paying load was found and mined at the Little Giant vein in Arrastre Gulch (Voynick 1992). Since then, there have been over 15,000 prospects in just the San Juan

Mountains. The exposure of altered rock related to the prospects and abandoned mines has released an excessive amount of metals into the surface waters. Difficulties in regulations include not having an established baseline concentration for the various base metals in a natural, highly mineralized zone.

The EPA has mandated federal land agencies such as the National Forest Service (NFS) and the Bureau of Land Management (BLM) to clean up metal contamination associated with abandoned mines or point sources on their property. Problems associated with this include determining clean up limits, identifying priority sites, and determining cost effective methods.

The BLM is presently concerned with point source contamination. They are interested in using the Forest Queen site as a pilot project for design and construction of a cost effective treatment method. Initially, the concern was that water discharging from the wetland exceeded the state water quality limits. Data collected show that Fe was being removed from the water, but the metal of concern, Zn, was not. They have commenced constructing a passive treatment system to treat the effluent from the collapsed adit prior to discharging it into the wetland. However, interest in the processes naturally occurring in this wetland may be used in constructed wetlands and passive treatment systems to meet water quality criteria.

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Site Description

The two-acre Forest Queen Wetland is located on a west-facing slope of a glaciated U-shaped valley at an elevation of 9800 feet. The valley is in a topographic reversal of a volcanic rim, which was active in the Tertiary (35 million years ago) prior to the glaciation. The over-steepened sides of the valley have a tremendous amount of mass-wastage processes currently active. The valley is filled with colluvium, alluvium and glacial deposits. The Animas River, which is undersized for the valley, flows braided through the reach of the river adjacent to the study site. The braided nature of the river can be attributed to the over-abundance of sediment. Maximum flows of the Animas River are recorded, typically, in May during the spring runoff.

The average precipitation for the five years, 1993-1997, at Silverton is 21.8 inches (Colorado Climate Center 1999). The precipitation at Silverton closely approximates the precipitation at the site and is the best available data.

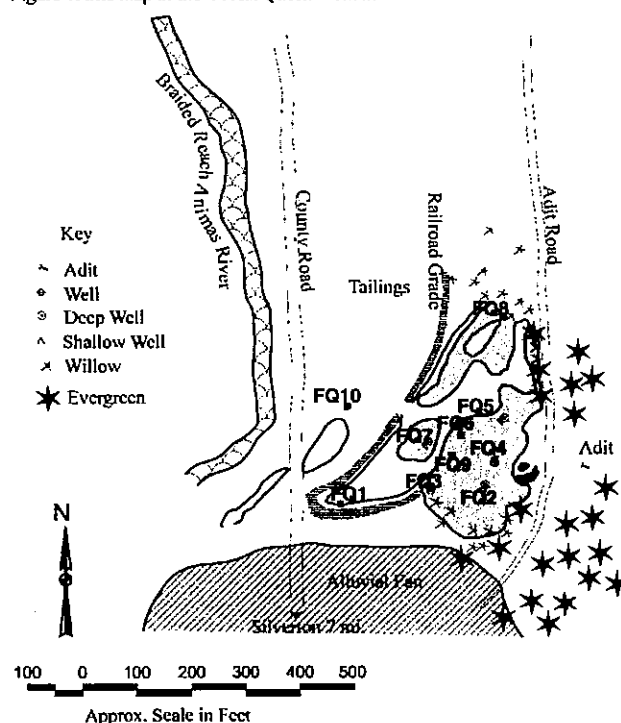
Surface water consistently enters the wetland from the collapsed adit by way of a small pond, which overflows into the wetland. Figure 1 shows the location of the collapsed adit, ponds, and railroad grade. During the high runoff in the snowmelt period, surface water also enters the wetland through beaver channels to the north and springs at the base of the slope to the east. A pond dammed by an abandoned railroad grade and beaver dams bounds the west side of the wetland. The surface water typically discharges through a break in the railroad grade, and then flows over flood deposited tailings and under the road through a culvert into a braided reach of the Animas River. The surface of the wetland has visible Fe and Al precipitates.

The wetland can be separated into two hydrogeologic units: an upper peat layer and a lower unconsolidated layer composed of sand, gravel and boulders. The peat layer, which has a saturated thickness up to 10 feet, serves as a low hydraulic conductivity unit. The unconsolidated layer located beneath and around the peat serves as a high hydraulic conductivity unit. The vegetation cover of the wetland is primarily sedges and mosses. The plant community is primarily composed of *Carex aquatilis*, *C. utriculata*, and *C. praegracilis*, *Hordeum jubatum*, *Calamagrostis canadensis* and *C. stricta*, *Deschampsia caespitosa*, *Juncus balticus*, and *Sphagnum* moss. Willows bound the perimeter along the north and south sides. Blue spruce and Douglas fir grow up the slope on the east side of the wetland. The west side past the railroad grade is mostly devoid of vegetation due to the tailings.

Purpose and Objectives

The first objective is to characterize and determine the hydrology of a sub-alpine wetland. This

Figure 1. Site map of the Forest Queen Wetland



involves defining the source or sources of water and how it flows through the system. Understanding the seasonal fluctuations of the hydrology is important because different geochemical processes may be dominant under different hydrologic regimes. Because the transport of chemical substances is dependent on the hydrologic flow path, there is an interdependence of the hydrology and the geochemistry that is important to define.

The second objective is to characterize and determine the geochemistry of a sub-alpine wetland. The first step of this objective is to define the source or sources of metals and their concentrations. The next step is to determine the distribution of the metals and relate the distribution to the hydrology. By looking at the distribution of metals retained in the wetland, in particular Fe, Al and Zn, it is possible to determine the accumulation zones of metals being retained in the wetland.

Hypotheses

Hydrological-Hypothesis. A positive water budget and peat accumulation is essential for peatland development and survival (Mitsch and Gosselink 1993). The Forest Queen Wetland has a relatively high accumulation of peat for the Southern Rocky Mountains. We would expect to find that there is a sustainable water source for this wetland. The first hypothesis is that the peat

receives discharge year-round from ground water sources originating from the hillslope.

The beaver dams present on the wetland indicate flowing surface water through the wetland. A significant surface water source would be the Animas River and/or the seeps and springs at the base of the hillslope.

From visual observations we know that the connection to the Animas River is seasonal, but the relationship to the hillslope ground water is not clear. We hypothesize that, for most of the year, a large portion of the peatland is perched and the low conductivity peat controls the water level at the surface.

Geochemical-Hypothesis. Currently, the recognition, value, and applied use of wetlands for improving water quality is increasing (Kadlec and Knight 1996). We hypothesize that Fe and Al from the mine adit water are retained in the surface sediments as oxyhydroxide precipitates across the surface of the wetland, and Zn is not. The presence of red-orange precipitates on the wetland surface indicates Fe oxyhydroxides and the white precipitates, Al oxyhydroxides. We hypothesize that iron and aluminum are retained by the natural wetland system as oxyhydroxides.

We hypothesize that Zinc from the mine effluent is not retained in the wetland. During high runoff, a greater load of Zn enters the wetland from water that has flowed over and through the tailings to the north and west of the wetland. The concentration of Zn is also typically higher in the Animas River than the effluent from the collapsed adit. The multiple sources of Zn make analysis and treatment more difficult. The geochemical environment is unsuitable for precipitating zinc as an oxyhydroxide.

Lastly, we hypothesize a strong connection between the hydrology and the geochemistry. The treatment of the mine water is closely related to how and where the water moves through the system. When natural wetlands have been compared to constructed treatment systems, it has been assumed that the competing aerobic and anaerobic processes may limit the treatment capability of a natural system (Wildeman et al. 1993). However, the degree of metal accumulation in the natural wetland may be more closely related to the hydrology.

Methods

Objective 1

To determine hydrology and geochemistry of the peat layers, fifteen wells were installed with screening at deep, middle, or shallow depths. The wells were drilled using a power auger, for up to a depth of four feet, and/or a hand auger for depths deeper than four

feet. The screened section of casing was lined with silica sand, sealed off with bentonite, and capped with concrete. Ten of the wells are nested at five locations such that in a group of two wells, one is shallow and the other deep. Wells were installed in October 1997. The wells, FQ1, FQ10 and FQ8 are screened in alluvium. The wells FQ7D and FQ2D reach the bottom of the peat, but do not extend into the colluvium. The remaining wells are solely screened in the peat at different depths. To understand the seasonal fluctuations, water levels were taken October 1997, April 1998, June 1998, and August 1998.

Objective 2

The wetland was characterized chemically by field measurements and samples analyzed in the laboratory. Eh, pH, ionic conductivity, temperature, and alkalinity were measured in the field. Additionally, ground water samples were tested for dissolved oxygen using a Hach spectrophotometer kit. Dissolved concentrations of cations, particularly Fe, Al and Zn, were measured in the laboratory using a Perkin Elmer Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). The ICP-AES analyses were performed on .45 μ m filtered water samples, which had been preserved with nitric acid. A Dionex Ion Chromatograph (IC) was used to measure concentrations of flouride, chloride, bromide, nitrate, phosphate, and sulfate. The samples were filtered with a .45 μ m filter and were not acidified; however, they were frozen to significantly reduce bacterial degradation.

Peat samples were collected in October 1997 at varying depths. We assumed that metal concentrations in the peat would not change significantly with the seasons. The metal content of the peat was analyzed using a strong hydrochloric acid/nitric acid digestion. A filtered sample of each extract was tested for metals on the ICP-AES.

The spatial distribution of metal concentrations was used to identify sources of contamination and areas of metal accumulation.

Results

Objective 1 – Hydrological

The first objective is to characterize and determine the hydrology of a sub-alpine wetland. The geology and the hydrogeology control the hydrology of the wetland. Figure 2 is a schematic of the hydrogeology. The peat is a low permeable layer that sits on a highly permeable layer of colluvium and alluvium. The colluvium and alluvium is composed of glacial outwash, river alluvium, and probably mass

wastage deposits. The low permeable peat controls the ground water flow into and out of the wetland.

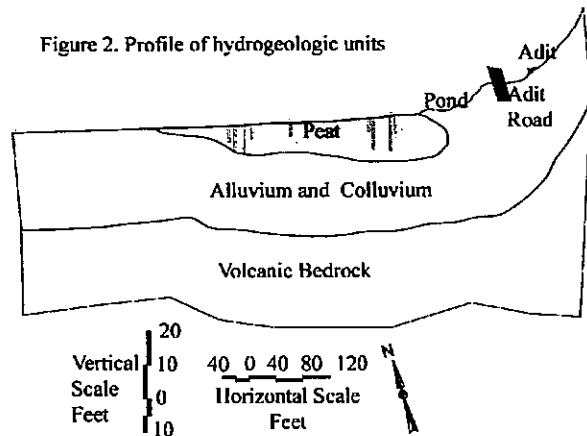


Figure 2. Profile of hydrogeologic units

Typically, peat accumulation in the Southern Rocky Mountain Region, peat accumulation is very slow. Because the accumulation of peat is near 10 feet at this site, there is good reason to believe the hydraulic functions have been stable since the end of the last glaciation. We can show that there is a long-term source of ground water that provides a consistent source of water. In addition to the ground water source, the low hydraulic conductivity of the peat maintains saturated conditions when the ground water discharge function is low. Figure 3 shows ground water contours for 5 episodes of ground water level monitoring. The area covered in the Figure 3 is only the center of the wetland and the area west of the adit road.

The water level near the surface fluctuates, seasonally, on the order of one foot. The water levels around the wetland fluctuate more than 3 feet. Analyzing the heads from the deep wells relative to the heads from the shallow wells, the vertical gradient fluctuates with the hydrologic cycle. The western part of the wetland typically has a downward gradient. The vertical gradient in the western part of the wetland has a slight upward gradient during the periods of ground water discharge in the spring and likely after precipitation events. Otherwise, horizontal flow is predominant.

Table 1 contains the water level elevation measurements for each of the ground water monitoring events. Data from the deep wells in October, 1997 is suspect, as there was not enough time for the water level in the wells to equilibrate between completing the well and measuring the water level.

Four episodes of ground water monitoring from April 1998, June 1998, August 1998 and October 1998 show the seasonal variation in the ground water flow. Profiles of the ground water (Figure 4) reveal that annually there is a ground water source that discharges into the wetland. April 1998 and August 1998 show a

horizontal flow of ground water through the wetland, and in June 1998 and October 1998 show a vertical component to the discharge. The source is still the eastern slope. All the profiles show a recharge component in the western half of the wetland.

The wetland is located in the transition from a discharge zone at the slope break and a recharge to the Animas River Basin. The ground water regime changes seasonally within the wetland with respect to the hydrologic cycle.

Water Sources. This system has two primary water sources, ground water and surface water. Precipitation plays a minor role, but at this elevation it is not significant (about 21.8 inches/year). However, precipitation is most likely the source for the ground water and extremely important for the ground water source area.

There is a consistent source of ground water from the steep, eastern slope. Observations of seeps and springs on the northeastern side of the wetland, during the spring runoff, confirm the ground water discharge. The seeps and springs also add to the surface water that enters the wetland from the north.

The surface water from the Animas River Basin that enters the wetland from the north through abandoned river and beaver channels floods the western portion of the wetland. This happens during the spring runoff typically in May and June. The water is stored in ponds and depressions on the wetland surface, flows out through the break in the railroad grade, or recharges the alluvium and colluvium through the wetland.

A consistent source of surface water flows from the collapsed adit year round. Seasonally, when the climate is dry, the primary source of surface water is the drainage from the adit. There are also minor amounts of surface water entering the wetland through seeps at the slope break.

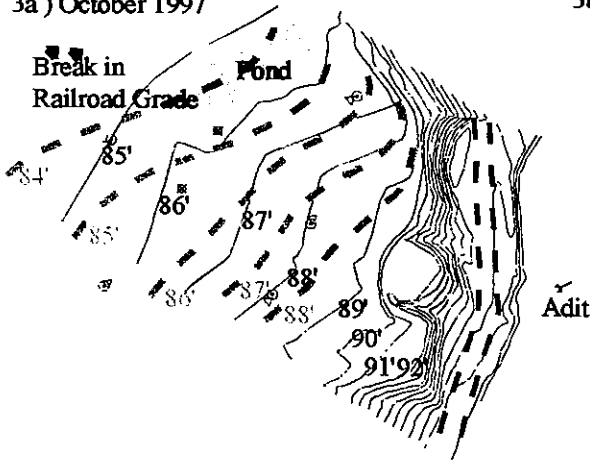
Objective 2 – Geochemical

The first step of this objective is to define the source of metals to the wetland and their concentrations. The sources of metals to the wetland include effluent from the adit, and, seasonally, seeps, springs, and surface water from the Animas River Basin. The best-defined sources are listed in Table 2 with the corresponding metal concentrations.

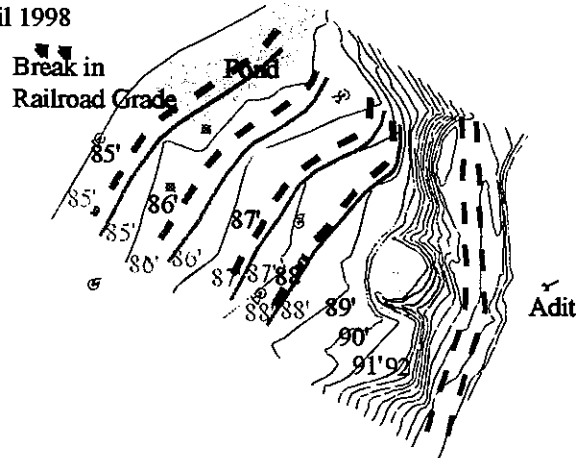
The adit is the only known constant source of metals to the wetland. Many of the seeps and springs flow seasonally at the surface where the metal concentrations can be measured. Well FQ8 flows artesian in the spring and may to be a good representation of ground water entering the wetland from the slope north of the wetland. The sample collected from the bio-

Figure 3. Ground water potentiometric surface from measured water table elevations

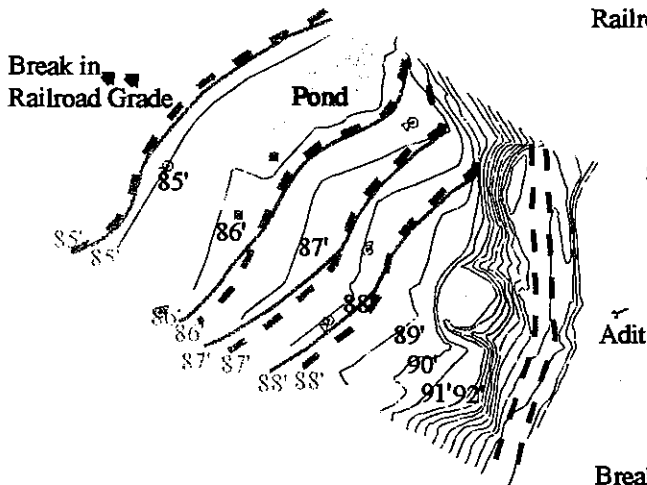
3a) October 1997



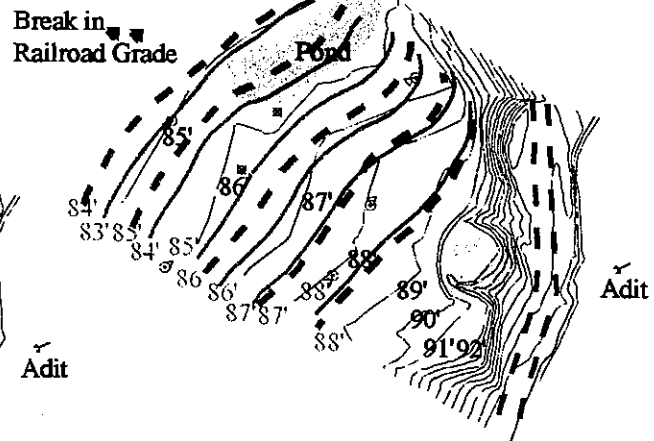
3b) April 1998



3c) June 1998



3d) August 1998



3e) October 1998

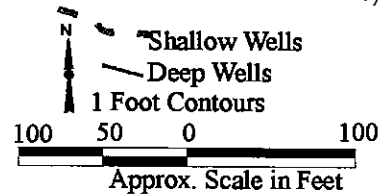
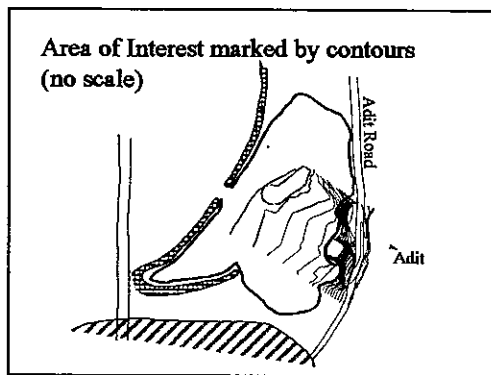
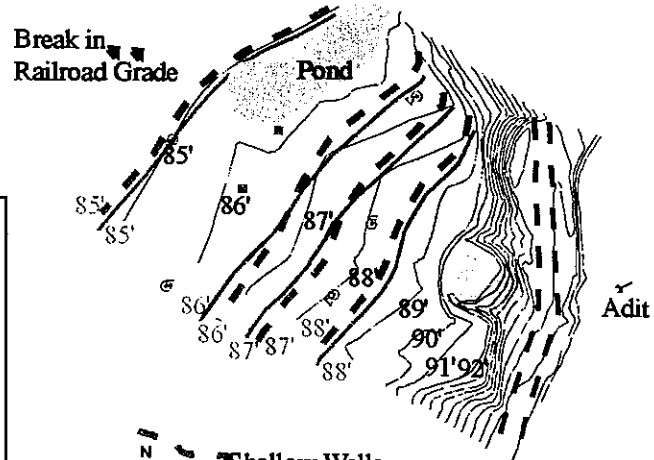


Figure 4 Profile of ground water hydrologic equi-potential surfaces and flow lines

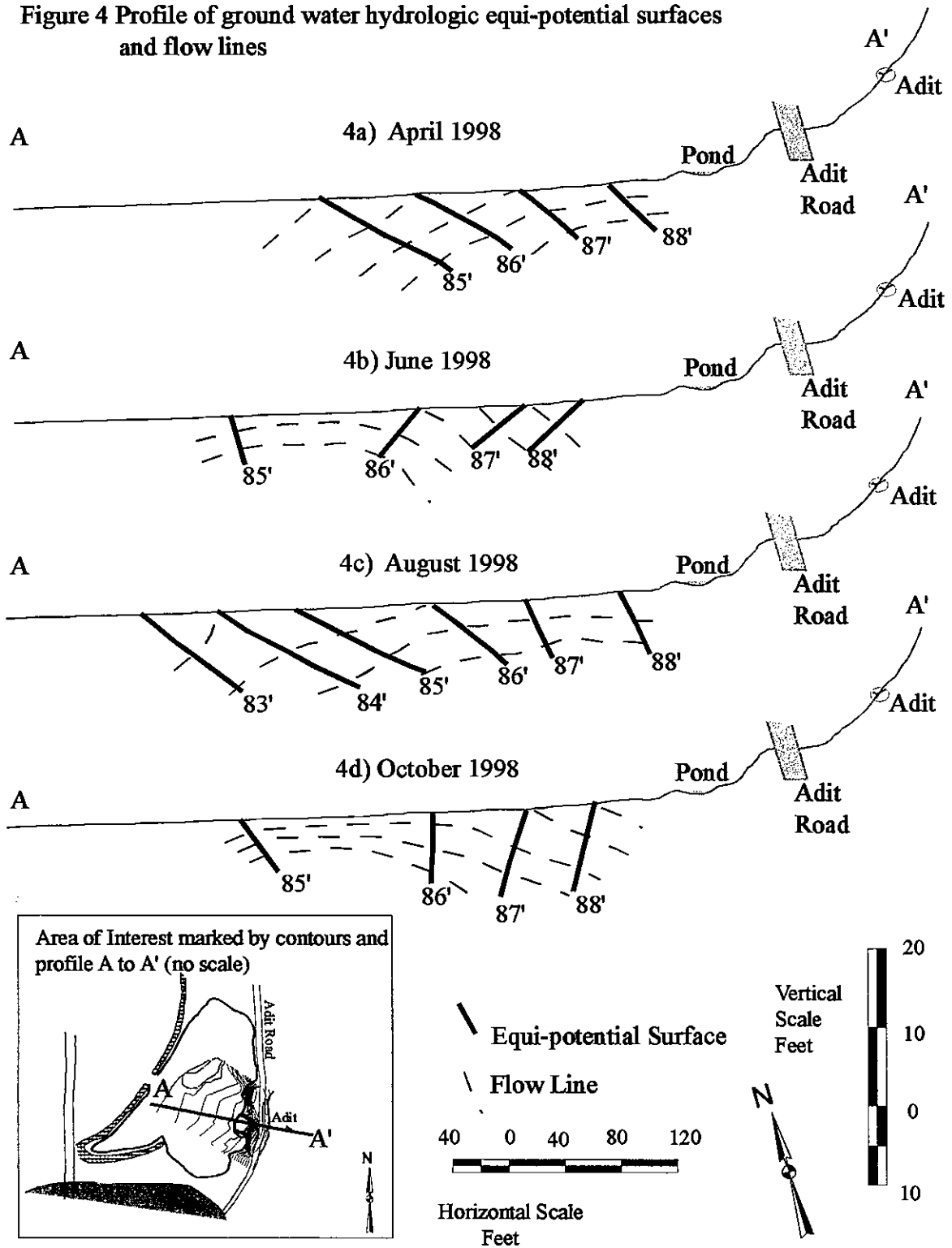


Table 1. Ground water and well elevations (all elevations in feet).

Well	Casing	Ground	Bottom	Screen	Oct-97	Apr-98	Jun-98	Aug-98	Oct-98
FQ1	85.69	84.59	80.01	81.42	81.70		83.51	80.01	80.59
FQ10	84.38	82.08	78.61	80.57	80.62	dry	81.09	80.02	81.89
FQ2D	86.89	85.58	77.87	78.85	78.41		85.77	84.92	85.76
FQ2S	86.89	85.79	82.71	84.15	85.59		85.59	85.51	85.66
FQ3D	88.46	87.54	78.37	79.91	81.54		87.99	87.90	87.75
FQ3S	89.33	87.89	84.89	85.97	87.69		87.78	87.76	87.84
FQ4D	88.58	87.50	78.49	79.51	79.87	87.23	87.15	87.50	87.56
FQ4S	89.09	87.61	84.09	86.45	87.45	87.38	87.39	87.48	87.57
FQ5	87.61	86.35	80.97	83.98	86.07	86.13	86.25	86.17	86.36
FQ5S	87.59	86.51	84.19	86.73	86.24	86.41	86.30	86.34	86.47
FQ6	87.09	85.78	81.15	82.12	81.61	85.48	85.93	85.65	85.69
FQ7D	86.41	85.16	78.14	79.13	78.59		85.12	83.06	85.06
FQ7S	86.15	85.36	81.77	82.49	84.99		85.43	84.67	85.23
FQ8	87.79	86.41	81.82	85.43	86.31		86.99	85.92	86.36
FQ9	87.12	85.84	82.94	83.64	85.81	85.63	85.97	85.74	85.65

Table 2. Sources of metals.

Date	Description	Al	Fe	S	Zn
October 1997					
10/4/97	Adit	1.831	23.691	143.079	0.661
10/5/97	Adit, co-located with FQ0104	1.880	24.023	145.320	0.677
10/19/97	Seep adjacent to collapsed portal	4.062	0.589	202.296	1.353
10/18/97	FQ8	2.024	0.136	60.755	0.451
April 1998					
4/11/98	Adit	1.223	15.576	err	0.514
June 1998					
6/16/98	Adit	1.782	22.719	143.574	0.730
6/16/98	Co-located mine adit	1.827	22.323	156.995	0.622
6/16/98	Seep off the slope in the forest south of system	0.059	0.876	10.879	0.035
6/16/98	Seep hole south of wetland close to wetland	0.157	0.403	126.383	0.039
6/16/98	By slope between wells FQ8 and FQ5S at obvious seep from slope	0.825	0.036	32.329	0.154
6/16/98	Seep beside adit	2.196	3.217	75.592	0.715
6/16/98	FQ8	1.447	0.0433	67.727	0.605
August 1998					
8/12/98	Adit	1.093	15.038	224.727	0.390
8/12/98	Mine Adit (Co-located w/ FQ1002)	1.764	21.179	169.165	0.501
8/12/98	Bottom of east bio-reactor pit	<.015	<.005	229.174	<.001
8/12/98	Seep by adit	3.482	1.272	151.325	1.100
8/12/98	Seep in forest west of wetland	0.076	0.210	7.986	<.001
8/12/98	Wetland Seeps just west of mine dump	0.135	0.383	247.846	<.001
8/12/98	FQ8	0.861	<.005	47.418	0.364
8/13/98	FQ8	1.547	0.106	47.521	0.390
October 1998					
10/10/98	Source of mine drainage above the wetlands at the collapsed adit	0.810	8.665	220.716	0.505
10/10/98	Source of mine drainage above the wetlands at the collapsed adit, co-located	1.192	9.422	232.607	0.526
10/10/98	FQ8	1.287	0.177	71.592	0.795

reactor pit is representative of ground water south of the wetland.

The second step of this objective was to characterize and determine the geochemistry of a sub-alpine wetland. The geochemical environment of the wetland can be described by using the measurements collected in the field. The depth is relative to the thickness of the peat. Figure 5 outlines the structure and geochemical environment within the wetland. The thickness and depth of the geochemical zones varies proportionately with the thickness of the peat. Field measurements used to obtain values for the geochemical environment include pH, dissolved oxygen (DO), alkalinity, and conductivity. Eh measurements were taken, but the method used was inadequate to capture low redox potential. Although Eh values were collected in the field, the values were inconsistent with other measurements and observations.

Field data collected from wells and the surface of the wetland were used to determine the values that describe the geochemical environment. The wells were split into shallow, middle, and deep ranges that correspond to the surface water/peat interface in the peat, peat, and ground water/peat interface in peat respectively. Samples collected from the surface of the peat, excluding ponds, were used to characterize the surface water. The ranges of values were obtained from the annual averages. In the case of the DO of the peat, the median value was used.

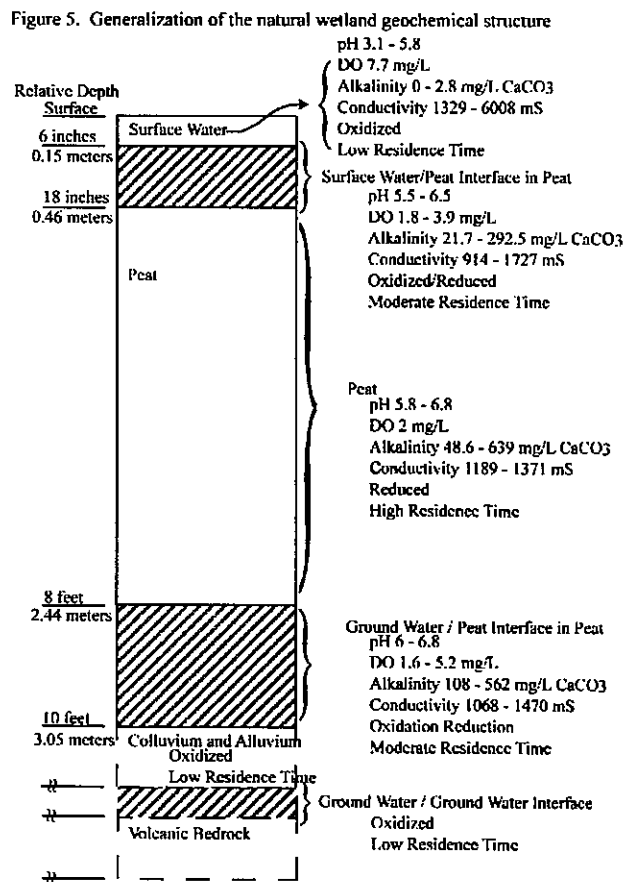
The surface water in Figure 5 includes the water above the surface of the peat and extends to the root zone at a depth of about 6 inches (0.15 m). This water is oxidized and typically has a pH between 3.1 and 5.8. The alkalinity is very low to none, and the conductivity can be as high as 6008 μ S. The water moves horizontally, characteristic of sheet flow, and has a low residence time.

The surface water/peat interface in the peat starts at the top of the root zone and extends to a depth of 18 inches (0.46 m). This water in some places is oxidized and others it is reduced. The pH is typically between 5.5 and 6.5 and has alkalinity between 21.7 and 292.5 mg/L. The conductivity is between 914 and 1727 μ S. The hydraulic conductivity is lower than the surface water and not as low as the peat. The residence time is moderate between the peat and the surface water, and the direction of movement varies over the wetland, but is transitional between horizontal and vertical movement.

The peat section, starting at a depth about 18 inches (0.46 m), extends 6.5 feet (1.98 m) down to a depth of 8 feet (2.44 m). Sulfur reduction occurs in this zone. It may occur in microcosms that have a Eh that is in the range of -250 mV and near a pH of 7. The ground water has an odor of sulfide. The average pH is 5.8 to 6.8. However, in some places the pH was measured above 7.5. The median for the DO was 2 mg/L, the range of conductivity

1189 - 1371 μ S, and the alkalinity 48.6 to 639 mg/L. The ground water flow changes seasonally, but is predominantly horizontal and has a high residence time due to the low permeability of the peat.

The ground water/peat interface in the peat is the zone between the lowest peat and the colluvium and alluvium. In the eastern part of the wetland, seasonally, this 2-foot zone is where the oxidized ground water enters the wetland with an upward vertical gradient. In the western part of the wetland, where the recharge function is dominant, the wetland is perched above the colluvium and alluvium. Mixing between the reduced and oxidized water results in a DO between 1.6 and 5.2 mg/L, an alkalinity between 108 to 562 mg/L, and conductivity 1068 to 1470 μ S. The peat in this zone has a low hydraulic conductivity and moderate residence time.



Distribution of Metals

The distribution of metals, in particular Fe, Al and Zn, in the surface water, ground water, and peat, are closely tied to the hydrology and geochemical environment. The distribution of metals is also related to

the active processes in the wetland. By looking at the distribution of metals within the wetland in both the water and peat the geochemical function can be determined.

Figures 6, 7, and 8 have three components describing the distribution Fe, Al and Zn in a) surface water, b) ground water, and c) peat soil concentrations. Statistically there is more variation in the spatial distribution than the seasonal distribution of metals. The concentrations used for the plots were annual averages in the case of more than one measurement per location, or the single concentration from one sampling event, typical of the soil and some surface water concentrations. More samples were collected in June and August, as there was more surface water. April and October 1997 and October 1998 had limited sampling.

Iron

The distribution of iron in the surface water is closely tied to the main source of iron, the adit. Fe concentration in the water flowing from the adit ranges from 15.58 - 23.86 mg/L. The concentration declines with distance from the adit. As the iron is removed from the surface water by precipitation, mixing with ground water and other surface water dilutes it. There is also a minor source of iron entering the wetland from the north. Figure 6a shows the distribution Fe in the surface water. The distribution of iron in the ground water is also related to the main source of iron, the adit. Iron that makes it to the reduced zone as shown in Figure 6b, becomes soluble (Fe^{2+}) is highly concentrated. The highest concentration measured in well FQ5 was 97 mg/L. During the dry months of the year, the ground water discharge into the wetland is limited. There is opportunity for water from the pond below the adit to discharge high concentrations of iron into the reduced zone of the peat.

As the pH rises above 3.5 and the water is oxidized, the iron precipitates as iron oxyhydroxide ($Fe(OH)_3$). This lowers the pH or produces acidity. However, this concentrates the iron as in the peat soils at the surface as oxyhydroxides. In the interface between the ground water and the peat (Figure 5) the environment is oxygenated and has a pH near and above six, the environment is conducive for precipitating iron as an oxyhydroxide at depth in the peat. The iron oxyhydroxide, may also contribute to iron concentrations in the reduced zone as it slowly moves vertically through the water column. The increased concentration of iron in the lower peat zone may also be elevated due to the precipitation of FeS. Laterally, the concentration of iron in the peat soils also declines with distance from the adit shown on Figure 6c.

Aluminum

The distribution of aluminum in the surface water is closely tied to the main source of aluminum, which is the adit. There is also a significant contribution of Al from seeps and seasonal springs along the base of the slope. During high runoff in the early spring some of the aluminum enters the wetland in the surface water. This surface water is a mixture of ground water from the Animas River Basin that rises above the ground surface and seeps and springs at the base of the slope. Al concentration in the water flowing from the adit ranges from 1.09-1.82 mg/L. The concentration declines with distance from the adit. The decline is closely connected to the pH. The surface water stored in ponds along the periphery of the wetland, typically, has a pH between 3.5 and 4. This keeps Al in solution. Figure 7a shows the distribution Al in the surface water.

The distribution of aluminum in the ground water is related to the sources of aluminum. The cross-section in Figure 7b shows the primary source originating near the adit. The concentration of aluminum in the ground water decreases with distance from the adit. At a depth of 2 feet the ground water concentration in the reduced zone drops off radically.

Where the pH rises above 4 (Martell and Motekaitis 1989), aluminum precipitates as aluminum oxyhydroxide ($Al(OH)_3$). This concentrates the aluminum precipitates in the peat soils. As the vertical gradient is downward in the eastern part of the wetland, the reduced zone of the peat has an elevated concentration of Al. The pH is on the order of 6.5 to 7 and high alkalinity. The maximum accumulation of Al in the soils is located between 1.5 and 4 feet shown on Figure 7c. The maximum concentration of Al in the peat in the reduced zone was measured to be on the order of 14 mg/Kg.

Zinc

The distribution of zinc in the surface water shown on Figure 8a is closely tied to the consistent source of zinc, the adit. Although the concentration of zinc in seasonal seeps, springs, and Animas River is higher than the concentration in the adit, the adit supplies a constant significant load of zinc to the wetland. The concentration of zinc from the adit ranges from 0.39 to 0.73 mg/L. Concentrations of sources other than the adit were measured as high as 1.353 mg/L at the seep adjacent to the adit. FQ8 also showed a significant contribution of zinc. As the hydraulic head in FQ8 is higher than the ground surface during the spring runoff, the zinc entering the wetland is most likely from ground water that may have been in contact with the tailings north of the wetland.

Zn concentration in the surface water around the wetland is typically around 0.3 mg/L. The gradient

Figure 6. The distribution of iron in a) surface water, b) ground water and c) peat

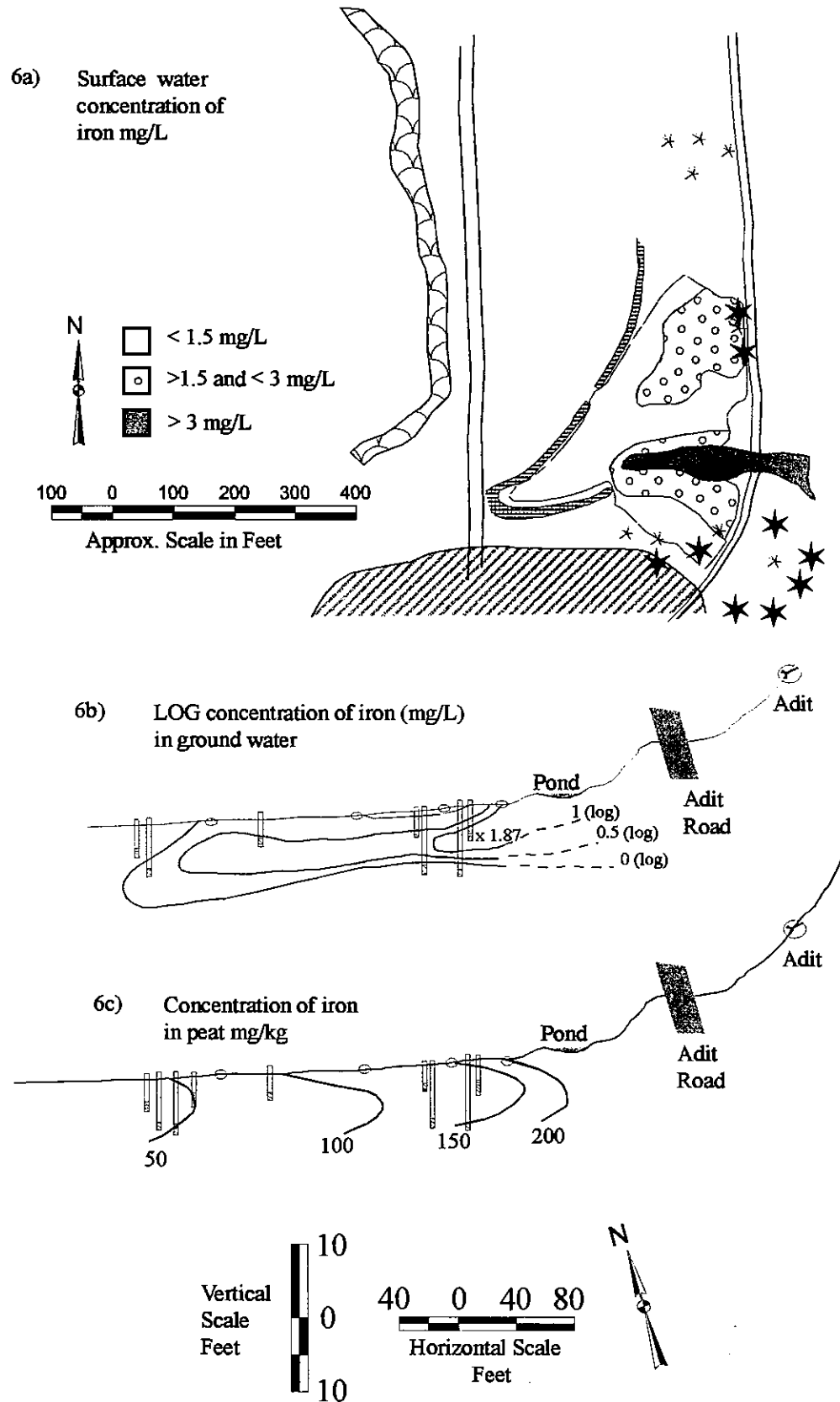


Figure 7. The distribution of aluminum in a) surface water, b) ground water and c) peat

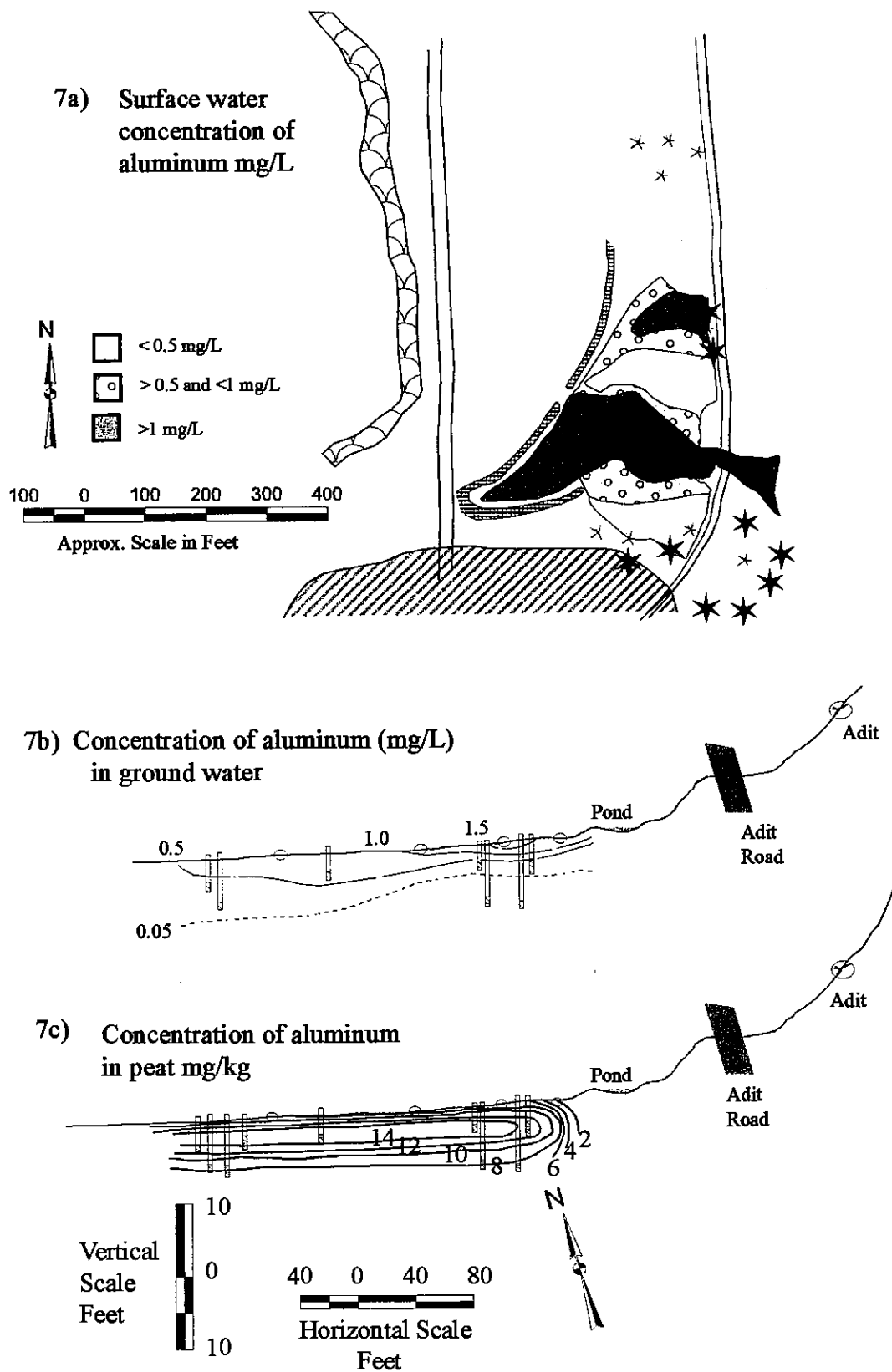
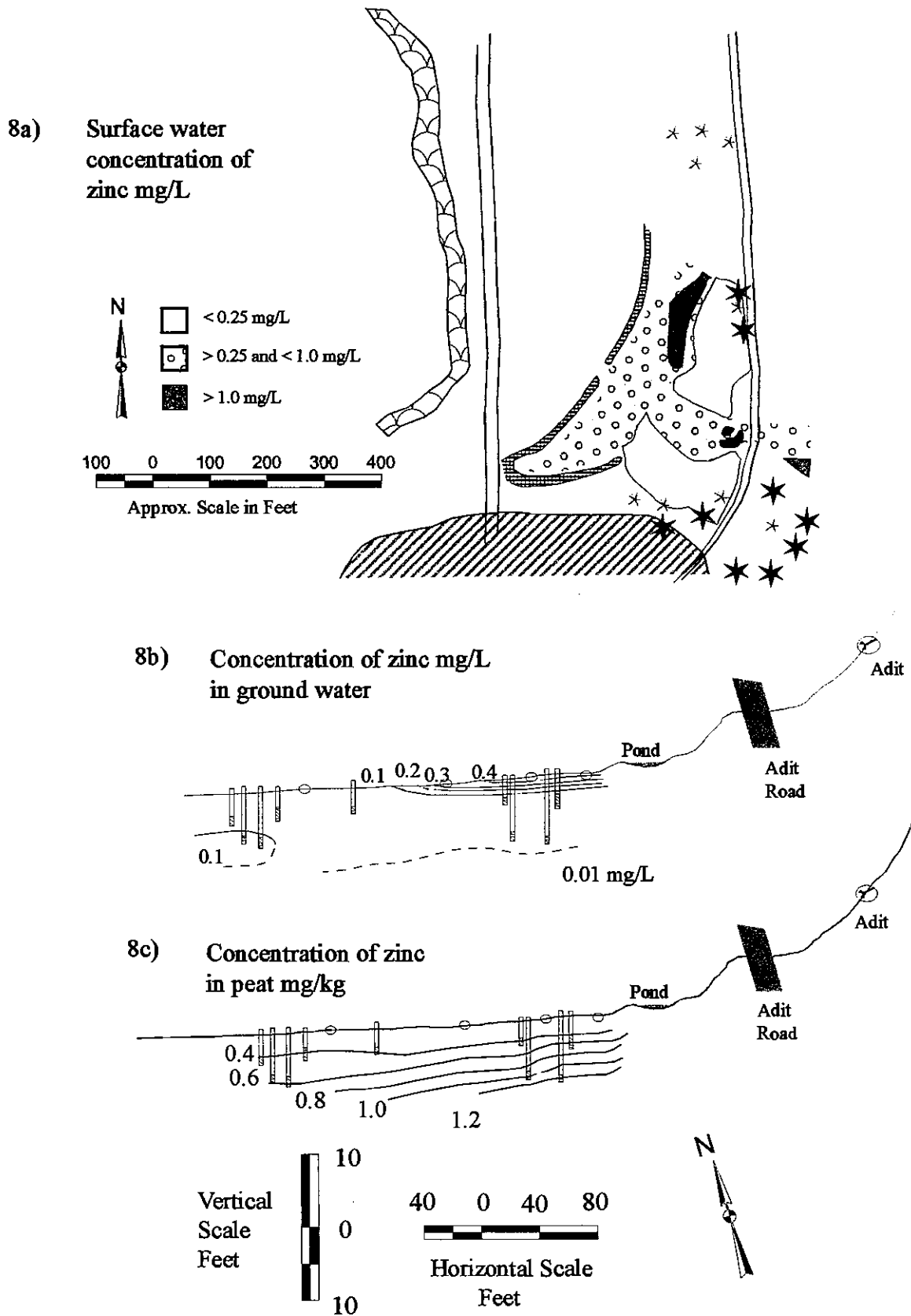


Figure 8 The distribution of zinc in a) surface water, b) ground water and c) peat



declines with distance from the adit, but the additional sources of zinc mix for an average concentration leaving the wetland nearing the same 0.3 mg/L. Some of the seeps and springs north and south of the adit along the base of the slope dilute the concentration of zinc.

The distribution of zinc in the ground water shown on Figure 8b is related to the sources of zinc. The cross-section shows the primary source originating from the adit. The concentration of zinc in the ground water decreases with distance from the adit. There is horizontal layering in the ground water with a steep gradient near a depth of 2 feet. Any deeper and the concentration of zinc in the ground water drops off radically.

The distribution of the concentration of zinc in the peat soil shows a low gradient increase with depth (Figure 8c). The highest concentration measured was 1.36 mg/Kg at the bottom of well FQ4D.

Fate and Transport of Metals

The processes in the wetland that affect the fate and transport of metals are closely tied to the hydrology. The long residence time of the metal laden water allows for sulfate reduction, precipitation and sedimentation of oxides, oxyhydroxide and sulfides, and reactions to proceed (Dvorak et al. 1992; Boto and Patrick 1978).

The low permeable peat layer controls the rate of ground water movement through the wetland. Surface water flows a tortuous path through the thick *Carex* and *Sphagnum* moss. Both processes are conducive for precipitation of oxides, oxyhydroxides, and sulfides. Once the metals are precipitated, their residence time is also extended.

Primarily advective transport then diffusion propagate movement of the metals. The advective transport moves the precipitates or dissolved metals along the hydrologic flow paths. Diffusion moves from high gradient to low gradient, and is a slow process. However, the diffusion gradient is in the same direction as the advective transport.

Finally, cation exchange and adsorption are two processes that can account for minor amounts of metal retention.

By analyzing the spatial distribution of metals and looking at transport mechanisms, we can define locations where metal concentrations change. The changes of concentrations in the distribution of metals (Figures 6-8) give an indication where biological, chemical or hydrological processes are active.

Discussion

The distribution of metals shows significant concentrations within the wetland. This accumulation is a result of both aerobic and anaerobic processes. The major mechanisms involved for removal of metals from

solution includes 1) cation exchange, 2) adsorption, and 3) precipitation of oxides and oxyhydroxides. Cation exchange and adsorption are important for initial metal removal; they potentially have limitations for elements like Fe and Al, which are likely to form insoluble precipitates (Tarutis et al. 1992; Wieder et al. 1988; Henrot and Wieder 1990; Wieder et al. 1990). Cation exchange may only represent a minor contribution to metal retention in wetlands (Wieder et al. 1990; Wieder et al. 1988; Henrot and Wieder 1990). Long-term retention of metals is dependent on the redox profile, and the conversion of oxidized phases in the sediments to the reduced mineral phases at depth during diagenesis (Tarutis et al. 1992; Wieder and Lang 1986). However, for elements less likely to form insoluble inorganic precipitates, such as zinc, retention may be controlled by the interaction with organic matter, including cation exchange (Wieder 1990). A study done by Kolm and others (1998) showed that less than 5% of the heavy metals was partitioned in the plants and the greatest percentage of heavy metals was partitioned in the soil.

The following is a discussion of the accumulation of metals and the processes proposed to account for the metal distribution. The processes are strongly related to the geochemical environment, which is controlled by the redox profile. To understand the redox profile, first an emphasis must be made that the water flows extremely slowly within the peat, and secondly, the production of alkalinity in the reduced zone of the peat affects the production of oxides, oxyhydroxides, and sulfides throughout the wetland. The production of oxides, oxyhydroxides, and sulfides as precipitates are most likely the predominant long-term removal mechanism for Fe, Al and Zn in this wetland.

Alkalinity

The alkalinity generation in this wetland is a very important component for the retention of metals. Alkalinity reduces acidity and adds buffering capacity to the ground water. This is conducive for precipitating oxyhydroxides and raising the residence time for both iron and aluminum.

According to Vile and Wieder (1993) there are three components that contribute to alkalinity generation. 1) abiotic reaction with acid mine drainage with a neutralization substance in the substrate such as CaCO_3 or cation exchange sites to remove protons to decrease acidity or enhance alkalinity, 2) dissimilatory sulfate reduction, and 3) the reduction of ferric oxyhydroxides to Fe^{2+} and result in alkalinity generation by proton consumption or bicarbonate formation. The first component, the abiotic mechanism, is limited. When the neutralizing agents become exhausted or the exchange sites occupied, the acidity is no longer reduced.

In this system there is very little carbonate. However, there is an abundance of iron and sulfur; the median concentration sulfur within the wetland is 190 mg/L. There was no correlation evident between total sulfur concentration and alkalinity, or sulfate and alkalinity.

The median for the alkalinity in the shallow wells runs near 174 mg/L, the deep wells - 194 mg/L, middle wells - 170 mg/L, and the wells along the boundary of the wetland near 11 mg/L. The surface water in and around the wetland including the sources has a median alkalinity of 9 mg/L. Certainly, alkalinity generation is occurring within the wetland. The two microbial facilitated processes sulfate reduction and the reduction of ferric oxyhydroxides are most likely contributing factors.

The process of consuming protons by dissimilatory sulfate reduction or biologically mediated Fe (III) reduction are the predominant processes operating in the Forest Queen and attribute to metal retention (Kalin et al. 1991). The reduction of iron oxyhydroxide and reaction with H₂S generates alkalinity with a net consumption of 8 and 16 protons (Anderson and Schiff 1987). Reduced iron reacting with H₂S to form FeS has no net change in the proton budget (Anderson and Schiff 1987) and can actually produce protons or acidity.

The combination of oxygenated portion of the peat being conducive for the formation of iron oxyhydroxides and the reduction and reaction of iron with sulfate is a potential mechanism for producing large quantities of alkalinity in the Forest Queen Wetland.

Iron

Iron is found in different form in the wetland depending on the redox potential. Ferric iron (Fe III) is dominant in oxidized conditions and ferrous iron (Fe II) is dominant under reduced conditions. Ferric iron can form stable complexes in particular the reddish-brown ferric hydroxide (Fe(OH)₃) which is insoluble and precipitates or remains in suspension (Kadlec and Knight 1996). This is potentially the dominant process occurring at the surface of the wetland. The hypothesis states that the iron would be retained in the surface of the wetland. This process proceeds as long as the pH environment is near and above 3.5, and oxygen is present. This process is thought to be catalyzed by bacteria in the aerobic zone (Wildeman, et al. 1994). However, this process also generates H⁺ depleting alkalinity and lowering the pH.

Cation exchange may affect the iron concentration, but it is most likely not a dominant process for metal retention. Wieder (1990) found that iron retention was similar in peat-based mesocosms with or without Sphagnum or cattails. In these studies he

found that the cation exchange rapidly reached saturation and may represent only a minor contributor to metal retention in wetlands. He also found that oxide formation continued up to saturation of 40 to 200 times the dry weight concentration as the cation exchange capacity. Plant uptake of iron is also limited (Spratt and Wieder 1988).

Fe is highly concentrated in both the reduced zone and the oxidized zone. The concentration of Fe in the reduced water and as oxides in the peat is almost 5 times that as the influent from the adit. The Fe oxides in the peat can contribute to the Fe II concentration in the water indefinitely, because the Fe II is highly soluble. Iron in contact with the reduced sulfur or in the reduced zone is likely FeS. FeS is important for the retention of iron in sulfate reducing environments (Dietz and Unz 1988).

Aluminum

Abiotic processes are responsible for the retention of Al. Whitish precipitates on the surface of the wetland are evidence of aluminum oxide and oxyhydroxide precipitates. These precipitates are present on the surface of the Forest Queen wetland. The contributing factors for aluminum precipitation are the Al³⁺ concentration, pH, and oxygen availability (Wieder et al. 1988).

The alkalinity produced in the reduced zone is evident in the rise of pH. The recharge function of the wetland moves surface water through the reduced zone, where the pH is typically between 6 and 7. The extended residence time of the Al precipitates as an oxyhydroxide effectively removes it from solution and Al is retained within the wetland.

In a study performed by Wieder and others (1988), they found that 50% of the increase of retention between control and impacted peat in man-made sphagnum wetland is accounted for in the cation exchange sites and specific adsorption onto both inorganic and organic sites. Oxide formation contributed to another 33% of total aluminum retention. Because of the size and the charge of Al³⁺, cation exchange and adsorption processes are very effective for removing Al from solution (Wieder et al. 1988; Wieder 1990). The data collected and tested in this study does not differentiate between cation exchange, adsorption, or precipitation, but the discrete processes would be an interesting study.

Zinc

The distribution of Zn in the wetland is closely tied to the surface hydrologic regime. The pH never reaches the value necessary to precipitate zinc as an oxyhydroxide. The majority of the zinc remains in solution and has a low residence time. Two other potential pathways for the removal of zinc include

adsorption and plant uptake (Mitsch and Gosselink 1993; Machemer and Wildeman 1992). Zinc has to compete with iron and aluminum for the adsorption sites. The competition is fierce because both occur at higher concentrations than zinc. Wieder (1990) showed that the maximum capacity and affinity of Zn^{2+} for sites on Sphagnum are equal to Al^{3+} and greater than Fe^{2+} . However, he also showed that the affinity Al^{3+} and Fe^{2+} are both higher than Zn^{2+} . Kolm and others (1998) found that a larger percent of organic matter correlated with the removal of zinc. The process is related to the sorptive capacity of the peat and a large volume of pore space that allows a high volume of water to react with the peat. The adsorption process is important initially, but not as effective long term (Machemer and Wildeman 1992). Because zinc is a required macronutrient for plants, a small amount of zinc is removed by plant uptake.

The recharge function of the peat moves some water through the reduced zone putting a small amount of Zn in contact with reduced sulfur and potentially elemental sulfur where it can form zinc-sulfide. The precipitation of the sulfide mineral dominates the soils chemistry for Zn^{2+} (Evans 1989). The ZnS accumulates in the sediments, but this process is slow and inefficient, and overall not effective for removing high loads of zinc from the surface water (Wildeman, personal communication 1999). The highest concentration of zinc in the sediments was found from FQ4, at a depth between 6.5 and 7.5 feet. The concentration was 1.36 mg/Kg. The highest concentration entering the wetlands was 1.35 mg/L from the seep near the adit.

Conclusions

Hydrological

There is a seasonal fluctuation in the ground water system. However, the ground water system provides discharge to the peatland year-round, which provides a suitable environment for sustaining this ecosystem. The consistent ground water source limits the fluctuation in the geochemical function by maintaining the geochemical environment within the wetland. The predominant flow path in the wetland is horizontal and is maintained year-round. The hydrologic flow is slow, which allows the biogeochemical reactions to maintain their environment. The vertical hydraulic flow is closely related to the hydrologic cycle.

Geochemical

The primary source for metal loading into the wetland is the adit. The concentration of metals decreases with distance from the adit. Geochemical function calculations show that a substantial amount of iron and aluminum are retained in the peatland. While

iron has shown consistent retention by ecosystems, elements such as zinc often show less than half of the amount entering the wetland retained (Giblin 1985). The evidence for the retention of zinc retained in the wetland is marginal. For practical purposes it would be safe to assume that only minor amounts of zinc are retained in the wetland. Identification of the process responsible for the retention of zinc at the Forest Queen Wetland would involve a close comparison of plant uptake, cation exchange, adsorption, and reaction with sulfide.

The distribution shows high concentration of soluble iron in the reduced zone and elevated concentrations in the peat soils near the surface and at depth in the peat. The concentration within the wetland nears 5 times the concentration at the adit and is most likely retained in these areas.

Aluminum has high concentrations along the surface of the wetland and elevated concentrations in the peat soils in the reduced zone. These concentrations are near 3 times the concentration at the adit. The aluminum is most likely retained in these areas.

Elevated concentrations of zinc are not found in the wetland. However, there is a gradient increasing with depth in the wetland. The accumulation of zinc in the soils and water is minor and essentially does not exceed the concentrations from the adit.

References

- Anderson, R.F. and S.L. Schiff. 1987. Alkalinity generation and fate of sulfur in lake sediments. *Can. J. Fish. Aquat. Sci.* 44: 188-193.
<https://doi.org/10.1139/f87-294>
- Boto, K.G. and W.H. Patrick, Jr. 1978. The role of wetlands in the removal of suspended sediments. *Wetland Functions and Values: The State of Our Understanding*, eds. P.E. Greeson, J.R. Clark, and J.E. Clark, American Water Resources Association, Minneapolis, MN: 344-376.
- Dietz, J.M. and R.F. Unz. 1988. Effects of a Sphagnum peat on the quality of a synthetic acidic mine drainage. *Mine Drainage and Surface Mine Reclamation, Proceedings of a Conference in Pittsburgh, Pennsylvania, April 9-12, 1988*, v. 1, Mine Water and Mine Waste: U.S. Bureau of Mines, Information Circular 183: 279-285.
<https://doi.org/10.21000/JASMR88010310>
- Dvorak, D.H., R.S. Hedin, N.M. Edenborn, and N.D. McIntyre, P.E. 1988. Treatment of metal-contaminated water using bacterial sulfate reduction-results from pilot-scale bioreactors. *Biotechnology and Bioengineering* 40: (5) 609-616.
<https://doi.org/10.1002/bit.260400508>

- Evans, L.J. 1989. Chemistry of metal retention by soils. *Environmental Science Technology* 23: (9) 1046-1056.
<https://doi.org/10.1021/es00067a001>
- Giblin, A.E. 1985. Comparisons of the Processes of Elements by Ecosystems, II: Metals. P.J. Godfrey et al. (eds), *Ecological Considerations in Wetlands Treatment of Municipal Wastewaters*. New York: Van Nostrand Reinhold: Chapter 10: 158-179.
- Henrot, J. and R.K. Wieder. 1990. Processes of iron and manganese retention in laboratory peat microcosms subjected to acid mine drainage. *Journal of Environmental Quality* 23: 730-738.
<https://doi.org/10.2134/jeq1990.00472425001900020018x>
- Kadlec, R.H. and R.L. Knight. 1996. *Treatment Wetlands*, CRC Press Lewis Publishers: p. 893.
- Kalin, M., J. Cairns, and R. McCready. 1991. Ecological engineering methods for acid mine drainage treatment of coal wastes. *Resources, Conservation, and Recycling* 5: (2-3) 265-275.
[https://doi.org/10.1016/0921-3449\(91\)90030-R](https://doi.org/10.1016/0921-3449(91)90030-R)
- Kolm, K., R. Harper and J. Emerick. 1998. HGM hydrologic and geochemical functions, Characterization and Functional Assessment of Reference Wetlands in Colorado. Colorado Geological Survey, Denver, Colorado.
- Kolm, K.E. Conceptualization and Characterization of Hydrologic Systems. Research Report GWMI 93-01, International Ground-water Modeling Center, Golden, CO, 1993.
- Machemer, S.D., and T.R. Wildeman. 1992. Adsorption compared with sulfide precipitation as metal removal processes from acid mine drainage in a constructed wetland. *Journal of Contaminant Hydrology* 9: 115-131.
[https://doi.org/10.1016/0169-7722\(92\)90054-I](https://doi.org/10.1016/0169-7722(92)90054-I)
- Mitsch, William J. and James G. Gosselink. *Wetlands*. 2nd Edition, Von Nostrand Reinhold, New York: 1993. pp722.
- Spratt, A.K. and R.K. Wieder. 1988 Growth responses and iron uptake in Sphagnum plants and their relation to acid mine drainage treatment. *Proceedings of a Conference on Mine Drainage and Surface Mine Reclamation, Vol. I: Mine Water and Mine Waste*. U.S. Dep. Inter., Bur. Mines Info. Circ. No. IC-9183: 382-388.
<https://doi.org/10.21000/JASMR88010279>
- Tarutis, W.J. Jr., R.F. Unz, and R.P. Brooks. 1992. Behavior of sedimentary Fe and Mn in a natural wetland receiving acidic mine drainage, Pennsylvania, USA. *Applied Geochemistry* 7: 77-85.
[https://doi.org/10.1016/0883-2927\(92\)90016-V](https://doi.org/10.1016/0883-2927(92)90016-V)
- Vile, M.A. and R.K. Wieder. 1993. Alkalinity generation by Fe (III) reduction versus sulfate reduction in wetlands constructed for acid mine drainage treatment. *Water, Air and Soil Pollution* 69: 425-441.
- Voynick, S.M. *Colorado Gold from the Pike's Peak Rush to the Present*. Mountain Press Publishing Company, Missoula: 1992. pp206.
- Wieder, R.K., G.E. Lang. 1986. Fe, Al, Mn, and S chemistry of Sphagnum peat in four peatlands with different metal and sulfur input. *Water, Air and Soil Pollution* 29: 309-320.
<https://doi.org/10.1007/BF00158762>
- Wieder, R.K., K.P. Heston, E.M. O'Hara. 1988. Aluminum retention in a man-made Sphagnum wetland. *Water, Air and Soil Pollution* 37: 177-191.
- Wieder, R.K. 1990. Metal cation binding to Sphagnum peat and sawdust: relation to wetland treatment of metal polluted waters. *Water, Air and Soil Pollution* 53: 391-400.
- Wieder, R.K., M.N. Linton, and K.P. Heston. 1990. Laboratory mesocosms studies of Fe, Al, Mn, Ca, and Mg dynamics in wetlands exposed to synthetic acid coal mine drainage. *Water, Air and Soil Pollution* 51: 181-196.
<https://doi.org/10.1007/BF00211515>
- Wildeman, T.R., G. Brodie, and J.J. Gusek. 1993. *Wetland Design for Mining Operations*, Richmond, B.C: BiTech Publishers: 408.
- Wildeman, T.R., L.A. Duggan, D.M. Updegraff, and J.C. Emerick. 1993. The role of macrophytes and algae in the removal of metal contaminants in wetland processes. 86th Annual Meeting of the Air and Waste Management Association, June 1993, Denver, Colorado.
- Wildeman, T.R., D.M. Updegraff, J.S. Reynolds, and J.L. Bolis. 1994. Passive Bioremediation of Metals from Water using Reactors or Constructed Wetlands. J.L. Means and R.E. Hinchee (eds.) *Emerging Technology for Bioremediation of Metals*, Lewis Publishers: Boca Raton, Florida: 13-24.