

Toxic Metals Removal in Acid Mine Drainage Treatment Wetlands

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Abstract

The removal of trace metals from acid mine drainage was studied in four constructed wetlands on abandoned mine lands in southwestern Indiana. The wetlands vary in the constraints of their settings, their design, the materials used in their construction, and their effectiveness at removing metals. Aqueous and sediment samples were collected twice a year at each of sixteen sampling locations. Water, pore water, and sediment extracts were analyzed for their physicochemical characteristics, major ions, and the trace metals arsenic, beryllium, boron, cadmium, chromium, copper, lead, molybdenum, nickel, selenium, and vanadium. A simplified sequential extraction was used to distinguish between bio-available and residual metals. The relative distributions of metals between the bio-available and residual fractions were compared with one another in order to determine the factors which control precipitation, sorption, and mineralization of trace metals, and assess their potential mobility. Data representing late winter and late summer conditions were compared to identify seasonal differences in metals concentrations in the various wetland cells. The overall percentage of major metals removed from the AMD was determined. The Aquachem computer program was used to generate a diagram of the prevalent chemical character of the wetlands waters and to introduce data to a water chemistry modeling program, PhreeqC. The PhreeqC program determined saturation indices for mineral phases in water entering and leaving the wetlands. The water and sediment metals values were compared with published criteria for water and sediment quality.

Introduction

Acid mine drainage

The oxidation of pyritic materials is the primary source of acidity in disturbed mine lands. Coal beds throughout the midwestern United States contain several percent pyritic sulfur in the form of fine crystals which rapidly oxidize in the presence of water and oxygen (Langmuir, 1997). Above pH 4.0 the ferrous iron spontaneously oxidizes to ferric iron, which in turn reacts with water to release three hydrogen ions for every ferric ion reacted, driving the pH further down. When the pH is below 3.0, iron-oxidizing bacteria such as *Thiobacillus ferrooxidans* thrive, rapidly converting ferrous iron to ferric iron, producing additional acidity.

The presence of calcareous rock can help abate the acidity of acidic drainage; however, the production of alkalinity is limited by the solubility of the carbonate rock. In contrast, the oxidation of pyritic materials initiates a cascade of acidity-producing reactions; in a typical natural setting, pyritic material can yield several orders of magnitude more acidity than the calcareous material can neutralize by dissolution (ATEC, 1984). When the materials are mixed together, the maximum alkalinity is quickly achieved and exhausted, whereas the iron and sulfur oxidation continues, causing acidity to increase over time. Although calcium carbonate can temporarily stabilize pyrite by inhibiting oxidation or neutralizing its acidity, once the carbonate has leached away or reacted, the pyrite once again becomes unstable.

The quality of water draining from mine lands is also influenced by overburden chemistry, the hydrology of the setting, the length of time between flushing by rain or thaws, the chemistry of the ground water, microbial activity, and the method of mining employed at the site. The changing dynamics over time mean that a simple balance of the amount of alkaline material and acid-generating material will not accurately predict the amount of acidity a site will

generate. In order to gain long-term control over these unfavorable dynamics, it is necessary to intervene by installing remedial measures.

While the tendency of a site to generate uncontrolled acidity is a problem in and of itself, another water quality issue arises from the burden of toxic metals present in the acid mine drainage (AMD). These metals either originate in the parent rock or are leached from other materials that the acidic water encounters on the site. Acidic water picks up metals either by direct dissolution of minerals or by cation exchange. Cation exchange involves the replacement of metal ions that are bound to charged surfaces with hydrogen ions (protons). Hydrogen ions have a stronger affinity for a charged surface than have the larger radius metal ions.

Raising the pH toward neutrality causes metals to precipitate from solution; so, to a large degree, treating water to remove acidity will significantly lower its burden of dissolved metals. Moreover, dissolved iron and manganese react with water to generate what is termed “mineral acidity;” precipitating these metals lowers the water’s overall potential acidity.

Acid mine drainage treatment wetlands

Of the methods available for treatment of AMD, passive designs are preferred because they do not require continuous maintenance. Among the passive designs, treatment wetlands have emerged as the only practical option for long-term treatment of acid mine drainage (McCleary and Keppler, 1994).

In order to address the problem of AMD originating in abandoned mine lands, the Indiana Department of Natural Resources Division of Reclamation has constructed several AMD treatment wetlands. These wetlands represent site-specific applications of the established scientific and engineering principles published by the U.S. Bureau of Mines (Bureau of Mines, 1994); (Hedin and Nairn, 1992). Passive mine drainage treatment systems are usually selected and sized according to a multi-step model proposed by the Bureau of Mines.

The first step is the chemical characterization of the AMD and the measurement of its flow. The second is to classify the water as net alkaline or net acidic. In order for water to be classified as net alkaline there must be at least 1.8 mg/l of alkalinity for every 1 mg/l of dissolved iron. In general the pH must exceed 6 or the oxidation of ferrous iron will be slow. Net alkaline mine water is treated by aeration to enhance metal oxidation processes. The most appropriate treatment structure to achieve oxidation and settling is the aerobic wetland.

Water classified as net acidic must be rendered alkaline before treatment will be successful. This is because oxidation drives the precipitation of metals, and the oxidation reaction rates decrease as much as one hundredfold per unit drop in pH (Behum and Kim, 1999, p.7). Alkalinity buffers mineral acidity, allowing pH to remain in a range where metal precipitation is possible. If alkalinity is to be introduced using some solid medium such as limestone, contact with the alkalinity source should take place before the AMD is exposed to air because the reaction of metals with oxygen causes rapid precipitation which armors solid surfaces, preventing any further dissolution of the alkaline material. To prevent this, alkalinity-generating structures are placed as early in the treatment sequence as possible. These may consist of anoxic limestone drains, compost wetlands, successive alkalinity producing systems, limestone ponds, or concentrated alkaline recharge pits (Behum and Kim, 1999, p. 26).

The type of treatment structure and its size is determined from the flow data and the water chemistry. The chemical parameters of the greatest importance are the acidity, alkalinity, dissolved oxygen, iron, and aluminum levels. If the acidity is not exceptionally high and there is

very little dissolved oxygen in the AMD, then a compact structure such as an anoxic limestone drain (ALD) will suffice to produce the initial alkalinity. However, if aluminum levels are high, an ALD should be avoided, since aluminum will precipitate as the pH approaches neutrality, plugging the drain. In general, if the AMD is too acidic or if it contains too much ferric iron, aluminum, or dissolved oxygen, the situation calls for a compost wetland as a means of introducing alkalinity.

Once a means of introducing alkalinity has been established, the later stages of treatment generally provide for aeration and the collection and storage of precipitated metals. Ultimately the amount of metals removed depends upon the chemical composition of the AMD, the presence of active microbes, the surface area of the wetland, and the retention time of the water in the wetland (Behum and Kim, 1999, p. 55).

The fate of trace metals in AMD treatment wetlands

Trace metals in solution seldom precipitate directly because their concentrations are so low that they are far below their saturation point. To some extent, these metals do tend to co-precipitate when the most abundant dissolved species, such as iron, coalesce into solid phases and fall from solution. However, the chemistry of trace metals is complex. The behavior of each of these elements is determined by its solubility, valence state, uptake by organisms, tendency to form complexes with other substances, and affinity for the solid phases formed from the precipitation of the major elements (Freeze and Cherry, 1979, p. 420). Even after the major acid-producing elements such as iron have precipitated and the pH of the AMD has improved, enough trace metals may remain in solution to impair the water quality. Some trace metals are considered toxic at very low levels and while dilution alone might allow certain types of AMD to meet general water quality guidelines for sulfate, total dissolved solids, or pH, the water may still exceed the guidelines for one or more regulated metals. In order to meet all treatment goals, it is usually necessary to design the AMD remediation structures so that they not only reduce the acidity and improve the pH of the water, but also provide for the adequate removal and storage of metals on the site.

Sediments formed in AMD treatment wetlands serve as a sink for potentially toxic metals; they may also serve as a source if conditions change sufficiently to make them available for dissolution and biological activity (Chapman and others, 1999). The ability of sediments to become a source of metals is expressed in terms of the metal's "availability," that is, the extent to which it may be taken up by organisms or transported from the site. Although specific routes of diffusion, active or passive transport, biogeochemical cycling, uptake, and dispersion are difficult to assess, a basic distinction can be made between available and unavailable metals based upon the tightness of a metal's bond to the other materials in the sediment. If a metal is so tightly bound to another substance that it cannot be freed even under the harshest conditions it is likely to encounter within its natural setting, then it can be considered unavailable. The strength of the bond holding a particular element to solid phase material can be determined empirically by subjecting sediment to a series of increasingly severe solvents. This procedure, known as "sequential extraction," can separate the fraction of metal that has been permanently fixed in a mineral phase from the fraction which is more loosely bound to sediment surfaces. The distribution of metals between the available and unavailable fractions is useful in determining to what extent remedial efforts are likely to achieve long-term as well as short-term treatment goals. The true effectiveness of AMD treatment cannot be known without addressing the issue of toxic

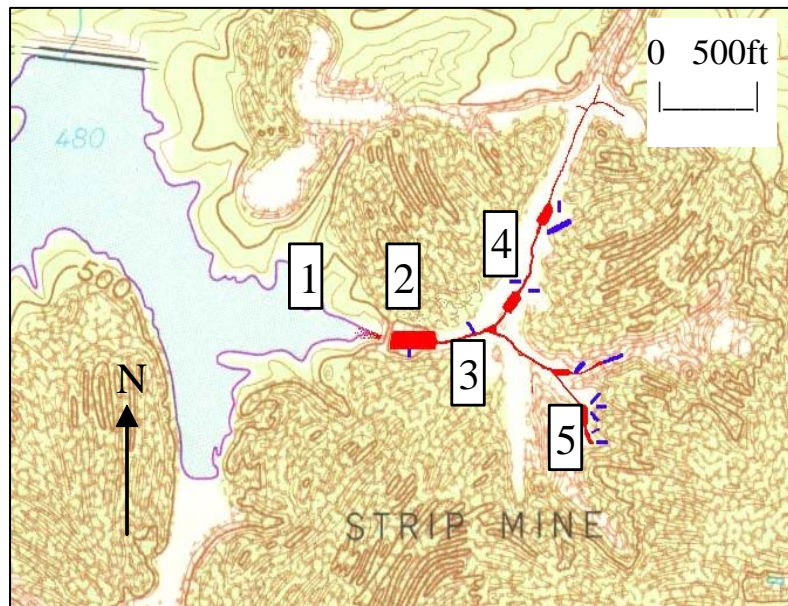
metals availability.

Study areas

Augusta Lake

Augusta Lake is located in Section 15 of Township 2S and Range 7W in Pike County, Indiana, within a 6,000-acre tract of land designated the Mill Creek Abandoned Mine Land Area. The eastern and southern boundary of the Augusta Lake drainage basin are associated with the eastern boundary of the Springfield coal field (ATEC, 1984). The ground-water divide follows a structural contour at 530-ft elevation separating the Mill Creek drainage system, in which the lake lies, from the Midwestern drainage area to the southeast. The entire basin has been disturbed by surface and underground mining and was identified as a source of AMD as early as 1949. The surface features within the study area are composed entirely of rock refuse from the Dugger Formation, and the bed of Augusta Lake is in contact with the Springfield (V) Coal Member. Augusta Lake discharges highly acidic water northward into Mill Creek and the Patoka River. Gob piles, spoil ridges, and abandoned underground mines to the east and northeast have been found to be major sources of acidity, sulfate, iron, and manganese in the lake (Comer and others, 2000).

Figure 1. Map showing Augusta Lake wetland sampling points. Drainage channels, ponds, and the successive alkalinity producing system are indicated by red lines, and anoxic limestone drains are portrayed in blue. Sample locations are (1) Lake inlet, (2) SAPS Pond, (3) Pond PD-1, (4) Pond PC-1, (5) Southeast Drain.



Augusta Lake wetland (Figure 1) is a multi-celled system consisting of a series of fifteen anoxic limestone drains (ALDs) which intercept seeps originating from spoil ridges and at least one outflow from an abandoned underground mine located to the south. The ALDs vary in size from about six by fifty ft. to two or three times this size. The anoxic limestone drains discharge into wetland oxidation ponds and *Typha* (cattail) wetlands before the flows merge into a single stream which feeds into a successive alkalinity

producing system (SAPS). The SAPS is forty by one hundred forty ft. long, and six segments of perforated PVC pipe are embedded in its base. Acid mine drainage is meant to percolate through a submerged bed comprising 2-inch crushed limestone on the bottom, a 2-ft. layer of lime-stabilized compost above, and 6 inches of wood waste and sewage sludge on top. In the bottom layer of crushed limestone, the AMD is collected by the PVC pipes and conveyed to a 4-inch pipe which discharges beneath the spillway. The majority of the AMD flows over the spillway and mixes with the treated water in a *Typha* wetland below before entering the easternmost arm of Augusta Lake.

The Augusta Lake system of scattered wetlands was sampled at five locations on February 28, 2000. Sampling points were: (1) oxidation Pond PC-1, which drains the problematic northern spoils deposits; (2) the combined flow from the northern, central and southern tributaries at Pond PD-1; (3) the water at the SAPS spillway, named SAPS Pond; and (4) the wetland below the SAPS at its confluence with Augusta Lake, a sample named "Lake Inlet."

A prior study indicated that levels of aluminum as high as 76 parts per million were present in drainage throughout the upper portion of the watershed (Comer and others, 2000). It is the opinion of Bill McCoy, the site manager, that aluminum has precipitated inside the ALDs causing them to become plugged, no longer generating alkalinity. Without alkalinity, the wetland system was unable to improve the quality of the basin's drainage.

Analysis of the February 2000 samples indicated that there was little difference in the chemistry of the water flowing from the northeastern portion of the watershed and the water which entered Augusta Lake at the downstream end of the drainage system. Consequently, the uppermost sampling points were moved to the southeastern watershed where prior work had established the presence of some alkalinity. The move was intended to gather information on the shortage of alkalinity throughout the system by observing the fate of the alkaline waters present in this part of the watershed at Pond PC-2 and Pond PB. In an effort to determine why metals are not precipitating completely before leaving the system, the lake inlet sampling point was replaced by a sample named "Mixing Zone" taken at the point where the water which percolates through the SAPS mixes with water which flows over the weir.

Midwestern reclamation site

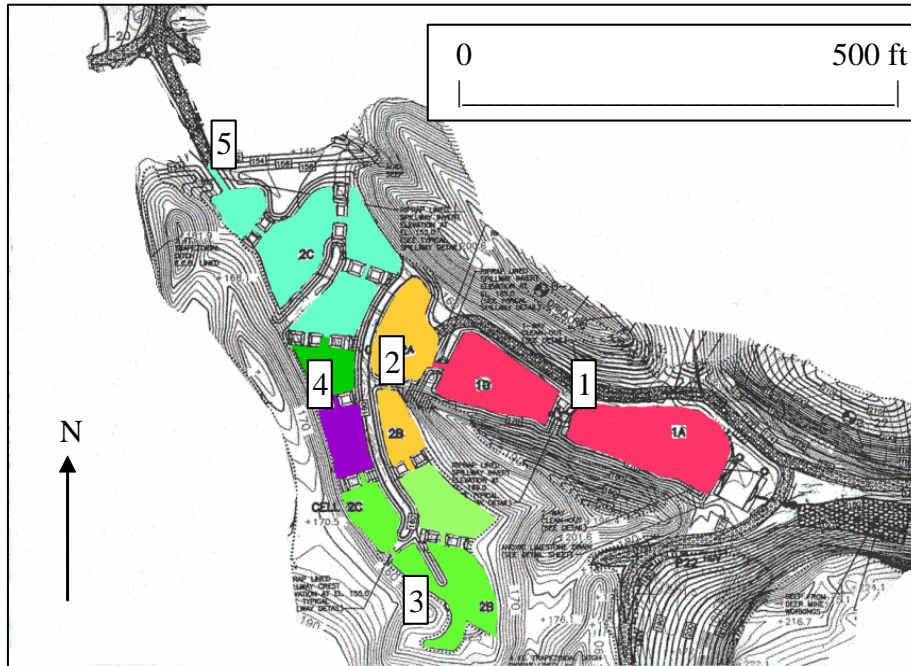
The Midwestern reclamation site wetland (Figure 2) is located north of State Highway 64 in the southern portion of Reclamation Site 1087 (Midwestern) southeast of the Augusta Lake watershed. It lies entirely within Sections 22 and 27 of Township 2S and Range 7W in Pike County, Indiana. Site 1087 consists of about 550 acres of surface-mined land that adjoins and, in some cases, intersects deep mine workings in the same coal seam (Bryenton, 1994, p. 6). Although the central portion of Midwestern was regraded during the 1995 reclamation work, in this part of the site vegetated spoil ridges and gob piles remain that discharge acidic drainage. Most of the lower wetland formerly consisted of an acidic pond that was drained prior to its bed being sealed with stabilized fly ash. Berms and baffles were constructed of mine spoil and baffle spillways were lined with riprap.

The primary source of AMD at this site has been intercepted beneath the surface and directed into a large ALD. The outlet drains into a compost wetland designated Cell 1A, which is composed of a mixture of 4 parts manure to 1 part hay by weight with 10 percent lime added. The surface of the cell is covered with a layer of pea gravel and a standpipe has been set to maintain the water level beneath the surface level of the cell, creating anaerobic conditions. The cell is sparsely vegetated with *Typha*. Water emitted from the standpipe is aerated in a steep riprap channel, then enters Cell 1B, an oxidation pond containing the same manure and hay substrate. The level in Cell 1B is kept constant by a riser and is about 40 percent vegetated with *Typha*. Its effluent flows through a series of shallow cells which contain an organic substrate of 3 parts soil to 1 part turkey manure and which maintain healthy stands of *Typha*. These cells were constructed over a base of coal fly ash (Bryenton, 1994, p. 6).

At Cell 2C2 the substrate was changed to a mixture of 70 percent wood chip compost and

30 percent fixated sewage sludge and lime placed over a base of ash. The final three cell chambers received the soil and manure substrate, with a higher ratio of turkey manure to soil than in the initial cells.

Figure 2. Midwestern wetland. AMD enters red cells from the right. Red cells contain 4:1 manure/hay; yellow contain 3:1 soil/manure, green contain 3:1 soil/manure mix over an ash base, purple contains municipal sludge with ash base, and aqua contain 2.5:1 or 2:1 soil/manure mix without an ash base.



Cells 2C5 and 2C6 received a soil to turkey manure ratio of 2 to 1 and the final cell, Cell 2C7, received a ratio of 1.5 parts soil to 1 part manure. These higher ratios of turkey manure content inhibited the establishment of vegetation in the final cells for the first two years of operation. During this period, vegetation did not grow on the substrate itself, but only along the

edges of the cells. At present, *Typha* is established throughout all of the wetland where the water depth is less than 2 feet. The wetland apparently is successful, as iron oxidation and precipitation is evident in the upper cells, vegetation predominates, and wildlife, including frogs, are plentiful.

The sampling locations chosen were: (1) the discharge from the Cell 1A standpipe into the oxidation pond, called Cell 1A; (2) the baffle between Cell 2A and 2B, known as Cell 2A; (3) Cell 2B3, where an intermittent seep enters the system; (4) Cell 2C3, downstream from the wood chip and sewage sludge substrate; (5) the effluent from the final treatment cell, called the outlet.

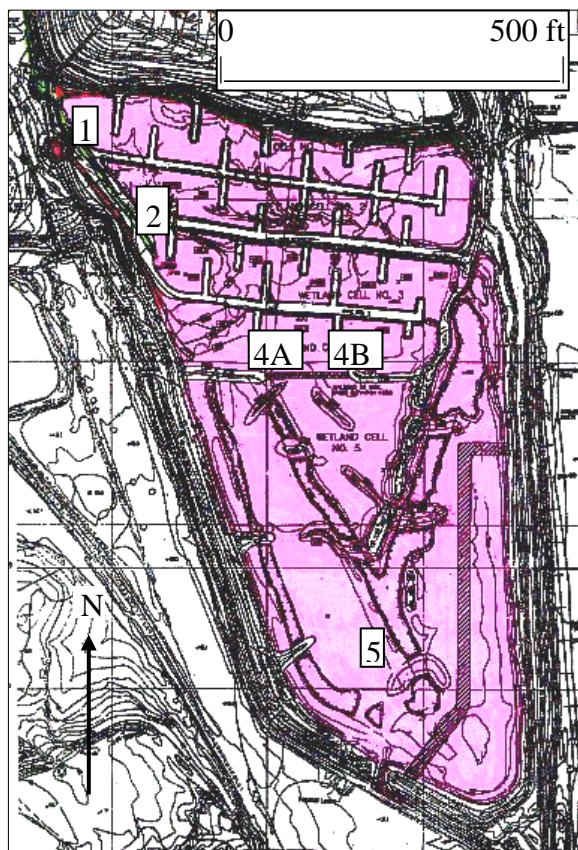
An effort was made to sample the upper part of Cell 1A where the ALD discharges by digging a hole in the pea gravel and allowing the water to settle. The sediment here consisted of a thin coating of iron precipitate on pea gravel. It was too difficult to separate this layer from the gravel and was impossible to obtain an interstitial water sample from the thin layer of iron oxide, therefore, this sampling point was abandoned.

Tecumseh reclaimed mine land

The Tecumseh wetland occupies the site of the abandoned Tecumseh Mine and coal processing plant in R7W, T4S, Owen Township Section 17, Warrick County, Indiana. The site is marked by a broad, gently contoured mound of spoil and gob and low-lying tailings situated just to the east of a series of flooded mine pits. A perennial stream known as Barren Fork has been diverted to the east by the presence of the main refuse mound. To the west of the pond are

acid seeps originating in the abandoned tailing ponds, some smaller spoil ridges, and perhaps subsurface flow from the nearby flooded pits. Since the broad, graded hill of spoil materials is situated in the flood plain of Barren Fork, the hill has served as an impoundment creating a lake upstream. Though surface drainage flows both east and west of the mound, water also seeps from the downgradient edge of the mound, creating at least four acid seeps that were identified in pre-reclamation surveys.

Figure 3. Map of Tecumseh wetland (pink area) showing sample sites designated according to cell number.



The DNR constructed an AMD treatment wetland in the broad flood plain below the Tecumseh spoil hill. The former bed of Barren Fork was incorporated into the largest wetland cell and a dike was built to divert the stream around the periphery of the wetland. Fresh water is introduced from the northwest along the western edge of the gob pile and directed to flow laterally along the toe of the hill to collect AMD from the seeps. Anoxic limestone drains have been installed within the main hill to intercept the seeps and these drains discharge at several points along wetland Cell 1. The combined flow follows a serpentine path around a sequence of baffles directing it back and forth across the area of the first three cells. Acid mine drainage from the tailings and spoil to the west is channeled through a riprap-lined ditch and introduced in a controlled manner into treatment Cell 4. The AMD flows through Cell 4 along a berm and then discharges across a long railroad tie weir into Cell 5. Flow from the upper wetland also enters Cell 5 along the opposite end of the weir. The bottom of this very large final cell has been sloped to drain and

contains a number of islands and other structures to baffle flow.

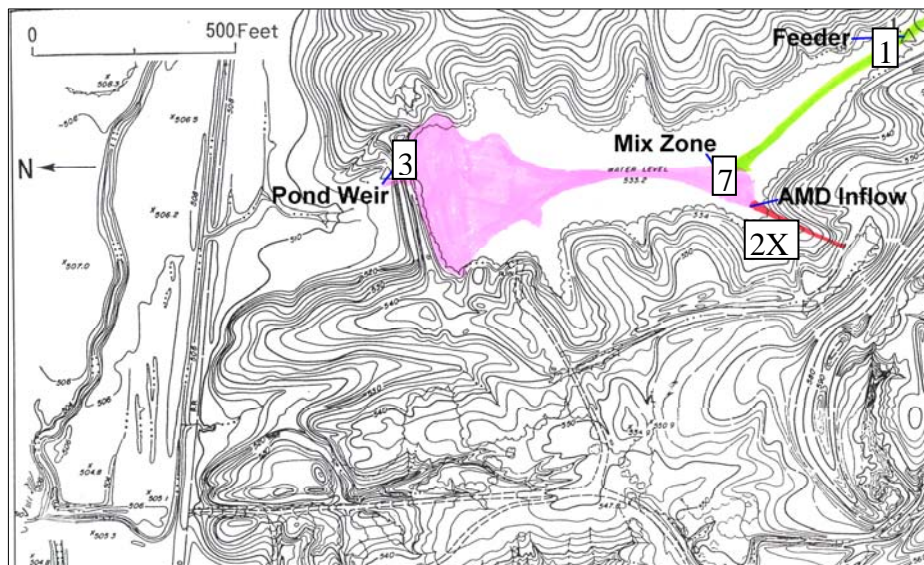
The base of the treatment cells consists of a bottom layer of sand covered with a 1 foot layer of turkey manure compost over which the water flows. The turkey manure compost consisted of a mixture of 3 parts soil to 1 part turkey manure. Agricultural lime was applied as well at a concentration of 200 tons per acre. The upper four treatment cells are shallow and support dense stands of *Typha*; however, the water in much of Cell 5 exceeds 2 feet in depth and *Typha* can be found only along the bank. The effluent at the end of the wetland remains somewhat acidic.

The wetland was sampled at the following points: (1) Cell 1, the fresh water supply near the base of the dam; (2) Cell 2, the outlet from the second wetland cell; (3) Cell 4A, the AMD flowing along the western berm of treatment Cell 4; (4) Cell 4B, the effluent from the upper wetland from the eastern side of Cell 4; (5) Cell 5, the outfall from the wetland. The Cell 1 sampling point was determined to contain AMD as well as fresh water and was abandoned.

Friar Tuck reclamation site

The Friar Tuck site is located northeast of Dugger, Indiana, in T8N, R7W, Wright Township Section 31, Greene County. The wetland (Figure 4) occupies the bed of an artificial lake whose dam was breached after its water became too acidic to support aquatic life. Formerly, extensive surface and underground mines, a power plant and a coal processing plant were operated on the property. Four coal beds were mined in the past; the spoil was heaped in a series of steep ridges and a large gob pile was created on the southeast part of the site. During the preceding decades, these features were directly revegetated with pine trees. The southeast gob pile stores a large volume of acidic water which seeps from the toe of a smaller spoil ridge into the study area. Until recently this water was retained by a berm and diverted along a backslope perimeter drain into a containment area informally known as Oxblood Pond. During the years when the AMD was diverted, a wetland of *Typha* and *Phragmites* became established in the former lake bed. To the north of the gob pile there is a flooded underground mine void which may feed into the wetland during times of elevated water levels. The mixing of water from sources, including this mine void, results in the formation of suspended precipitates which sometimes can be observed in the pond above the reconstructed dam.

Figure 4. Map of Friar Tuck wetland depicting fresh water as green and AMD as pink.



The primary source of fresh water for the wetland follows a drainage channel that enters the former lake bed from reclaimed land south of the site. In 1998, after the vegetation was established in the former lake bed, the dam was reconstructed, raising the water level to an elevation several feet

lower than that of the original lake. A long channel lined with limestone riprap was constructed to carry AMD from Oxblood Pond to the central part of the lake bed where it could mix with the fresh water stream, and then Oxblood Pond was breached. The AMD entering the wetland from this breached pool is severely acidic, but its flow is relatively low. Though prior studies have indicated that the water at the dam and spillway remains somewhat acidic, (pH~5), there is considerable use of the water by aquatic and terrestrial animals. A beaver dam situated atop the spillway has raised the surface level of the impounded water by approximately 18 inches. The effluent from the wetland flows through a long channel eroded through an expanse of bottom land before entering Mud Creek, which flows westward along the northern edge of the Friar Tuck Reclamation Site.

The Friar Tuck wetland was sampled at these points: (1) the alkalinity-bearing stream where it enters the wetland; (2X) the major AMD seep issuing from the base of the southeast gob deposit at the discharge point of the rip rap channel; (3) the wetland pond at the discharge weir of the reconstructed dam; (7) the zone where acidic and alkaline waters mix and precipitation mechanisms can be observed. In order to avoid confusion with the sampling sites designated during a prior study, the numbers 4,5 and 6 were omitted when naming samples.

Experimental

Reagents and labware

Only certified reference materials, trace metal grade reagents, and Class A labware were used to prepare samples for analysis. Barnstead Nanopure 18 Mega-Ohm de-ionized water was used to prepare standards, blanks, and sample dilutions. The nitric acid used in sample preservation, standard preparation, and precleaning was “Baker Instra-analyzed.” Hydrochloric acid extraction solution was prepared by diluting Fisher Certified ACS Plus acid to 1 Normal strength. Ammonium oxalate/oxalic acid extraction solution (0.175 M ammonium oxalate with 0.1 M oxalic acid) was prepared from ammonium oxalate monohydrate and oxalic acid dihydrate, both “Baker Analyzed.” A method blank of this extractant was carried through with the samples. The hydrogen peroxide used was Fisher ACS Certified 30 percent. All labware used in sample preparation was washed in Micro detergent, triple rinsed with de-ionized water, soaked in 7 percent reagent grade nitric acid and triple rinsed with Barnstead ultra-pure water. All standards were prepared from J.T. Baker Instra-analyzed ICP or AA grade-certified standard solutions. Sample bottles and jars were pre-cleaned I-Chem 300 Series HDPE containers which exceed all U.S. EPA analyte specifications.

Sampling and sample preservation

Field measurements were taken at each location prior to sampling so that the readings would not be influenced by sampling activities. Water samples were collected in precleaned 1-liter polyethylene bottles with Teflon-lined caps. The samples were collected at a depth approximately 10 inches below the water surface, as close as possible to the exit point of the wetland cell being sampled. Sediment samples were collected at the same locations using either a wooden spatula or a plastic scoop to transfer the surficial sediment layer into a pre-cleaned wide-mouth 500-ml polyethylene jar with a Teflon-lined cap. The remainder of the container was filled to the top from the water column above the sampling spot, and the lid was replaced while the jar remained immersed so that all air was excluded from the sample container. All samples were immediately placed in coolers precooled with cold-packs. Filtration of water samples took place as soon as possible after sampling, always within the initial 8 hours after collection. Alkalinity determinations were performed immediately after filtration. Aliquots of filtered water for metals analysis were acidified to below pH 2 directly after filtration. All water sample aliquots and sediment samples were preserved by refrigeration at 45 degrees Fahrenheit prior to extraction and analysis.

Sequential extraction of sediments

Sediment samples were extracted as soon as possible after collection. The chemistry of the sediments, including the distribution of metals among the various physical phases, changes rapidly when the sediment is brought from an anoxic to an aerobic environment. Because of this, the samples were prepared while wet so that exposure to air would be minimal. Prior to removing a subsample, the supernatant water was decanted from each sample into a precleaned, acid washed 400-milliliter glass beaker so that after sampling the liquid could be returned and the jar resealed in case further sub-sampling should prove necessary. The jar of sediment was thoroughly stirred using a wooden spatula then a 2 gram-portion of wet sediment was transferred to a dry, preweighed evaporating dish for total solids determination using Standard Methods 16th Edition, Method 209 A (APHA, 1985). Immediately after the removal of the aliquot for total solids, from 3 to 4 grams of the sediment was placed in a preweighed, acid-washed 100-milliliter Teflon beaker. A Teflon stir bar was added along with 45 milliliters of ammonium oxalate/oxalic acid extractant. The sample was stirred and the pH was checked to ensure that the extraction would take place at pH 3.0 or below. Any sample solution exceeding this pH was acidified to pH 3.0 or below using 1 N HCl. A Teflon watch glass was placed on top of the beaker and the solution was magnetically stirred for 2 hours. The impingement of direct light upon the solution has been shown to alter the efficiency of the extraction, so although Teflon-ware is somewhat opaque, ambient light in the work area was maintained at a low level.

At the end of the extraction period, the solution was decanted into a clean centrifuge tube. The sediment remaining in the beaker was rinsed with ultra-pure water and the rinsate added to the tube. The solution was spun at 1,200 rpm until the solids settled from solution. The liquid was transferred to a vacuum filtration apparatus and filtered through a 0.45-micron cellulose nitrate membrane filter into a precleaned 125 Erlenmeyer flask. Solids remaining in the tube were washed into the filtration apparatus with a minimum of water and vacuum filtered and washed with a few milliliters of water. The filtered oxalate/oxalic acid extract was transferred to a clean graduated cylinder, then the flask was rinsed with a few more milliliters of water. The extract was then acidified to pH 2 and the final volume of the extract was measured before transferring it to a precleaned 60-ml. polyethylene bottle for storage.

Both the sediment collected on the filtration membrane and the remnant in the centrifuge tube were returned to the extraction beaker using a rubber policeman and a stream of water. Four milliliters of 30 percent hydrogen peroxide were added to the solids and the solution was stirred and warmed to initiate oxidation. Heat was reduced and oxidation was allowed to continue overnight. In the morning, excess water was removed by further warming until the residue appeared moist but not dry. Then 45 milliliters of 1 N HCl were added to the moist residue and the contents were stirred with a magnetic stir bar to extract the metals from both the oxidized organic phase and the acid-soluble minerals. The HCl extract was vacuum filtered as before and the final volume recorded. The remaining residue was collected, air-dried, and weighed.

Preparation of pore waters

Pore water was removed from the sediment samples according to the following procedure. The supernatant liquid was decanted from the sediment, and a subsample of the sediment was loaded into a round-bottomed 60-milliliter centrifuge tube. A small amount of

head space was allowed to remain inside the top of the tube. A rubber septum was stretched over the mouth of the tube and the tube was tapped to free any entrapped air. A valve attached to a hypodermic needle was inserted through the septum so that the tip remained near the inside surface of the septum. A second hypodermic needle attached to a regulated nitrogen supply by means of plastic tubing was inserted through the septum so that the tip was just above the surface of the sediment. The sample was purged with nitrogen at 5 psi for 5 minutes, while tapping the tube to free trapped air. The pressure relief valve was closed, the nitrogen shut off, and the two needles removed from the septum. The tube was weighed and another tube prepared to serve as a counterweight, then both were placed in a Damon HT Centrifuge and centrifuged at 8,000 rpm for one hour. Most of the pore water was poured off and the remnant suctioned off using a clean glass syringe and the combined water was vacuum filtered through a 0.45-micron cellulose nitrate filter into a 30-milliliter bottle, diluted with an equal weight of ultra pure water, acidified to below pH 2, and stored at 45 degrees Fahrenheit prior to metals analysis. The dilution step is necessary to generate sufficient volume for a full suite of metals analyses.

Analytical methods

Samples were divided into aliquots to meet the requirements of the various analytical methods and preserved with concentrated nitric acid as appropriate. The aliquots were stored in the IGS walk-in refrigeration unit, which is equipped with 24-hour temperature monitors and alarms.

Field parameters, including pH, dissolved oxygen, redox potential, temperature, and specific conductivity, were measured using a YSI 600XL sonde and a YSI Model 610DM data logger calibrated as specified in EPA's Methods for Chemical Analysis of Water and Wastes (U.S. EPA, 1979). Alkalinity was measured using a Hach Model 16900-01 digital titrator according to the method presented in Hach's Water Analysis Handbook (Hach Company, 1992). Acidity was measured using the APHA standard method (APHA, 1985). Ferrous iron was determined using the Cerium-IV titration method adapted to a Radiometer TIM900 electronic titrator (Peters and others, 1974).

Chloride, nitrate, and sulfate were determined by ion chromatography. A Dionex AS40 Autosampler introduced the samples to a DX100 chromatograph controlled and monitored by a computer running Dionex AI-450 software. The separation of ions was performed using an AS-4A column and the results were quantified using a five-point calibration curve constructed from certified reference standards according to the procedures set forth in EPA Method 300 (Pfaff, 1991).

Metals analysis

Three types of analytical techniques were available for metals determinations: flame atomic absorption, graphite furnace atomic absorption, and inductively coupled plasma emission spectrometry. The choice of techniques was based upon both the suitability of the technique for the element in question and the concentration at which the element was present. Inductively Coupled Plasma is well-suited to high concentrations of elements and is unable to accurately quantify elements at concentrations of less than a few parts per million. The optimum range for flame AA varies from element to element, but generally lies between 0.1 and 10 parts per million for the elements studied. Flame AA was used whenever a moderate degree of dilution (less than

a factor of 200) could bring the analyte within the AA's optimal analytical range. Graphite furnace must be used for trace level analyses, as this technique offers the ability to detect subpart per billion concentrations of several elements. The optimal range for most elements on GF/AA is generally from 1 to 100 parts per billion.

Aluminum, barium, sodium, strontium, and silicon were analyzed using ICP. Samples were introduced to the plasma by a Rainin peristaltic pump and a Hildebrand grid nebulizer as described in EPA Method 6010A (EPA, 1992). The ICP used is a Jarrell Ash Atomcomp II Model 975 simultaneous instrument modified with a ADAM-II 30 channel, high-speed digital data acquisition system and Seren 11600 solid state RF generator. Some surface water and sediment extracts from the wetland outlets were also analyzed for boron, which was subcontracted to Test America, Indianapolis, for analysis by dedicated ICP. Results from the major cation analyses were checked on a second ICP, the Leeman Labs PS900 ICP/Echelle Spectrophotometer, located at the Center for Earth and Environmental Research at IUPUI.

Flame atomic absorption was used to determine calcium, iron, magnesium, manganese, nickel, potassium, and zinc. The atomic absorption spectrophotometer used was a Perkin Elmer 5100PC Zeeman Corrected Graphite Furnace Atomic Absorption Spectrophotometer interfaced to a PC-based data station running PE Winlab software. Flame atomic absorption methods were taken from EPA's Methods for the Analysis of Water and Wastes, (EPA, 1979) and the EPA Solid Waste Manual, SW-846, (EPA 1992).

Trace metals were analyzed by GF/AA techniques described in the above-referenced EPA manuals, as well as methods published by the instrument's manufacturer. When concentrations exceeded the upper linear range of the instrument, the furnace autosampler was used to dilute the samples into the linear range for that element. When the analyte is present at levels requiring a dilution greater than fourfold, the samples were either manually diluted or analyzed using conventional flame atomic absorption. Analysis was performed on the furnace for the following metals: arsenic, beryllium, cadmium, chromium, copper, lead, molybdenum, nickel, selenium, and vanadium. All AA analyses were done in triplicate, except for the refractory metals vanadium and molybdenum, which were sometimes done in duplicate to minimize attrition of the analytical system's graphite components. The selenium analytical procedure was modified to incorporate a furnace program developed by the USGS (Jones and Garbarino, 1998). Arsenic and selenium values were checked using the PE Model 5100's hydride generation system.

Results

Wetlands performance

The four wetlands differed widely in the constraints of their settings, the complexity of their designs, and the substrates used in their construction. They also varied in their capacity to remove metals from AMD. The analytical results appear in Table 1.

At Augusta Lake, the largest ALDs have apparently failed and alkalinity only appears in some parts of the upper watershed during summer. Acidity predominates throughout the majority of the system and the removal of trace metals from the water is inconsistent at best.

At the Midwestern site, the outlet of the primary ALD discharges beneath the surface of a compost wetland cell. As the water emerges from the standpipe at the lower end of this cell, iron precipitates from solution. Only a small proportion of the other dissolved metals co-precipitate

with the iron at this point. Five years after construction, this ALD still works well. The pH of the water leaving Cell 1A is only slightly acidic and its quality improves further as it travels through the first three aerobic treatment cells. During the winter, an untreated seep was observed entering Cell 2B3, as evidenced by a visible precipitate; a decrease in pH from 7.3 to 5.5; an increase in oxidation potential, iron, nickel, cadmium, and acidity; and a decrease in alkalinity. Cell 2C2, a second sampling point downstream from the seep, contained elevated levels of calcium, nickel, and zinc during the winter as well. The seep was not observed in the summer and its flow is apparently intermittent. Its influence most likely explains the elevated metals concentrations downstream during the winter sampling. Although Cell 2B3 was constructed with a base of fixated fly ash beneath the usual substrate, it is unlikely that this difference in construction materials accounts for the alteration in water chemistry because the same effects were not observed in the summer samples.

In general, the water quality at Midwestern improves as the water flows through successive cells; the water is of better quality at the outlet of the final cell with respect to all parameters except for iron, which increased from 0.4 to 4.0 between Cell 2C3 and the outlet during the winter. No such increase in iron was observed in the summer samples.

Tecumseh wetland makes use of a large water volume, an ample surface area of organic substrate, and a serpentine flow pattern to achieve its treatment objectives. The long flow path through the first few cells allows time for precipitation and neutralization of much of the initial metals burden. The main influx of AMD is not introduced to the flow path until Cell 4A. Unfortunately, mixing between this AMD and the water from the upper wetland does not take place in Cell 4 because the two streams of water approach the outlet from opposite directions along two separate channels. In Cell 5, the water remains poorly mixed. In those areas where AMD is present, the turkey manure compost and ag lime substrate mixture seems to create adequate alkalinity to promote bacterial sulfate reduction and the binding of metals by organic processes. The amount of iron in the wetland effluent is low in the summer, only 0.2 ppm. In winter, iron removal is less effective at Tecumseh.

At Tecumseh, boron ranges from 1.2 to 3.0 ppm in the AMD at Cell 4A. The higher value is in the range known to be phytotoxic. It is possible that the boron could inhibit plant growth in the upper portion of Cell 5 where concentrated AMD comes into contact with the *Typha*. However, the boron was only 0.4 ppm at the outlet of Cell 5, a level which is unlikely to impair the vitality of aquatic vegetation. The presence of boron is not the only factor which could explain the failure of cattails to become established throughout Cell 5. The water depth in much of the cell exceeds the 18-inch maximum preferred by *Typha*. Destruction of the plants by wild boar and muskrats has been documented as well.

Table 1. Wetlands water chemistry

Sample ID	Sampling Date	Field Temp °C	SpC @25°C μmhos	pH @25°C S.U.	Eh vs SHE mV	Acid. eq CaCO3 mg/L	Alkal. mg/L	HCO3- mg/L	CO3= mg/L	Fe mg/L	Fe++ mg/L	Mn mg/L	Na mg/L	Cl- mg/L	NO3- mg/L	SO4- mg/L
<i>WINTER</i>																
Augusta Lake wetland																
PondPC1	03/07/00	17.8	3660	2.70	672	NA	0	0	0	104.4	NA	32.2	NA	9	<5	2787
PondPD1	03/07/00	18.0	3440	2.50	749	NA	0	0	0	133.6	NA	31.9	9.0	10	<5	2670
SAPS inlet	03/07/00	16.6	3290	2.80	658	280	0	0	0	49.8	25.0	24.6	11.0	4	<1	2317
SAPSpond	03/07/00	19.7	3320	2.60	643	233	0	0	0	42.9	25.0	23.2	12.8	3	<1	2310
Lake inlet	03/07/00	22.2	3320	3.35	551	151	0	0	0	5.0	4.0	23.8	13.8	4	<1	2344
Friar Tuck wetland																
Feeder	02/28/00	14.1	2370	7.30	388	30	173	210	0	4.1	0.0	2.0	22.3	3	<1	1304
AMDinflow	02/28/00	16.9	6400	2.90	605	6220	0	0	0	2152	1564	21.4	30.0	<5	<1	11000
Mixzone	02/28/00	7.8	2160	4.60	446	32	132	160	0	14.7	NA	4.0	19.1	2	<1	1252
Pond weir	02/28/00	12.6	1610	5.30	438	34	85	100	0	1.2	0.9	8.3	15.3	2	<1	930
Midwestern wetland																
Cell1A_in	02/29/00	17.9	3710	6.45	184	171	315	380	0	78.6	68.0	8.7	23.1	NA	NA	NA
Cell1Aout	02/29/00	9.6	2960	6.50	172	122	310	380	0	49.9	45.0	15.6	15.7	17	<1	2272
Cell1B	02/29/00	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	10	<1	1720
Cell2A	02/29/00	12.7	2590	7.10	317	35	188	230	0	0.3	0.1	7.3	16.0	15	<1	1451
Cell2B2	02/29/00	15.3	2320	7.30	297	36	158	190	0	1.5	0.0	4.6	13.4	14	<1	1263
Cell2B3	02/29/00	11.4	2030	5.50	351	40	17	20	0	7.2	0.4	6.8	17.0	21	<1	1132
Cell2C2	02/29/00	13.3	2020	6.30	337	26	42	50	0	0.4	0.1	7.8	17.2	23	<1	1160
Outlet	02/29/00	9.6	1520	7.00	320	15	76	90	0	0.3	0.0	0.7	10.5	12	<1	763
Tecumseh wetland																
Cell01out	02/29/00	11.2	2690	6.10	248	22	123	150	0	6.0	1.5	0.7	12.8	5	<1	1522
Cell02out	02/29/00	12.9	2770	6.60	209	24	84	100	0	5.1	1.0	0.8	117	5	<1	1608
Cell4Aout	02/29/00	15.5	4330	3.10	590	1304	0	0	0	708	547.0	5.8	110	2	<1	3358
Cell4Bout	02/29/00	13.4	2710	6.90	236	27	111	140	0	4.6	0.0	0.6	121	5	<1	1520
Cell5out	02/29/00	16.8	2480	7.20	424	18	82	100	0	0.1	0.0	0.3	113	5	<1	1442

Table 1. Wetlands water chemistry, continued

Sample	Sampling	As	Be	B	Ca	Cd	Cr	Cu	K	Mg	Mo	Ni	Pb	Se	V	Zn
ID	Date															
		µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L
WINTER																
Augusta Lake wetland																
PondPC1	3/7/00	<1	19	NA	444	4.8	4	<1	7.3	194	11	750	1.9	<1	<1	3.32
PondPD1	3/7/00	<1	18	NA	420	6.7	5	<1	6.8	181	13	924	1.4	<1	<1	3.80
SAPS Inl.	3/7/00	<1	6	0.26	446	3.3	1	<1	6.0	NA	10	440	1.9	<1	<1	1.36
SAPSPond	3/7/00	<1	5	0.24	432	3.4	1	4	6.2	230	9	371	0.8	<1	<1	0.97
Lake_inlet	3/7/00	<1	4	0.19	446	3.2	<1	10	7.1	205	6	418	1.5	<1	<1	0.94
Friar Tuck wetland																
Feeder	2/28/00	<1	<1	0.3	308	<0.4	<1	<1	4.6	209	13	17	<0.5	<1	3	0.07
AMDinflow	2/28/00	<1	56	NA	765	30.4	42	47	8.0	215	8	1090	3.8	<1	168	9.50
Mixzone	2/28/00	<1	<1	0.23	198	0.8	<1	3	4.2	157	4	31	<0.5	<1	10	0.23
Pond_weir	2/28/00	<1	<1	0.21	163	0.7	1	<1	5.1	129	5	9	<0.5	<1	24	0.24
Midwestern wetland																
Cell1Aout	2/29/00	2	<1	0.52	476	<0.2	<1	1	9.4	190	8	47	<0.5	<1	<1	0.11
Cell1B	2/29/00	<1	<1	0.64	611	<0.2	1	<1	7.1	263	9	260	<0.5	<1	<1	0.59
Cell2A	2/29/00	<1	<1	0.45	397	0.6	<1	<1	11.2	184	7	54	<0.5	<1	<1	0.11
Cell2B2	2/29/00	<1	<1	0.39	350	0.4	<1	<1	10.9	161	6	37	<0.5	<1	<1	0.06
Cell2B3	2/29/00	<1	<1	NA	288	5.5	<1	<1	8.7	137	4	179	<0.5	<1	<1	0.30
Cell2C2	2/29/00	1	<1	0.26	316	4.4	<1	<1	8.5	137	5	163	<0.5	2	<1	1.26
Outlet	2/29/00	1	<1	0.18	230	0.6	<1	<1	8.9	85	4	37	<0.5	1	<1	0.09
Tecumseh wetland																
Cell01out	2/29/00	1	<1	0.4	198	<0.2	<1	<1	5.5	230	5	10	<0.5	<1	4	0.46
Cell02out	2/29/00	<1	<1	0.41	242	<0.2	<1	<1	10.1	233	4	14	1.2	1	<1	0.11
Cell4Aout	2/29/00	<1	3	1.2	314	0.9	2	2	18.4	231	5	106	1.0	<1	16	0.96
Cell4Bout	2/29/00	<1	<1	0.4	196	<0.2	<1	<1	8.0	235	6	6	<0.5	2	<1	0.09
Cell5out	2/29/00	<1	<1	0.36	223	<0.2	<1	<1	7.8	222	5	5	<0.5	1	1	0.51

Table 1. Wetlands water chemistry, continued.

Sample ID	Sampling Date	Field Temp °C	SpC @25°C µmhos	pH @25°C S.U.	Eh vs SHE mV	Acid. eq CaCO3 mg/L	Alkal. mg/L	HCO3- mg/L	CO3= mg/L	Fe mg/L	Fe++ mg/L	Mn mg/L	Na mg/L	Cl- mg/L	NO3- mg/L	SO4- mg/L
SUMMER																
Augusta Lake wetland																
Pond PC2	09/28/00	16.5	2970	6.75	270	89	102	120	0	33.1	NA	15.4	9.1	6	0	2052
Pond PB	09/28/00	13.1	2960	3.45	501	178	0	0	0	7.1	NA	20.5	7.5	0	0	2031
SAPSout	09/28/00	15.9	2860	9.10	185	24	140	150	9	38.7	NA	2.1	105.7	0	0	1936
Mixing Zone	09/28/00	15.7	2840	5.60	372	82	18.5	20	0	30.2	NA	18.7	10.0	0	0	1977
Friar Tuck wetland																
Feeder	09/22/00	19.3	2210	7.58	428	55	301	370	1	7.9	0.0	1.5	17.0	4	0	1126
AMDinflow	09/22/00	22.4	7750	2.55	607	6093	0	0	0	2504	NA	37.0	33.1	0	0	8620
Mixzone	09/22/00	19.5	1600	3.19	633	133	0	0	0	9.9	NA	7.5	16.0	2	0	972
Upper pond	09/22/00	20.5	1700	5.77	326	57	19	20	0	0.7	0.5	4.6	18.0	0	0	949
Pond weir	09/22/00	21	1760	6.05	246	70	28	30	0	7.5	NA	4.7	22.5	0	0	1075
Midwestern wetland																
Cell1Aout	09/19/00	21.7	3.72	6.07	131	142	248	300	0	145.5	129.2	13.8	24.9	0	0	2413
Cell1B	09/19/00	25.7	3.18	6.58	241	30	201	240	0	0.2	0.1	6.3	23.3	1	0	2093
Cell2B2	09/19/00	23.4	3070	6.60	232	64	205	250	0	0.2	NA	4.1	22.6	0	0	1980
Cell2B3	09/19/00	19.2	2490	6.32	271	32	186	230	0	0.2	0.1	6.2	22.4	0	0	1443
Cell2C2	09/19/00	21.3	2440	6.54	325	63	196	240	0	0.2	NA	6.6	20.2	0	3	1414
Outlet	09/19/00	18.5	2190	6.37	341	28	217	260	0	0.2	<0.1	8.4	19.8	0	0	1172
Tecumseh wetland																
Cell02out	09/19/00	25.0	2450	7.38	255	56	128	160	0	0.9	0.3	0.3	114	0	0	1466
Cell4Aout	09/19/00	25	7690	2.89	622	NA	0	0	0	2462	1709	17.3	111	0	0	8191
Cell4Bout	09/19/00	25	2660	4.61	515	73	12	10	0	20.7	20.0	2.2	119	0	0	2294
Cell5out	09/19/00	25.6	2330	8.29	342	39	103	120	1	0.3	0.3	0.2	106	0	0	1405

Table 1. Wetlands water chemistry, continued.

Sample	Sampling	As	Be	B	Ca	Cd	Cr	Cu	K	Mg	Mo	Ni	Pb	Se	V	Zn
ID	Date															
		µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L
<i>SUMMER</i>																
Augusta Lake wetland																
Pond PC2	9/28/00	2	<1	0.26	641	5.2	2	<1	9.2	151	<1	297	0.7	<1	<1	0.22
Pond PB	9/28/00	1	5	NA	580	3.8	<1	5	5.8	141	<1	391	32.9	<1	<1	0.67
SAPSout	9/28/00	<1	<1	0.16	371	<0.2	<1	0	6.3	147	5	398	<0.5	<1	<1	0.11
Mixzone	9/28/00	<1	1	0.22	645	0.2	3	<1	5.9	126	<1	422	2.1	<1	<1	0.56
Friar Tuck wetland																
Feeder	9/22/00	<1	<1	0.28	389	0.2	<1	<1	4.5	91	<1	5	<0.5	<1	<1	0.14
AMDinflow	9/22/00	<1	25	2.9	789	28.8	40	11	17.9	230	<1	1310	0.8	<1	320	8.04
Mixzone	9/22/00	<1	3	0.25	391	1.6	0	2	6.0	184	<1	45	1.7	<1	<1	0.36
Up. Pond	9/22/00	<1	<1	NA	391	0.3	<1	<1	5.1	104	<1	13	0.6	<1	<1	0.15
Pond_weir	9/22/00	<1	1	0.29	455	0.2	4	2	4.9	158	<1	7	5.3	<1	11	0.11
Midwestern wetland																
Cell1Aout	9/19/00	1	<1	NA	697	<0.2	6	<1	8.7	202	<1	250	<0.5	<1	<1	0.13
Cell1B	9/19/00	<1	<1	0.5	644	<0.2	0	<1	NA	183	<1	18	<0.5	<1	<1	0.11
Cell2B2	9/19/00	2	<1	0.44	656	0.4	0	<1	12.1	173	<1	233	5.2	<1	<1	0.10
Cell2B3	9/19/00	<1	<1	0.25	566	0.2	0	<1	11.6	126	<1	53	<0.5	<1	<1	0.09
Cell2C2	9/19/00	<1	<1	0.29	556	0.1	0	<1	13.6	115	<1	20	<0.5	1	<1	0.12
Outlet	9/19/00	1	<1	0.2	510	1.4	1	<1	18.0	97	<1	13	1.1	<1	<1	0.12
Tecumseh wetland																
Cell02out	9/19/00	<1	<1	0.39	414	3.4	<1	<1	10.4	158	<1	37	0.6	<1	<1	0.13
Cell4Aout	9/19/00	<1	18	3	1021	4.5	5	3	27.3	228	<1	343	<0.5	<1	45	2.83
Cell4Bout	9/19/00	1	<1	0.41	437	0.2	4	1	11.2	160	<1	29	<0.5	<1	<1	0.12
Cell5out	9/19/00	1	<1	0.35	701	0.3	1	<1	7.6	89	<1	15	<0.5	1	<1	0.08

At Friar Tuck, the relatively large volume of the feeder stream overwhelms the small volume of AMD flowing from the known seep, and the feeder stream's alkalinity neutralizes the AMD. Beryllium, cadmium, chromium, nickel, and vanadium are all reduced to insignificant levels in the wetland effluent.

In the three wetlands where significant improvement is observed-- Midwestern, Tecumseh and Friar Tuck-- dilution may account for most of the water quality improvement, including the decrease in metals concentrations. The fact that simple dilution is the most important influence upon water quality does not indicate that a wetland is not performing as desired. Dilution with fresh water can increase the pH, precipitate metals, and eliminate mineral acidity. These effects may contribute to the beneficiation of AMD such that quality improves more than the dilution ratio suggests.

Iron, aluminum, and manganese generate the majority of mineral acidity in AMD. The removal of mineral acidity is an essential aspect of water quality improvement. The effectiveness of the four wetlands at removing these acid-forming metals can be seen in the four graphs in Figure 5. There was insufficient manganese present at Tecumseh to warrant plotting on the graph.

Figure 5. Graphs of the concentrations of acid-forming cations in the four wetlands.

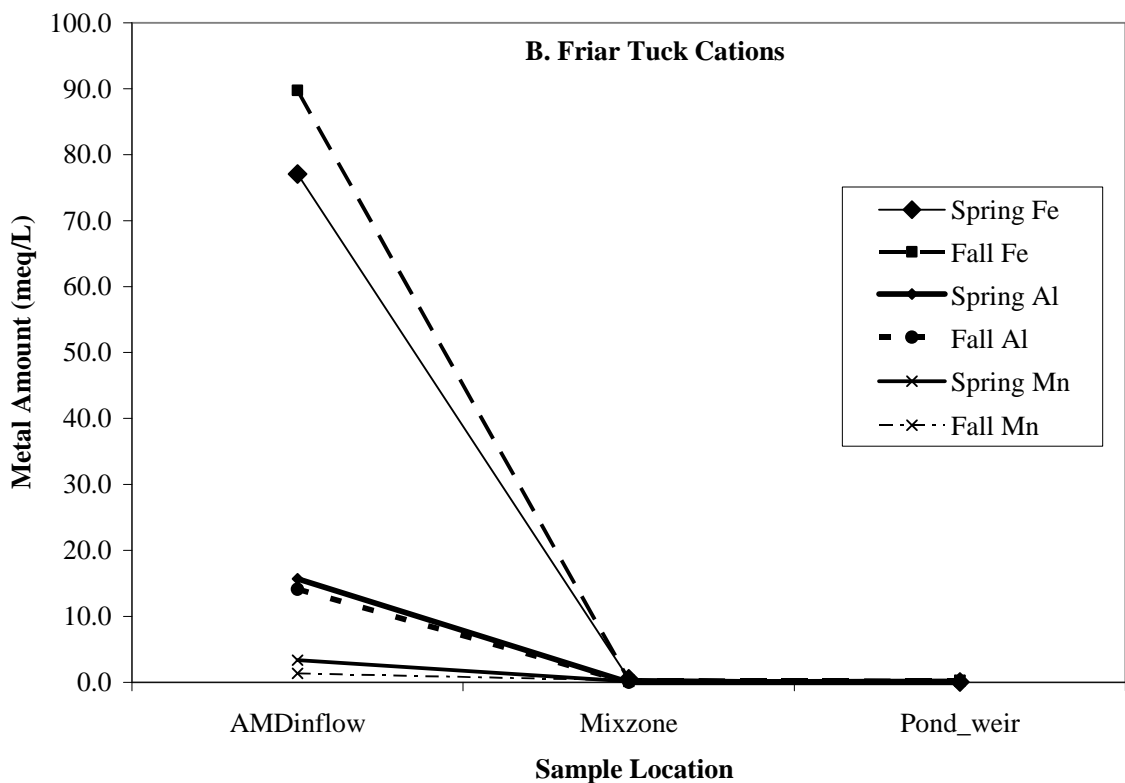
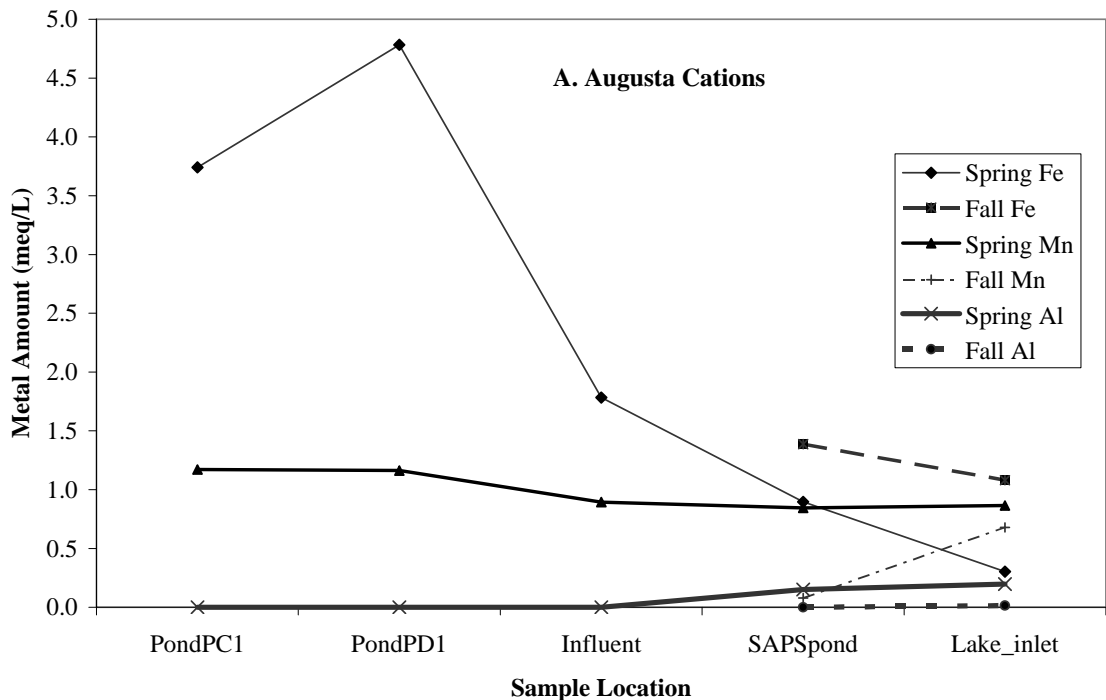
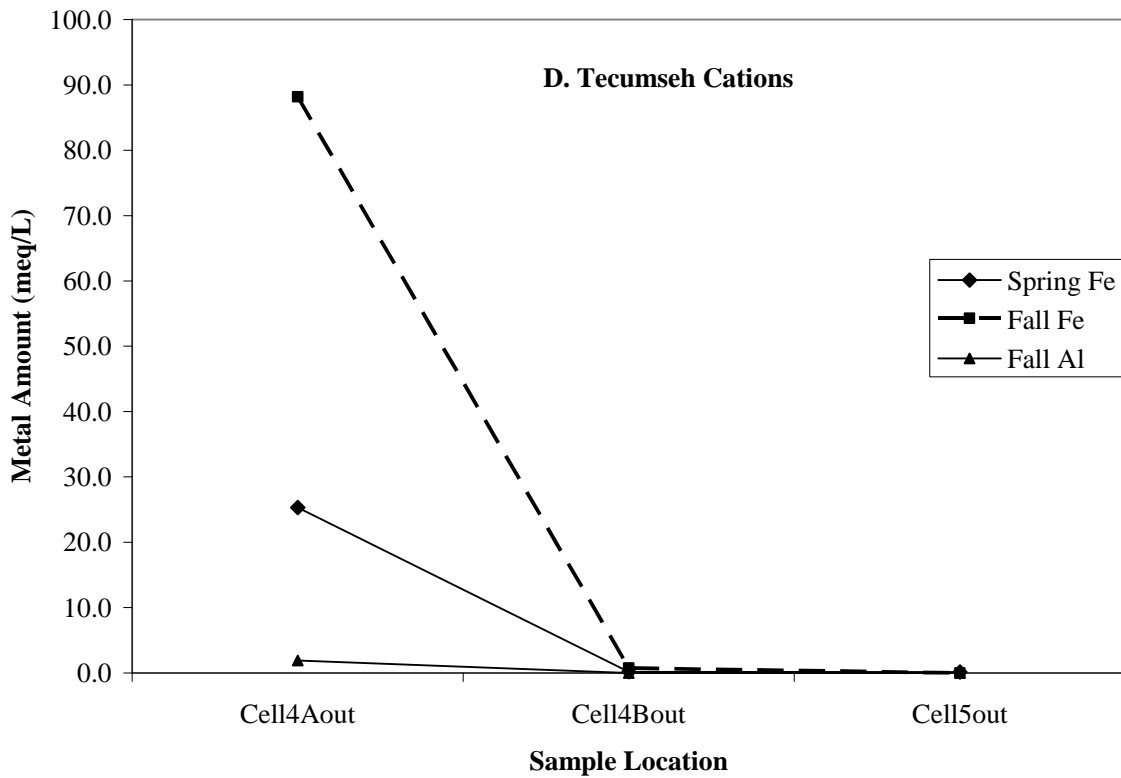
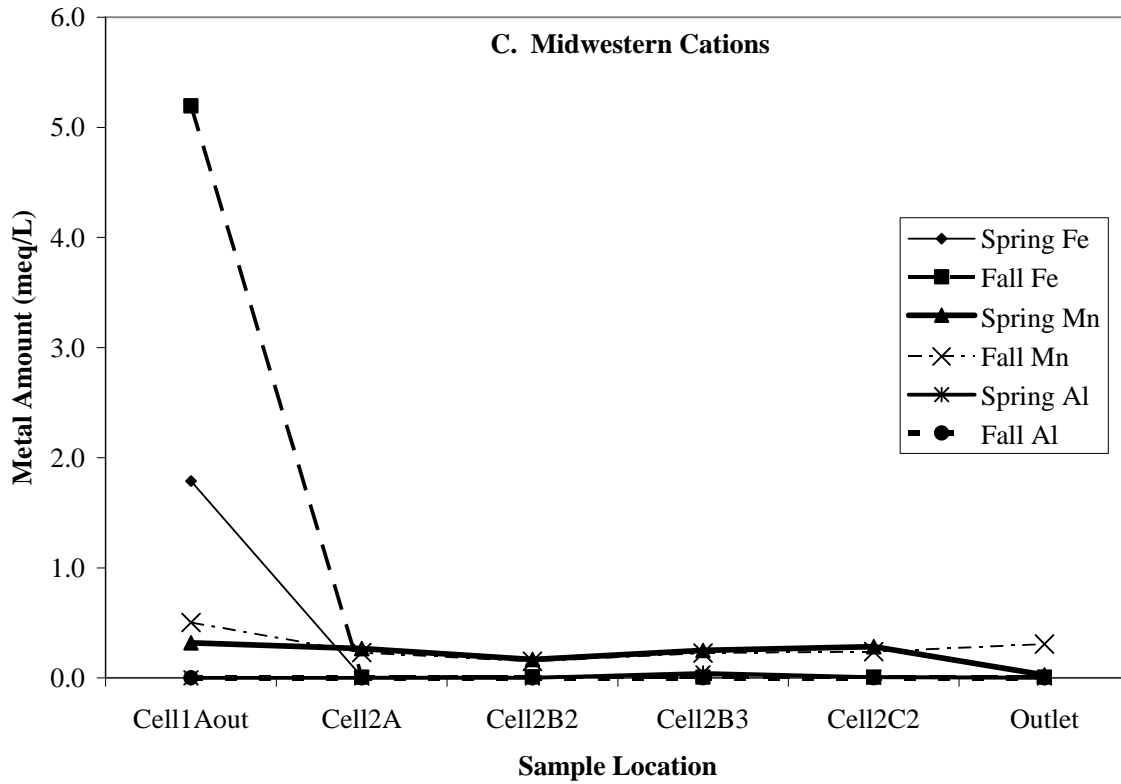


Figure 5 continued. Graphs of acid-forming cations in the four wetlands.



Of the three acid-forming metals, iron is by far the most important contributor of mineral acidity; its removal and sequestration is one of the primary treatment objectives in the design of AMD wetlands. The iron removal rates in the four wetlands (Table 3) were estimated to generate a comparison of the measured iron removal rates with the theoretical removal rates used to size constructed wetlands. Rough estimates were made of the surface areas of the wetland cells by measuring the area of the wetland cells depicted on engineering design sheets. No scale was available for these drawings, therefore, cell areas had to be estimated by comparison of the drawings with USGS quadrangles; hence, the size estimates are approximate.

The mass of iron removed was obtained by averaging the winter and summer iron concentrations and comparing the difference between the average value for the AMD influent and the average value for the wetland effluent. The flow rates appearing in Table 2 were determined by direct measurement when possible. In the case of the AMD inflow at Tecumseh Cell 4A, the channel was too broad and diffuse to measure so the arbitrary assumption was made that the flow from 4A was 10 percent that of the total flow through the wetland. This assumption accounts for what is most likely an overestimate of the mass of iron removed.

Table 2. Estimated flow rates in the study areas	
Augusta Lake*	SAPS discharge: 1 gal per minute SAPS weir discharge: 170gal per minute
Friar Tuck**	AMD discharge: 2.4 gal per minute Freshwater influent: 212 gal per minute Wetland effluent: 268.8 gal per minute
Midwestern Cell 1A standpipe***	Summer: 8 gal per minute Winter: 11 gal per minute
Tecumseh Cell 5 discharge***	929 gal per minute
* Measured by USGS survey team using electronic velocity meter, 9/28/00. ** IGS flow measurements by Tracy Branam in 1998. *** Measured by stop watch and bucket or velocity meter by Adam Flege, Barry Maynard, and Ron Smith in March, June and September 2000.	

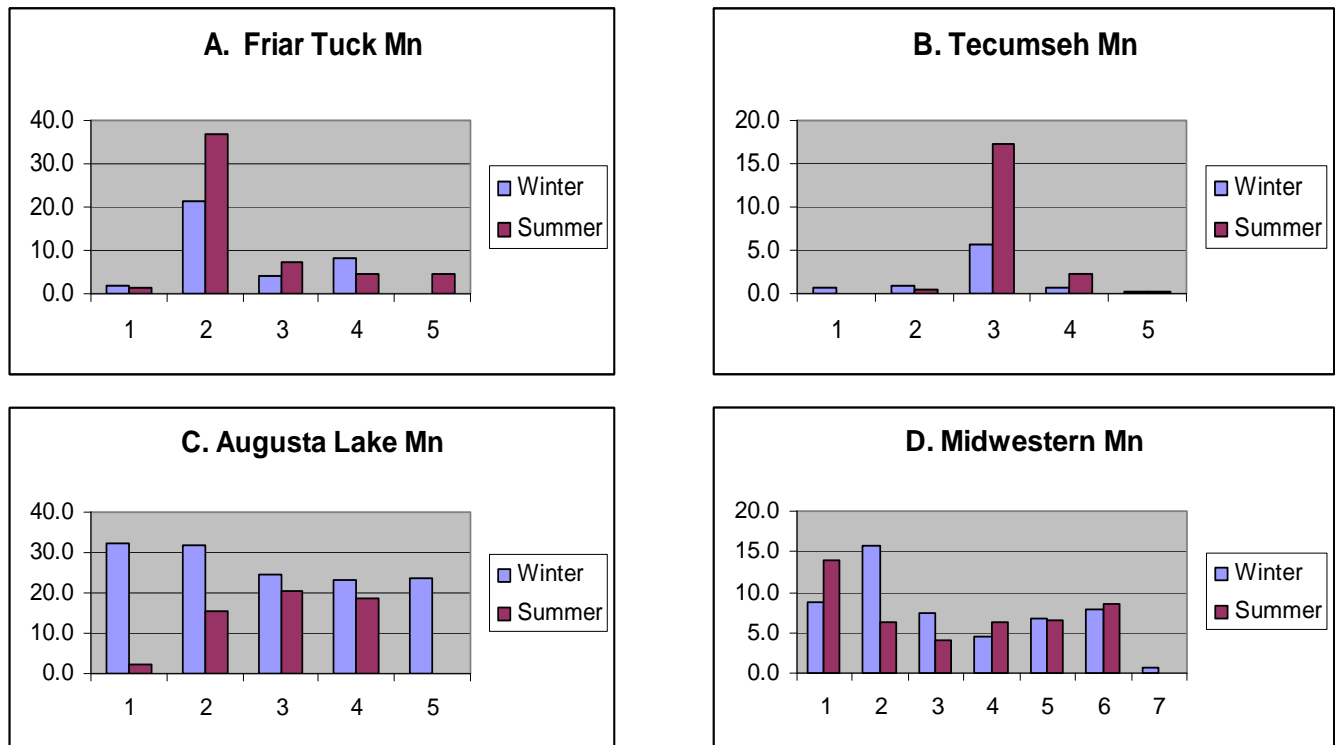
Table 3. Estimated iron removal rates			
Site	Approximate Area*	Iron removed per day	Iron/m ² /day
Augusta	2,000 m ²	6.05 kg.	3 g/m ² /day
Friar Tuck	16,260 m ²	30.2 kg.	2 g/m ² /day
Midwestern	17,800 m ²	4.3 kg.	<0.5g/m ² /day
Tecumseh	236,000 m ²	814 kg.**	3.5 g/m ² /day
* Areas are rough estimates from maps and may be inaccurate. ** Assumes the flow at Cell 4A is 1/10th of the flow at Cell 5 outlet.			

Despite the uncertainties involved in the estimates, the iron removal rates in all four

wetlands fall within the range proposed by the Bureau of Mines for use in sizing wetlands (Bureau of Mines, 1994). The Bureau of Mines design criteria indicate that wetlands can be relied upon to remove 5 g/m²/day of iron. Although the wetlands studied do not quite meet this level of efficiency, it is because they contain a larger surface area than is required to remove the iron present in the AMD. The inclusion of this excess surface area in the calculation makes the wetlands appear less efficient. Three of the four wetlands remove 99 percent the iron available in the influent AMD without requiring the use of their entire surface area. For instance, at Midwestern, about 99 percent of the iron precipitates from solution in the first aeration cell. The poorest performing wetland, Augusta Lake, removes 96 percent of the iron entering the system during winter. (The summer Augusta Lake data do not accurately reflect the wetland's overall iron removal because one of the sampling points was relocated to a mixing zone where precipitation is incomplete).

The water analyses show that, in general, there is a gradual reduction in the content of most metals as the water approaches the wetland outlet. The most notable exception is manganese (Figure 6), an acid-generating metal that is capable of electron exchange reactions with iron. Manganese oxidation is slower than iron oxidation and does not occur in the presence of ferric iron. Manganese does not precipitate until all the iron has precipitated, usually in the later stages of the wetland (Behum and Kim, 1999, p. 41). Manganese is not appreciably removed at Augusta Lake, and in fact, it passes through all the wetlands except Tecumseh, where it is not abundant.

Figure 6. Wetland manganese concentrations in order from the wetland inlets to the outlets.



Manganese oxide precipitates are unstable in the presence of ferric iron; this can cause the precipitates to release manganese into solution (Behum and Kim, 1999,). This is apparent in the Midwestern Wetland, where in summer, manganese decreases to 4.1 ppm in Cell 2B2, then rises to 8.4 ppm. at the outlet. In winter manganese again decreases to 4.6 ppm in Cell2B2 then rises again to 7.8 ppm in Cell2C2 before declining to 0.7 ppm at the outlet.

A second exception to the uniform decrease in metals concentrations as the water flows through these systems concerns elements which form oxy-anions in solution. Within a wide range, the solubility of these elements does not decrease as pH increases as is the case for metals which form cations in solution. In the case of the wetlands studied here, the data indicate negligible removal of boron and only small decreases in molybdenum throughout the wetlands. Neither of these elements are at levels that are likely to adversely affect human health or the environment.

Water chemistry modeling

The water chemistry results were used to create a data set for input to the water chemistry modeling program, PhreeqC. The program calculated the activity of all major dissolved species. The test results for water entering the four wetlands were compared with the water exiting the wetlands during both winter and summer. The prevalent chemical character for these eight pairs of influent and effluent was calculated using the Aquachem computer program. The results were plotted in a trilinear Piper chart (Figure 7), with the influent waters appearing as triangles and the effluent waters as stars. The chart demonstrates that the wetlands mitigate the influence of iron as a major cation. While all the influents contain varying amounts of iron, the effluents are all dominated by calcium or magnesium. The predominance of sulfate as the major anion is not changed. Anion concentrations in both the influent and effluent samples plot close together, indicating that although sulfate is being removed, it is not being replaced by bicarbonate or chloride. Aquachem provides an interface to the PhreeqC program developed by the USGS (Parkhurst, 1995). PhreeqC was instructed to use the list of minerals from the MINTEQA database to calculate saturation indices for those mineral phases present in the wetland waters.

Twelve solutions representing AMD and outlet water from each of the sites were entered for simulation of reactions by the programs. The minerals that are super-saturated at each site are summarized below, in order of decreasing saturation.

Augusta Lake

Winter: hematite, goethite, quartz.

Summer: goethite, K-mica, alunite, kaolinite, gibbsite, jarosite-K, Fe(OH)₃, illite, quartz, gypsum.

Friar Tuck

Winter: hematite, goethite, alunite, K-mica, kaolinite, gibbsite, Fe(OH)₃.

Summer: hematite, goethite.

Midwestern

Winter: hematite, goethite, Fe(OH)₃, quartz, chalcedony.

Summer: hematite, goethite, Fe(OH)₃, quartz, rhodochrosite.

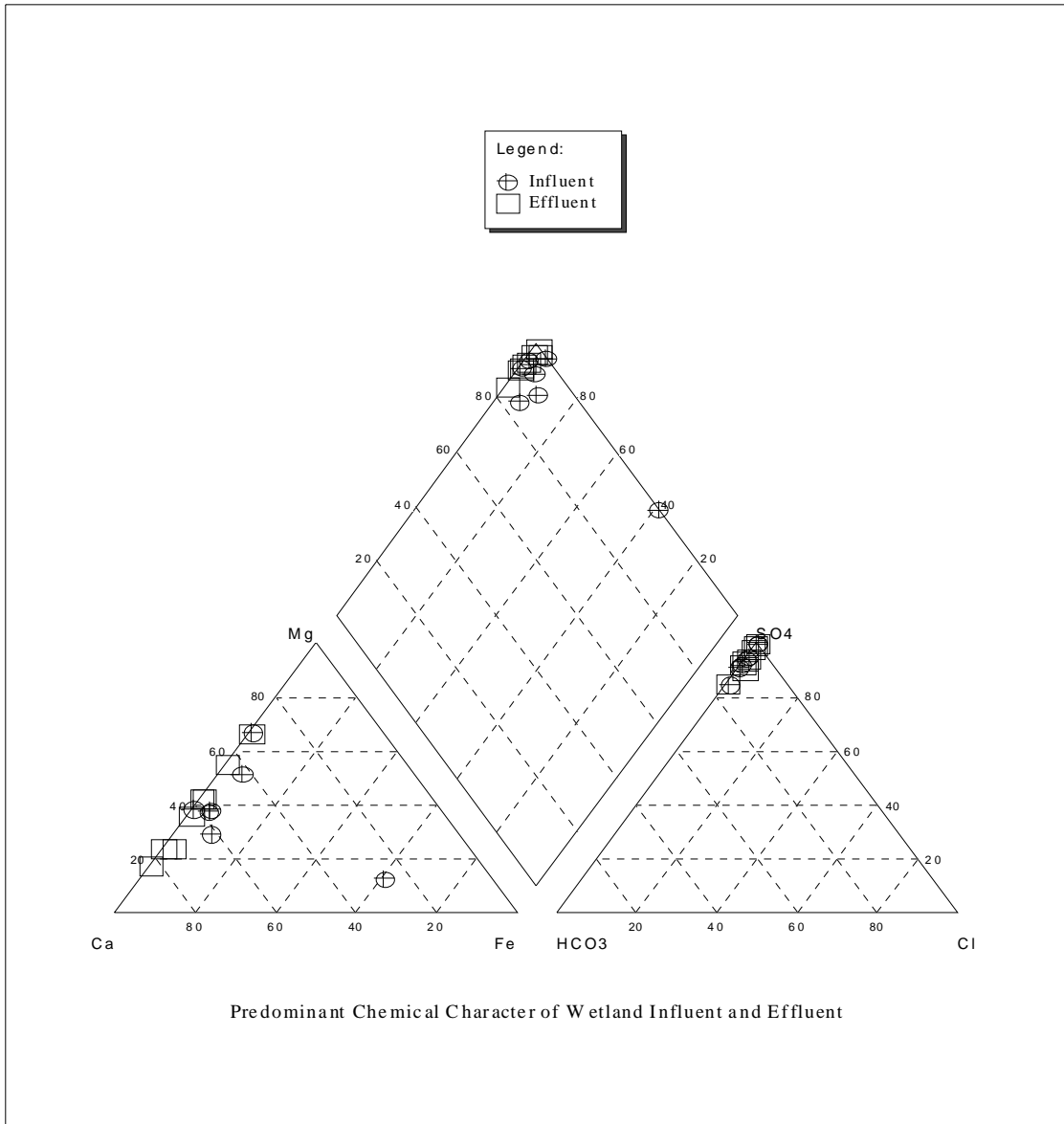
(List of supersaturated minerals, continued.)

Tecumseh

Winter: hematite, goethite, jarosite-K, $\text{Fe}(\text{OH})_3$.

Summer: hematite, goethite, talc, dolomite, $\text{Fe}(\text{OH})_3$, calcite, aragonite, chrysotile, rhodochrosite, siderite, gypsum.

Figure 7. Piper diagram showing the predominant chemical character of wetland influents and effluents.



Although the wetland waters are supersaturated with respect to these minerals, this does not mean they will all necessarily appear in the wetland sediments. These saturation indices indicate only that the concentrations of chemical constituents present in the water will tend to drive precipitation reactions rather than dissolution reactions for these minerals. Due to the constraints presented by activation energies and reaction rates, the precipitation of some of these phases (especially silicates) would require a time span far greater than the residence time of the water in the wetland. Any change in temperature, dilution, or other alteration by physical or biological processes can also disrupt the system's ability to precipitate solid phases.

An important determinant of phase transition is the tendency for minerals to precipitate in meta-stable forms, particularly hydrous oxides. Water chemistry modeling programs include only those minerals for which adequate thermodynamic data exist, which excludes many meta-stable and poorly crystalline forms. Recent studies have shown that one of the most abundant minerals in AMD wetlands is schwertmannite, $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$, a mineral that was not recognized until 1995 (Bigham and Schwertmann, 1996, p. 848). Schwertmannite is not included in the MINTEQ database and there is a paucity of thermodynamic data available regarding its formation, even though it is the most common phase formed from AMD in the pH range of 3.0 to 4.5 (Bigham and Schwertmann, 1996, p. 847). The abundance of metastable phases in wetlands underscores the importance of empirical techniques like sequential extraction for determining the composition and chemical properties of the sediments.

Sediment extracts

The results of the analysis of the sediment extracts appear in Appendix A. The metals concentrations in the data tables are expressed in terms of wet weight as opposed to dry weight in order to more accurately portray their composition in their natural setting. Appendix B contains a second set of tables that present the distribution of each element between the two extracts as percentages.

Although the concentrations of trace metals dissolved in wetland waters are generally negligible, the sediment extract data show that large quantities of metals have accumulated in the wetland sediments. The lack of correlation between water and sediment concentrations suggests that the two phases may not be in chemical equilibrium. There are a variety of reasons that disequilibrium might exist. As noted above, precipitation of mineral phases can require a time span that exceeds the residence time of the water in the wetlands. Also, the oxidized layer which coats the sediment isolates the bulk of the solid material from contact with the aqueous phase (Hsu and Maynard, 1999, p. 231). Furthermore, isotope data indicate that during both winter and summer, the majority of water present in the wetlands consisted of rainfall as opposed to ground water (Flege, 2001, p. 52). The influx of precipitation and its dilution effect would mask the relationship between sediments and water, as the duration of contact might be too short for the two phases to interact completely.

While the sediment data reveal the presence of elements not detected in the water samples, it is also true that certain highly soluble elements found in the water samples are not abundant in the sediments. The sediment values reflect the metals that have precipitated from the AMD; therefore, highly soluble elements such as sodium are not present at significant levels in the precipitates even though they are present in the water.

The precipitates collected for this study are the product of complex interactions among physical, chemical, and biological processes. These precipitates are not physically uniform and

vary considerably in their consistency, ranging from loose, hydrated gels to tight, dense crystalline particles. Because of their heterogeneity, it is necessary to exercise caution when comparing data from different sampling points. Nonetheless, the concentrations and distribution of metals in the oxalate and hydrochloric acid extracts provide information regarding the types of precipitates present in the sediments.

As expected, large proportions of iron, aluminum, and manganese are associated with the oxalate extracts, signifying an abundance of hydrous oxyhydroxides in the wetlands. The elements beryllium and vanadium are also predominantly associated with oxalate extracts. In most cases, the concentration of trace metals increases in the final wetland cells. The precipitates formed at the AMD sources are a notable exception to this general pattern. The AMD is often supersaturated with metals that precipitate rapidly upon contact with the air, accounting for high metals concentrations at locations where the AMD first encounters the atmosphere.

While scavenging by hydrous oxides is not significant at a pH of 3.0 or less, in the Midwestern wetland, the pH remains circum-neutral throughout the system. At Midwestern, in both the winter and summer, 99 percent of the iron in solution precipitates in the first aeration cell. After that, iron concentrations fall as the distance traveled from the source increases. At the same time, the data show that the trace metals present in the solid phases either increase or remain the same as the distance from the standpipe increases. Were co-precipitation with iron the controlling factor, then as iron precipitation decreases the accumulation of co-precipitated metals should also decrease. The fact that the metals are accumulating despite lower iron levels indicates other processes are at work, and is consistent with the possibility that scavenging by oxyhydroxides is taking place in the lower wetland cells.

The residual fraction represented by the hydrochloric acid extract contains metals that either were absorbed by organic materials, precipitated in relatively insoluble minerals, or transferred by the aging of amorphous phases to less soluble minerals. Rapidly precipitated iron compounds may incorporate up to 10 mole percent of substituted metals (Herbert, 1996). Since these metals are incorporated in the mineral's structure, substituted elements are more likely to appear in the residual fraction than in the oxalate fraction.

The mineral phases that precipitate at lower pH tend toward denser, more crystalline forms, including goethite and hematite. Their tighter structure, smaller surface area, and the lower pH of the surrounding water make these sediments less effective at scavenging metals from solution. In waters below pH 3, surface adsorption of Cu, Pb, and Zn to goethite is insignificant (Herbert, 1996, p. 229). Dense, ochreous sediments of this type interspersed with hematite crystals are abundant in the acidic Augusta Lake Wetland. This visual observation is confirmed by analysis of the extracts. The high concentrations of trace metals throughout this system suggests that metals are passing through the wetlands and accumulating at the Augusta Lake inlet rather than being scavenged from solution in the upper regions of the watershed. The lack of metals scavenging relative to the other wetlands is consistent with the scarcity of the loose, large-surface area precipitates formed at higher pHs.

The portion of metals bound within the residual fraction is elevated at the outlet of the Midwestern wetland. Here, aging is a contributing factor. Since precipitation of the most abundant metal—iron—is most rapid in the first few cells where the iron first encounters oxygen, the rate at which precipitates are deposited decreases in proportion to the distance from the source. Therefore, a sample of surficial solids collected where the precipitation rate is slower will contain sediment of more advanced age. As solids age in a wetland, metals migrate from the

less stable oxidized phases to the more stable anoxic phases. This is reflected in the accumulation of trace metals in the HCl extracts of the final treatment cells.

Another important mechanism of metals removal in wetlands is the binding of trace metals by organic materials, particularly high molecular weight substances such as humic acid (Fu and Allen, 1992, p. 1371). The increased ratio of manure used in the substrate at the final cells may also be a factor in the elevated metals concentrations found in the residual fraction near the Midwestern outlet. The sequential extraction used in this study separates organically bound metals into the hydrochloric acid extract. Lead is known to have a high affinity for the organic component of wetland sediments (Pickering, 1986, p. 126). The accumulation of high levels of lead in the hydrochloric acid extracts from the final cells of the Midwestern wetland may be due in part to its adsorption to the organic substrate there or to new organic matter formed by biological activity.

Discussion

There are several ways in which trace metals are known to leave solution and accumulate in the solid phases present in AMD treatment wetlands:

1. co-precipitation with major species, either substituted in lattice structure or physically entrained in the precipitate;
2. adsorption to hydrous oxide surfaces;
3. complex formation with humic acid, fulvic acid and other organic compounds;
4. sorption to cell walls of plants or micro-organisms;
5. ion exchange reactions;
6. uptake by organisms;
7. binding to ligands--organic or inorganic substances that bind the metal and which also bind other molecules.

Each of these types of processes are influenced by the water chemistry and other localized conditions. Some processes are strongly affected by the reduction/oxidation state, while others are relatively unaffected by this characteristic.

The aquatic environment in the wetlands may be divided into two zones in which the most important reactions may be characterized as being either predominantly aerobic or anaerobic in nature. Aerobic conditions prevail where oxygenated water is abundant, while anaerobic conditions exist where some barrier prevents the diffusion of oxygen into the system. Iron and sulfate are the two most important species contributing acidity to AMD. These species exist in oxidized form under aerobic conditions and reduced form under anaerobic conditions. The precipitation of trace metals also varies under these different conditions.

Aerobic water chemistry

In AMD wetlands, aerobic reactions are most prominent at locations where anoxic ground water comes into contact with oxygen or oxygenated water. Under these circumstances, iron, manganese, and aluminum are rapidly oxidized and fall from solution. This creates an abundant supply of hydrous oxide precipitates, which can scavenge trace metals from solution (Elliot and Dempsey, 1990, p.332). Hydrous oxides vary greatly in their surface areas, their

surface reactivity, and their ability to scavenge metals. One poorly crystallized iron oxy-hydroxide is schwertmannite, a mineral having a pincushion structure and a very large surface area of 175 to 225 square meters per gram (Bigham, 1996). In a study of 44 AMD wetlands, schwertmannite was found to be the most common phase formed from AMD in the pH range of 3.0 to 4.5. This mineral has a Fe/S mole ratio in the range of 4.6 to 8. In comparison, goethite and jarosite have high affinities for sulfate, and these minerals have Fe/S mole ratios in the range of 1.5 to 2.4.

In AMD systems, it is sulfate bound to solid phase oxide surfaces that most often serves as a ligand for binding metals. Such an assemblage is known as a ternary complex. An example of a common ternary complex in these systems is $=\text{FeOHCuSO}_4$. Material in which ternary complexes are abundant has been shown to contain higher concentrations of Pb, Cu and Zn bound to its hydrous oxide surfaces (Webster and others, 1998, p. 1361).

The ability of AMD precipitates to absorb sulfate and metals is dependent upon the type of precipitate present. The following factors determine the form that iron oxy-hydroxides assume as they precipitate (Herbert, 1996, p. 229).

1. the concentration of Fe in the solution;
2. the pH of the solution;
3. the Redox potential (Eh) of the solution;
4. the concentration of sulfate, carbonate and other ligands in the solution;
5. the partial pressure of CO_2 and O_2 ;
6. the activity of the H_2O ;
7. the presence of bacteria.

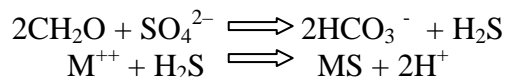
The form of the precipitate, in turn, determines how tightly trace metals are bound. Metals can be washed easily from the surfaces of many precipitates or displaced by other species, and loose gels can be physically swept away when flow increases. Some hydrous oxides readily dissolve if the water chemistry changes, releasing their load of metals so they become available for uptake by plants or for transport from the site. An example is schwertmannite, which readily releases bound metals. This mineral is characteristic of aerobic zones (Bigham and Schwertmann, 1996, p. 847). It is highly soluble in oxalate. In contrast, more highly crystalline minerals such as jarosite and goethite release the trace metals associated with them only when subjected to relatively strong acid, as in the hydrochloric acid extraction. Although the latter minerals may form in an aerobic environment, they also result from the aging of hydrous oxides under anaerobic conditions.

Anaerobic chemistry

Although the form of the iron precipitate present in wetland sediments affects sorption of trace metals from the aqueous phase, the ultimate fate of the metals sequestered in the sediments is determined by the stability of the sediments over time. If undisturbed, a loose iron hydroxide such as ferrihydrite ($\text{Fe}(\text{OH})_3$) ages into goethite (alpha FeOOH), which in turn ages to hematite (alpha- Fe_2O_3) (Herbert, 1996, p. 229). A portion of the surface-bound sulfate and metals may become incorporated into the crystalline lattice as the mineralization proceeds. These metals are securely bound and are rendered unavailable for subsequent remobilization. Goethite can contain up to 10 mole percent of Cr, Cu, Ni, or Zn or up to 30 mole percent of Al or Mn

incorporated in its structure, where it is relatively permanently fixed.

These chemical pathways for the mass transfer of metals to stable forms are augmented by biological processes, including microbial sulfate reduction (Hedin and Hammack, 1989, p.508). For the most part, sulfate reduction takes place in anoxic sediments rather than in the water column (Hsu and Maynard, 1999, p.229). It requires a source of organic carbon, anaerobic conditions, a circum-neutral pH and an active population of sulfate-reducing bacteria. The bacteria reduce sulfate to hydrogen sulfide while oxidizing organic compounds to form bicarbonate. Metal ions react with the hydrogen sulfide to form less soluble metal sulfides, releasing hydrogen ions. The sulfate reduction step is mediated by bacteria, while the reaction of metal with sulfide is controlled by the concentrations of reactants. In the following equations CH_2O represents an organic compound and M represents a metal:



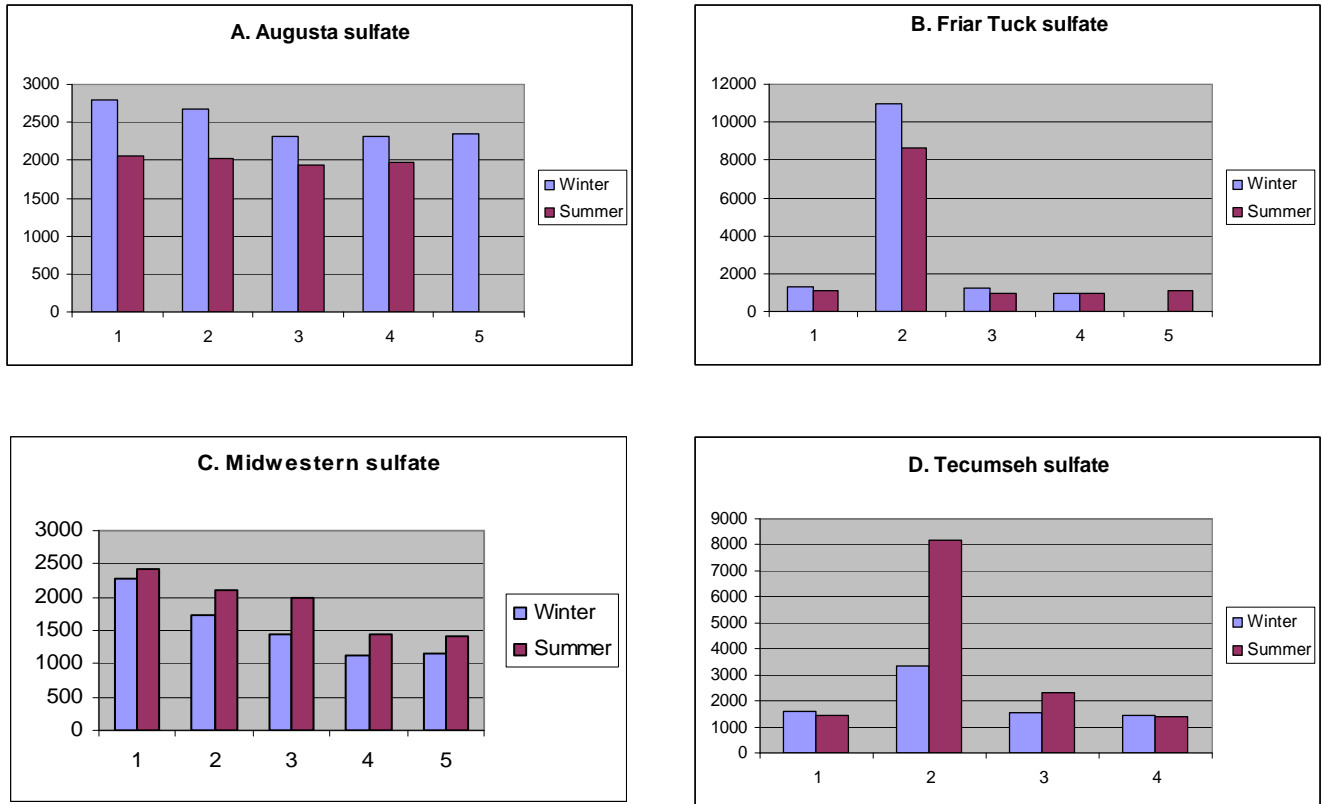
Sulfate hydrolyzes water to form acid, so its removal from solution, along with the removal of ferrous iron and the production of bicarbonate, bring about a net increase in alkalinity. Transfer of metals from hydrous oxides to sulfides represents a relatively permanent fixation of the metals. Thus, the mineralization of metals such as iron and manganese in wetlands correlates with the fate of the sulfur. Over time, sulfate reduction is among the most important of the remediation processes taking place in AMD wetlands because it facilitates the fixation of metals by continuously generating alkalinity and maintaining pH in a favorable range for metal precipitation (Hedin and Nairn, 1992, p. 1).

As long as some alkalinity is available, metals precipitation and scavenging by hydrous oxides can continue in winter despite a decreased level of sulfate reduction due to diminished microbial activity.

The sulfate data appear in Figure 8. Of the four wetlands studied in this investigation, the greatest degree of reduction in surface-water sulfate levels takes place in the Midwestern wetland. In this wetland system, the outlet sulfate level is only 34 percent that of the influent level in winter and 49 percent of the influent level in summer. The winter data show that the most dramatic decrease in sulfate levels takes place in the final cells and that the decrease in sulfate is accompanied by dramatic decreases in the concentrations of most of the dissolved metals. Appreciable sulfate reduction is not observed in the total absence of alkalinity. For example, the winter water samples at Augusta Lake show little pH improvement, only a small reduction in sulfate levels, no alkalinity, and little removal of calcium, cadmium, magnesium, manganese, nickel, and lead.

Overall, there is not a high degree of efficiency in the removal of sulfate from the water in the studied wetlands and the final sulfate level is seldom less than the influent by more than a factor of three. Sulfur isotope studies indicate that an oxidized layer of iron oxides, calcium sulfates, and aluminum sulfates coat the top of the wetland substrates, isolating the sediments from the overlying water. This causes sulfate-reducing bacteria to use sulfate from within the oxidized layer rather than the sulfate in the water (Hsu and Maynard, 1999). Likewise, the bacterial reduction processes tend to fix the metals present in the oxidized layer instead of removing metals from the water column.

Figure 8. Graphs of wetland sulfate levels in surface water, with sampling points arranged in order from the inlet to the outlet of each wetland.



Conclusions

Seasonal differences in treatment effectiveness

The performance of wetlands has been reported to decline during winter, owing either to microbial inactivity at low temperatures or physical factors such as changes in the hydrologic regime (Hsu and Maynard, 1999, p. 231). Biological processes are an important determinant of both sulfate reduction and long-term metals fixation, and microbiological activity is temperature dependent. Therefore, the use of wetlands for water-quality improvement is widely criticized as ineffective during winter. However, the results of this study indicate that metals removal continues during winter. There are several possible reasons. For one, the most biologically active zones lay within solid phases at the bottom of wetland cells where the temperature during winter may not drop so low as to preclude microbial action. Another possible explanation is that the ability of hydrous oxides to scavenge metals from solution is not as impaired by low temperatures as microbial activity may be. During summer, microbial reactions and alkalinity production enhance the transfer of sorbed metals from oxides to less soluble mineral phases, which is an important means of stabilizing metals for long-term storage. Even if these microbial processes slow during winter, precipitation continues to create fresh oxide surfaces which can effectively scavenge metals. While metals scavenging occurs throughout the year, enough microbe-mediated sulfate reduction and metals fixation may occur in the warmer weather to

maintain the wetland's ability to accumulate metals for years.

Wetland design considerations

At both Augusta Lake and Tecumseh, ALDs are armored with precipitates and have failed. There are three types of metal precipitates which commonly clog ALDs: iron oxides, aluminum hydroxides, and gypsum. Iron, typically the most abundant metal in these waters, precipitates from anoxic ground water when it encounters oxygen. Oxygen can enter a drain when highly aerated rainfall is channeled directly to a shallow drain by impervious materials. Oxygen may also enter through the exit of the ALD during drought or other low flow conditions if the earthen dike that serves as an air lock does not retain enough water. At Augusta Lake, the AMD seeps are scattered and some are at relatively high elevations in the watershed. Because flow is intermittent, the drains are vulnerable to oxidation and armoring by iron.

Oxygen is not required to trigger aluminum precipitation. Acid Mine Drainage typically leaches aluminum from shales and clays associated with coal; when this acidic drainage enters an ALD, its pH increases rapidly. At a pH of 5 or above, aluminum hydrolyzes water to form aluminum hydroxide, which drops from solution as a very fine-grained precipitate. The small particle size of this precipitate allows it to effectively seal the interstitial spaces within the crushed limestone matrix.

Gypsum, a hydrated form of calcium sulfate, will form when calcium released from limestone in the drain combines with sulfate from the AMD. The dissolution of calcium carbonate inside an ALD produces acid-neutralizing bicarbonate. For every mole of bicarbonate released, a mole of calcium is also released. If the water in the drain contains more than 1,500 mg/L sulfate, under most conditions the water becomes saturated with respect to gypsum and the mineral precipitates from solution and blocks the drain (Behum and Kim, 1999).

The type of mineral at fault is best determined by excavating the drain and examining its contents. In 1998, the crushed limestone inside the failed ALD at Tecumseh was removed for examination by the IGS Geochemistry Section. The material was bound into a solid mass by a hard mineral that did not possess the softness and fine grain size characteristic of aluminum hydroxide. Microscopic analysis of the precipitate revealed a predominance of large crystals, their size suggesting a condition of prolonged supersaturation inside the ALD. X-Ray Diffraction analysis of ALD solids collected indicated the presence of gypsum, brushite, and andrealite. PhreeqC modeling based upon the chemical analysis of water collected from the clogged drain indicated that gypsum was supersaturated in the water inside the drain. The clogging of ALDs is often attributed to aluminum precipitation; however, it appears that in this case, gypsum precipitation was responsible for the failure of the ALD.

In contrast, the ALD at Midwestern continues to work well more than five years after construction. The water level in the anoxic wetland cell at the terminus of the ALD is kept below the surface of a pea gravel bed by use of a standpipe at the lower end of the cell. The design provides a constant level of anoxic water and excludes air from entering the drain. Also, there is insufficient aluminum in the AMD at Midwestern to initiate precipitation of aluminum hydroxide.

The successive alkalinity producing system at Augusta Lake was originally designed so that no less than 5 percent of the total flow would pass through the alkaline substrate bed. Flow measurements made in 2000 indicate that the ratio of water passing over the weir to that passing through the bed is 170 to 1. While alkalinity continued to be generated, as evinced by a pH

above 9 in the treated water, there was not enough flow to effectively neutralize the large volume of untreated AMD flowing over the weir.

Except for the failed SAPS, the water flow in all four wetlands is horizontal and the designs rely primarily upon diffusion to disperse alkalinity. Therefore, these wetlands require more surface area than a wetland having a vertical flow pattern. The use of horizontal flow patterns gives rise to a general precept regarding the construction of AMD treatment wetlands which has been summed by the phrase, "the bigger, the better." Large, simple cells can work just as well as intricately designed smaller cells, provided there is adequate mixing of AMD with alkalinity-bearing water and little channeling. A prime example of a large-scale design is at Tecumseh, where a very large final cell provides a long residence time and adequate surface area for precipitation of metals. However, due to poor mixing, the AMD flows along the extreme western portion of the cell and the large expanse of organic substrate in the rest of the cell is presently underutilized. It can be assumed that over time, precipitated solids will accumulate in the western portion where the AMD now flows, raising the elevation of the bottom of the cell. It is possible that if the bed becomes raised uniformly, the flow path of the AMD from Cell 4A will shift toward the center of Cell 5 and more of the cell will be utilized. But it is more likely that the increased rate of precipitation in the zone where the AMD encounters neutral water will cause a barrier of accumulated precipitates to form. In that case, the AMD flow will create its own isolated channel through the mass of precipitates, further decreasing mixing and providing an undesired direct path to the outlet. Although the large size of the final cell would seem to promote longevity by providing ample space for storage of precipitates, without efficient mixing it may be pointless to create an overly large wetland cell.

Both the SAPS at Augusta Lake and the organic substrate layer in Midwestern Cell 2C3 are composed of a mixture of 70 percent wood chips and 30 percent sewage sludge. At Augusta Lake, this substrate clogged easily with aluminum despite periodic back-flushing (Behum and Kim, 1999). At Midwestern, the sulfate level in the water of the cell containing this substrate remains the same or actually increases, whereas in the other cells in this wetland, the sulfate level is always lower than in the previous cell. Analysis of pore water in Cell 2C3 shows an elevated level of manganese and the surface water shows an increase in Eh in the summer. It is not clear whether a redox reaction with iron in the pore water has solubilized manganese from precipitates or if the manganese originates in the wood chip substrate. Manganese is a cofactor in photosynthesis and significant amounts are present in leaves. Entire branches of leaves may have been chipped and composted in the substrate, and this may serve as a source of manganese. Regardless of the source, the inconsistent treatment efficiency in this cell relative to the rest of the wetland, along with the failure of the Augusta SAPS, suggests that the composted wood chips do not make the best substrate for AMD treatment. It is quite possible that wood chip compost does not provide the nutrients favored by sulfate-reducing bacteria (B. Maynard, oral commun. 2001).

Environmental impact of sediment-bound metals

In general, the wetlands serve the desirable goal of reconcentrating the oxidation products of pyritic materials in a more secure location where they are less likely to be subjected to further weathering. This is consistent with the general reclamation goal of relocating acid-generating deposits from areas of high relief to low-lying areas where they can be isolated from air by burial or by submersion beneath a water table. To some extent, the sediments become compact and

uniform as they age, having smaller grain size and less pore space than the original spoil. This tends to stabilize solids and inhibit the release of metals and acidity as the solids age. The beds of the wetlands can permanently protect the sequestered materials, especially if the wetland is located as low as is feasible in the drainage system.

Despite the overall beneficial impact of AMD treatment wetlands, their sediment can also be viewed as a source as well as a sink for toxic metals (Webster and others, 1998). The practical significance of the metals concentrations in wetland sediments is open to interpretation and depends in part upon the land-use goals of the wetland's setting. The uptake and the toxicity of these metals is influenced by a variety of factors, including: (1) the presence of metal binding phases, both organic and inorganic; (2) aqueous complexing factors and the chemistry of overlying water and pore water; (3) the redox state of the metal; (4) burrowing of benthic organisms; and (5) the sensitivity of organisms exposed to the sediments (Chapman and others, 1999).

The bioavailability and toxicity of a metal depend strongly upon the exact physical and chemical form of the metal (EPA, 1992b). The form of the metal in turn depends upon the chemical characteristics of the surrounding water (EPA, 1992b). The EPA Office of Science and Technology considers sediment toxicity to be primarily determined by the concentrations of pollutant dissolved in interstitial water (EPA, 1992b). For this reason, pore water samples were prepared from selected sediments and analyzed for metals. The results appear in Table 4.

Iron and manganese appear in higher concentrations in the pore water than in the surface water. The trace elements arsenic, copper, molybdenum, lead, and selenium are somewhat higher as well. In general, the trace metals in the pore waters remain below EPA safe drinking water standards and are not likely to exert a toxic effect upon plants and wildlife; except for those waters where the nickel exceeds 100 ppb, the Midwestern samples with marginal arsenic levels; and the Augusta winter samples containing beryllium. Safe Drinking Water Act criteria appear in Table 5, where they are presented as indicators of surface-water quality.

Sediment quality criteria

The EPA has published sediment ecotoxicological screening criteria for metals (Hellyer and Balog, 1999). The EPA approach attempts to reconcile existing methods for assessing sediment toxicity, including Ontario's Provincial Sediment Quality Guidelines, the St. Lawrence Center of Environment Canada Guidelines, the Washington State Sediment Quality Standards, the NOAA Sediment ER Criteria, the Florida Department of Environmental Protection Criteria, the Biological Effects Database for Sediment, the EPA Ecotoxicological Thresholds for Sediments (Office of Solid Waste and Emergency Response), the EPA Region IV Screening Values, the EPA ARCS Program, and the Canadian Sediment Quality Guidelines.

Table 4. Pore water chemistry: major cations.

Sample	Sampling	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Si ^o	Sr
ID	Date									(estimated)	
		mg/L	mg/L	mg/L	mg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<i>WINTER</i>											
Augusta Lake wetland											
PondPC-1	03/07/00	45.0	<1	458	130.7	6.8	188.6	28.8	18.0	20	0.8
SAPSp pond	03/07/00	<1	<1	581	89.3	NA	254.2	21.5	22.0	6	0.2
Lake_inlet	03/07/00	<1	<1	522	124.5	7.8	218.5	16.4	28.0	8	0.2
Friar Tuck wetland											
Pond_weir	02/28/00	<1	<1	269	109.7	11.5	171.5	11.1	17.9	3	0.4
Midwestern wetland											
Cell1Aout	02/29/00	<1	<1	450	4.1	6.9	165.6	6.5	14.0	6	0.6
Cell1Bout	02/29/00	<1	<1	429	50.6	10.9	164.9	42.2	10.0	6	0.6
Cell2B2	02/29/00	<1	<1	413	44.8	15.5	135.6	10.0	12.5	12	0.6
Cell2B3	02/29/00	<1	<1	358	138.1	8.7	111.2	13.7	20.0	6	0.6
Cell2C2	02/29/00	<1	<1	783	61.0	14.5	226.7	18.5	6.6	3	0.6
Outlet	02/29/00	<1	<1	552	18.0	10.9	97.4	44.0	7.1	12	0.6
Tecumseh wetland											
Cell04A	02/29/00	<1	<1	292	304.4	17.6	214.6	2.8	98.0	10	0.4
Cell04B	02/29/00	<1	<1	304	105.6	11.2	228.0	3.6	120.0	2	1.3
<i>SUMMER</i>											
Augusta Lake wetland											
AugSEdrain	09/28/00	<1	<1	535	340.4	6.6	225.0	9.3	12.1	6	1.2
SAPSp pond	09/28/00	<1	<1	394	776.4	5.4	212.9	22.1	9.9	8	0.2
SAPSp repl	09/28/00	<1	<1	397	124.4	5.5	229.6	22.0	10.8	8	0.2
Aug mixed	09/28/00	<1	<1	478	552.2	7.2	217.1	26.1	11.7	7	1.0
Friar Tuck wetland											
Feeder	09/22/00	<1	<1	197	7.8	4.3	235.7	22.4	12.1	3	0.5
AMDinflow	09/22/00	<1	<1	353	1332.8	5.8	208.2	33.3	38.0	2	0.0
Pond Weir	09/22/00	<1	<1	97	99.1	6.8	108.5	10.2	10.0	3	0.4
Mix Zone	09/22/00	<1	<1	249	1266.6	2.8	197.9	41.9	20.0	2	0.0
Midwestern wetland											
Cell1Bout	09/19/00	<1	<1	256	45.1	11.8	291.3	0.0	26.2	6	0.6
Cell2B2	09/19/00	2.6	<1	345	4.7	11.3	250.0	7.5	26.0	12	0.8
Cell2B3	09/19/00	<1	<1	249	7.7	13.2	199.9	3.9	26.0	7	0.4
Cell2C2	09/19/00	<1	<1	255	3.9	13.7	165.1	25.2	6.9	3	0.6
Outlet	09/19/00	<1	<1	161	44.4	12.8	115.7	9.6	10.2	13	0.4
Tecumseh wetland											
CellSed2	09/19/00	<1	<1	147	7.9	10.1	254.4	3.7	104.0	4	1.6
Cell04A	09/19/00	8.7	<1	446	4522.0	4.2	264.7	27.0	128.0	6	1.4
Cell04B	09/19/00	<1	<1	267	1896.0	13.1	237.2	3.7	104.0	1	1.8
Cell05	09/19/00	<1	<1	175	5.0	9.0	248.8	6.5	84.0	3	1.2

Table 4. Pore water chemistry continued: trace metals.

Sample ID	Sampling Date	As µg/L	Be ug/L	Cd µg/L	Cr µg/L	Cu µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Se ug/L	V ug/L	Zn mg/L
Augusta Lake wetland												
PondPC-1	03/07/00	<1	29	9.4	6	11	13	194	4.5	1	9	4.2
SAPSpnd	03/07/00	<1	9	12.3	1	4	14	394	15.6	1	13	2.8
Lake_inlet	03/07/00	<1	<1	<0.2	<1	<2	15	116	1.6	1	10	0.5
Friar Tuck wetland												
Pond_weir	02/28/00	6	<1	0.4	<1	<2	9	9	3.6	3	5	0.4
Midwestern wetland												
Cell1Aout	02/29/00	2	<1	0.5	<1	31	18	52	9.3	3	7	0.1
Cell1Bout	02/29/00	1	<1	<0.2	<1	2	20	18	<0.5	2	2	0.2
Cell2B2	02/29/00	4	<1	<0.2	<1	13	57	16	6.0	1	<1	1.5
Cell2B3	02/29/00	3	<1	<0.2	<1	2	22	13	4.2	2	1	0.1
Cell2C2	02/29/00	6	2	2.0	<1	3	180	211	2.4	2	5	0.9
Outlet	02/29/00	6	<1	1.0	<1	<2	55	131	1.2	2	<1	0.1
Tecumseh wetland												
Cell04A	02/29/00	3	12	4.0	3	11	17	105	13.6	3	24	3.4
Cell04B	02/29/00	4	<1	0.5	<1	<2	60	6	3.6	4	4	0.1
Augusta Lake wetland												
AugSEdrain	09/28/00	<1	<1	0.7	12	<2	<1	11	0.5	<1	9	0.2
SAPSpnd	09/28/00	<1	6	3.3	20	15	<1	262	11.6	0	5	3.6
SAPSrepl	09/28/00	<1	7	NA	21	14	<1	273	11.7	7	12	3.4
Aug mixed	09/28/00	<1	<1	1.1	14	5	<1	88	0.8	2	<1	0.5
Friar Tuck wetland												
Feeder	09/22/00	2	<1	0.2	<1	3	3	8	0.7	4	3	0.1
AMDinflow	09/22/00	2	<1	2.0	1	<2	19	96	0.3	82	113	10.1
Pond Weir	09/22/00	<1	<1	2.1	8	5	5	2	1.4	7	7	0.1
Mix Zone	09/22/00	2	<1	6.1	7	13	7	559	0.9	1	102	3.2
Midwestern wetland												
Cell1Bout	09/19/00	1	<1	0.3	5	3	<1	107	1.1	<1	<1	1.3
Cell2B2	09/19/00	7	<1	1.2	1	11	<1	5	3.7	<1	<1	1.6
Cell2B3	09/19/00	3	<1	0.4	<1	7	<1	12	1.5	<1	<1	0.1
Cell2C2	09/19/00	3	<1	<0.2	0	2	<1	28	1.0	5	9	1.5
Outlet	09/19/00	15	<1	<0.2	3	3	5	7	4.7	1	9	0.1
Tecumseh wetland												
CellSed2	09/19/00	2	<1	0.2	2	3	10	10	1.2	4	<1	0.2
Cell04A	09/19/00	1	<1	9.9	7	<2	87	27	0.6	32	100	6.3
Cell04B	09/19/00	2	<1	0.3	12	9	7	155	0.6	7	34	1.4
Cell05	09/19/00	<1	<1	0.8	4	9	9	35	3.8	1	<1	0.2

Table 5. Table showing wetland effluent chemistry and EPA Safe Drinking Water Act Standards. Conductivity and pH are in standard units, all other parameters are in terms of parts per million.

Sample ID	EPA Standards	Augusta Mar-00	Augusta Sep-00	Friar Tuck Mar-00	Friar Tuck Sep-00	Midwestern Mar-00	Midwestern Sep-00	Tecumseh Mar-00	Tecumseh Sep-00
Conductivity	<400	3320	2840	1610	1760	1520	2190	2480	2330
pH	6.5-8.5	3.35	5.6	5.3	6.05	7	6.37	7.2	8.29
Primary EPA Standards									
As	0.05	<.001	<.001	<.001	<.001	0.001	0.001	<.001	0.001
Ba	2	0	0	0	0	0	0	0	0
Be	0.004	0.004	0.001	<.001	0.001	<.001	<.001	<.001	<.001
Cd	0.005	0.003	0.0003	0.0007	<.0002	0.0006	0.001	0.0002	0.0003
Cr	0.1	<.001	0.003	0.001	0.004	0.005	<.001	<.001	<.001
Cu	1.3	0.01	<.001	<.001	0.002	<.001	<.001	<.001	<.001
Ni	0.1	0.418	0.422	0.009	0.007	0.037	0.013	0.005	0.015
Pb	0.015	0.002	0.002	<.001	0.005	<.001	0.001	<.001	<.001
Se	0.05	<.001	<.001	<.001	<.001	0.001	<.001	0.001	0.001
NO3-	1	0	0	0	0	0	0	0	0
SO4-	400/500	2344	1997	930	1075	763	1172	1442	1405
Secondary EPA Standards									
Ca	<100	446.4	333	191	455	203	510	212	306
Fe	<.05	8.46	30.16	4.66	7.81	4.02	0.163	4.48	0.158
K	12.0-10.0	7.14	5.858	5.112	4.94	8.876	18.032	7.764	7.648
Mg	<30	205.2	126.12	129	157.5	84.64	96.74	222.2	89.16
Mn	<.02	23.78	18.67	8.31	4.68	0.72	8.44	0.32	0.25
Zn	<.1	0.94	0.56	0.24	0.11	0.09	0.12	0.51	0.08
TDS	100-500	3498	2957	1395	1759	1220	2100	2018	1961

The EPA New England Regional Lab has released a template which allows the comparison of sediment metals values with each of these sets of standards (EPA, 1996). Of these standards, the 1996 EPA OSWER Standards were chosen as a benchmark for comparison of the metals values found in sediments collected at the outlets of the four treatment wetlands. For purposes of this comparison, the total quantity of each metal present in the sediment was used rather than the values determined for individual extracts. The data are presented in Table 6. Of the toxic metals, only 12 of the 80 data points exceed the OSWER criteria. These 12 data points represent 11 different elements that exceed the criteria in sediments collected near the wetland outlets. The majority of these high values occur in the final cell of the Midwestern wetland. It is reasonable to conclude that enough potentially toxic metals have accumulated near the outlets of the treatment wetlands to warrant future efforts to contain these sediments in the wetlands, and to maintain the hydrologic regime so that the sediments are not flushed from the sites.

Table 6. Sediment values compared with EPA OSWER sediment quality criteria.

Major Elements												
Sample ID	Date	Ca ⁺⁺	Mg ⁺⁺	K ⁺	Na ⁺	Fe	Mn	Zn ⁺⁺	Ba ⁺⁺	Sr ⁺⁺	Al ⁺⁺⁺	Si [°]
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Augusta Outlet	2/29/2000	5979	381.2	554	42.0	63855	145.1	74.0	8.5	1698.1	1543.4	230.8
Augusta Mixing Zone	9/1/2000	1148	549.7	72	80.6	84244	304.5	157.0	0.0	38.5	1568.2	1024.9
Friar Tuck Outlet	2/29/2000	4909	729.9	1972	178.7	13333	238.1	8.4	24.4	1254.2	1065.2	255.2
Friar Tuck Outlet	9/1/2000	8021	810.3	161	50.3	27124	164.1	12.3	10.3	16.4	572.4	738.5
Tecumseh Outlet	3/1/2000	6226	691.1	918	330.2	40135	814.6	36.1	37.8	720.1	1582.4	345.6
Tecumseh Outlet	9/1/2000	3655	649.6	23	179.1	43170	1639.7	0.0	13.0	24.3	400.6	921.3
Midwestern Outlet	3/1/2000	5576	644.4	795	68.8	21419	413.9	56.8	20.5	1562.7	2126.6	787.2
Midwestern Outlet	9/1/2000	13023	1168	140	75.6	15026	753.1	88.1	15.8	49.9	1872.7	650.6
Trace Metals												
Sample ID	Date		As	Be	Cd ⁺⁺	Cr	Cu	Mo	Ni ⁺⁺	Pb	Se	V
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Augusta Outlet	2/29/2000		1.4	1.2	0.9	3.2	7.7	4.4	29.8	6.7	0.1	11.6
Augusta Mixing Zone	9/1/2000		0.1	0.8	0.9	1.2	1.6	0.4	55.2	0.6	0.1	1.9
Friar Tuck Outlet	2/29/2000		3.2	0.6	0.2	8.3	7.9	1.2	14.9	8.9	0.0	23.2
Friar Tuck Outlet	9/1/2000		2.2	0.6	0.2	11.4	4.3	0.2	7.6	6.7	0.1	12.6
Tecumseh Outlet	3/1/2000		2.3	0.5	0.2	4.1	6.2	2.4	16.8	4.3	0.1	7.5
Tecumseh Outlet	9/1/2000		2.5	0.6	0.2	3.9	6.4	1.3	87.2	11.6	0.2	11.9
Midwestern Outlet	3/1/2000		6.6	0.7	1.0	6.1	12.7	2.2	37.1	11.1	0.1	9.8
Midwestern Outlet	9/1/2000		3.5	1.1	1.5	12.0	10.8	1.3	63.1	20.7	0.4	12.1
Shaded values exceed OSWER criteria												

Water quality criteria

The data indicate that although alkalinity is essential to the successful removal of acidity and sulfate, a wetland that does not possess sufficient alkalinity still can successfully sequester metals. The mineral phases that precipitate at the low pH of an acidic wetland are less likely to go back into solution and be transported from the site than precipitates formed at a higher pH. While a wetland having a higher pH may release metals when the pH is suddenly lowered, this is not likely in the case of an acidic wetland, as the solids were already under acidic conditions when they precipitated. Even wetlands that are incapable of improving the acidity of the water flowing through them can provide an effective sink for potentially toxic metals.

The water-quality data for the wetlands effluents appears in Table 5 along with the maximum contaminant goals established under the Safe Drinking Water Act. The samples which exceed primary standards are highlighted in orange and the samples which exceed secondary standards are highlighted in yellow.

For the most part, the effluents from all four wetlands meet the maximum contaminant goals for metals. Only at Augusta Lake does the effluent exceed the criteria for nickel, beryllium, and sulfate, and there the ALDs and SAPS have clogged and failed. Secondary standards are not being met at any of the wetlands for conductivity, TDS, calcium, iron, and magnesium, though simple dilution with a tenfold volume of fresh water would bring the water into compliance for secondary standards as well. The pH standard was met during the March

sampling at Midwestern and during both samplings at Tecumseh.

The water analysis data support the prevailing views about the effectiveness of hydrous oxide phases at removing trace metals from solution. Gels of iron, manganese and aluminum can achieve the absorption of close to 100 percent of most dissolved trace metals even under slightly acidic conditions (Elliott and Dempsey, 1990, p. 332).

Summary of conclusions

The data generated in this study support the following general statements regarding the effectiveness of AMD treatment wetlands.

- The wetlands are effective at removing and storing toxic metals even in the case of the Augusta Lake wetland, where there is little alkalinity or sulfate reduction.
- Dilution is a significant contributor to water-quality in these wetlands.
- The wetlands effluents generally meet water quality standards for toxic metals in winter as well as summer.
- The wetlands studied are not very effective at removing sulfate. Establishing alkalinity is essential for the successful removal of sulfate from AMD.
- The estimated iron removal rates suggest that the sizing criteria in general use are accurate and that the wetlands have been sized adequately for iron removal.
- Large wetland cells can be as effective for metals removal as a larger number of smaller cells as long as there is adequate mixing, little channelization, and the water level is kept shallow enough to encourage the growth of *typha*.
- The wetlands that are most successful at metals removal and sequestration are those which incorporate manure-based organic substrates.
- The percentage of metals that are bio-available in the sediments varies widely from element to element. The distribution of metals between available and residual forms depends on the type of precipitates present and the influence of biological processes, especially sulfate reduction, which are enhanced by the presence of organic substrates. Over time, wetlands should transfer metals from available forms to more stable residual forms, provided that anaerobic conditions persist.
- The rapid precipitation of iron in the initial treatment cells does not simultaneously remove most of the trace metals from the AMD. Significant amounts of these metals pass through to the final treatment cells.
- Potentially toxic metals have accumulated in sediments near the outlets of the wetlands in significant amounts, indicating that the integrity of these cells should be maintained to prevent the sediments from being flushed from the sites. Metals sequestered in anoxic sediments will become increasingly stabilized over time.

Drought conditions prevailed in southwestern Indiana during the summer of 2002. Inspection of the Midwestern wetland in August 2002 indicated that there was no surface water present except in the first two oxidation ponds. Formerly anoxic sediments lay exposed in most of the other cells. The dried sediments were coated with oxidized iron and metal salts. The oxidized layer extended about 3 inches beneath the surface and terminated in a black horizon where moisture was still present. The black horizon contained detritus from wetland vegetation

mixed with the organic substrate placed in the cells during construction. In Cell 1B of the Midwestern wetland, where a shallow layer of water still remained, the oxidized layer was about 1 to 2 inches deep. Measurements taken with the Eh probe indicated that reducing conditions persisted in the sediments in this cell at a depth of 1 foot or more beneath the sediment surface. It is likely that microbial processes important in metals fixation will require some time to become reestablished after the wetlands are flooded once again.

This serious disruption of the water regime may have a profound effect on the metals levels in the wetlands effluent. As the wetland fills with water, metals salts coating the surface of the wetland cells are likely to redissolve, creating high concentrations of metals. However, the final wetland cell will have to accumulate water to a depth of 2 or 3 feet before there will be any flow over the spillway. The intensity and timing of rain events will probably exert a strong influence upon the metals concentrations in the effluent when the flow of water resumes at the outfall.

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APPENDIX A: Sediment extract analysis.

Site ID	Sampling Date	Al mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	Si mg/L	Sr mg/L	Zn mg/L
<i>WINTER</i>												
Augusta Lake												
SAPS Pond OX	3/1/00	67.2	0.0	516.7	40060	346.6	183.1	0.0	22.2	1.0	117	0.9
Lake Ox	3/1/00	1037.6	3.3	918.0	55648	304.2	334.3	143.9	23.7	3.0	1687	0.0
SAPS Pond HCl	2/29/00	2.6	0.2	112.3	5103	190.3	16.7	6.3	10.8	31.1	0	0.4
Lake HCl	2/29/00	505.7	5.2	5061.5	8208	249.6	46.8	1.2	18.4	227.8	11	74.0
Friar Tuck												
AMD Ox	2/29/00	154.4	0.0	5291.6	55376	56.9	134.5	0.0	0.3	4.8	1114	0.0
Mix zone Ox	2/29/00	885.4	1.6	380.7	63318	332.7	114.6	83.6	0.0	1.5	3047	101.9
Weir Ox	2/29/00	419.4	15.9	13.5	11997	1396.7	658.5	176.6	127.5	1.6	1241	4.5
AMD HCl	2/29/00	413.8	5.2	1358.1	14292	931.7	26.2	0.0	46.7	177.5	0	2.1
Mix zone HCl	2/29/00	634.7	0.7	36.8	7915	274.0	24.7	0.0	14.1	122.0	5	34.1
Weir HCl	2/29/00	645.9	8.5	4895.4	1337	575.1	71.4	61.5	51.2	253.6	14	3.9
Tecumseh												
Cell 1 Inlet Ox	3/1/00	480.1	0.0	0.0	60194	1272.4	291.2	39.2	234.4	11.4	381	0.0
Cell 2 Ox	3/1/00	630.1	3.8	376.7	66304	915.5	425.0	83.4	45.9	7.6	964	0.0
Cell 4A Ox	3/1/00	0.0	0.0	208.4	100971	2439.3	243.9	9.9	220.5	4.5	0	0.0
Cell 4B Ox	3/1/00	484.8	2.2	0.0	25890	952.8	344.8	67.6	139.1	4.7	858	17.3
Cell 5 Ox	3/1/00	1026.0	9.9	57.2	35558	642.6	398.1	516.7	261.8	5.3	714	6.8
Cell 1 Inlet HCl	3/1/00	72.7	3.2	706.7	2240	349.4	20.1	10.3	9.5	50.7	0	6.4
Cell 2 HCl	3/1/00	122.0	2.7	532.6	1698	146.8	12.2	4.7	12.3	111.3	2	6.7
Cell 4A HCl	3/1/00	67.0	2.7	34.5	10351	780.5	27.3	1.5	106.6	26.9	0	2.0
Cell 4B HCl	3/1/00	457.4	7.4	1515.3	1493	573.3	85.3	10.5	61.6	103.2	3	6.2
Cell 5 HCl	3/1/00	556.4	27.8	6169.3	4577	275.4	293.0	297.9	68.4	340.3	6	29.3
Midwestern												
Upper Cell 1 Ox	3/1/00	6021.1	3.7	59.6	94654	1186.6	1828.7	59.3	0.0	3.2	2004	253.2
Cell 1A Ox	3/1/00	3030.7	2.7	1911.9	78890	2664.0	506.2	170.3	0.0	13.2	0	0.0
Cell 1B Ox	3/1/00	3694.7	4.5	0.0	22741	5622.9	261.9	677.8	0.0	0.0	0	0.0
Cell 2A Ox	3/1/00	881.9	3.2	0.0	13823	2954.5	259.4	520.3	76.2	1.9	749	0.0
Cell 2B2 Ox	3/1/00	1547.6	2.4	0.0	21606	2242.6	483.6	213.0	284.8	0.1	3892	0.0
Cell 2C2 Ox	3/1/00	2988.5	12.8	0.0	20115	7533.6	652.1	285.2	114.1	5.0	9306	68.5
Outlet Ox	3/1/00	932.6	11.3	0.0	17426	465.9	347.6	304.2	30.4	1.8	1547	36.8
Cell 1 HCl	2/29/00	133.1	12.3	10751.3	1990	387.3	0.0	104.5	50.5	163.6	2	2749.9
Cell 1A HCl	2/29/00	17.6	18.8	8141.9	23478	986.0	180.3	102.9	59.1	3061.2	20	3.8
Cell 1B HCl	2/29/00	67.7	3.7	3726.4	4469	558.0	34.9	851.3	36.6	114.3	2	14.7
Cell 2A HCl	2/29/00	221.1	4.8	3810.8	7739	334.8	206.4	521.0	11.4	298.7	8	18.0
Cell 2B2 HCl	3/1/00	192.1	3.5	2833.4	2817	197.3	41.1	229.8	49.0	99.8	1	18.1
Cell 2C2 HCl	3/1/00	1201.7	24.1	14221.0	2072	405.8	321.4	112.9	45.9	468.3	17	31.8
Outlet HCl	3/1/00	1194.0	9.3	5576.3	3993	329.0	296.8	109.6	38.4	785.4	16	20.1

Appendix A continued

Site ID	Sampling Date	As µg/L	Be µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Se µg/L	V µg/L
WINTER											
Augusta Lake											
SAPS Pond OX	3/1/00	108.8	19.1	10.5	420.1	248.2	201.5	3934	71.6	30.6	593.9
Lake Ox	3/1/00	863.2	1078.5	284.7	2173.0	344.7	2183.5	6744	401.6	36.0	10015.1
SAPS Pond HCl	2/29/00	67.9	5.1	9.3	205.7	246.8	376.4	5451	216.0	5.1	275.6
Lake HCl	2/29/00	540.5	124.2	616.0	1071.3	7377.4	2195.0	23009	6263.5	17.0	1576.5
Friar Tuck											
AMD Ox	2/29/00	29.1	105.9	31.8	4753.2	807.6	158.1	35285	6.6	17.2	5359.6
Mix zone Ox	2/29/00	34.4	829.3	373.7	1917.6	458.9	101.5	9015	614.6	13.1	11351.7
Weir Ox	2/29/00	2143.2	525.1	26.8	5750.9	321.5	517.4	5715	491.2	8.9	18860.2
AMD HCl	2/29/00	80.5	70.3	16.6	3067.2	1060.7	216.0	26058	493.3	15.3	86277.8
Mix zone HCl	2/29/00	134.9	213.4	174.9	702.3	3153.3	198.3	31148	1587.7	184.5	1892.0
Weir HCl	2/29/00	1103.7	76.8	128.6	2589.7	7590.5	725.1	9198	8426.3	8.9	4372.1
Tecumseh											
Cell 1 Inlet Ox	3/1/00	406.2	205.5	14.7	611.8	171.3	3066.1	7292	34.3	36.7	1168.2
Cell 2 Ox	3/1/00	564.0	259.9	50.7	784.7	1471.3	1101.9	8975	482.3	59.3	1490.9
Cell 4A Ox	3/1/00	202.0	12.3	9.9	295.7	221.8	1219.6	8156	93.6	64.1	1282.2
Cell 4B Ox	3/1/00	808.0	357.3	45.1	1963.6	3122.4	943.2	17865	189.9	83.7	4152.5
Cell 5 Ox	3/1/00	1218.5	472.9	44.5	2420.3	250.4	1605.2	8735	425.6	94.6	5658.4
Cell 1 Inlet HCl	3/1/00	60.2	7.3	41.1	2378.5	1071.8	205.0	2290	371.5	51.4	281.9
Cell 2 HCl	3/1/00	77.1	7.4	93.4	445.0	3455.9	168.3	3767	1080.5	72.7	404.9
Cell 4A HCl	3/1/00	59.1	7.4	56.2	1833.1	384.4	188.3	4169	130.8	35.5	510.0
Cell 4B HCl	3/1/00	439.8	13.1	89.0	3272.5	40395.7	227.8	26992	1848.3	62.8	1083.9
Cell 5 HCl	3/1/00	1031.9	34.9	160.4	1725.6	5995.9	772.1	8053	3902.6	8.7	1819.7
Midwestern											
Upper Cell 1 Ox	3/1/00	4160.3	9865.1	2979.3	1099.3	366.4	2494.5	37149	47.9	50.7	1124.6
Cell 1A Ox	3/1/00	56.1	60.1	4.0	270.4	10.0	463.3	12519	20.0	6.0	254.4
Cell 1B Ox	3/1/00	1064.2	260.6	49.4	630.9	329.1	737.8	39443	13.7	21.9	556.8
Cell 2A Ox	3/1/00	1948.5	357.2	68.4	2280.0	142.5	1013.7	7239	185.3	11.4	604.2
Cell 2B2 Ox	3/1/00	904.0	1018.5	198.6	1284.8	584.0	322.4	43987	240.6	63.1	197.6
Cell 2C2 Ox	3/1/00	3088.2	3304.6	171.1	5389.6	4681.5	1824.2	55214	143.6	61.0	3123.6
Outlet Ox	3/1/00	5368.1	588.2	106.8	3680.8	1904.8	1186.4	22535	231.7	38.6	1736.2
Cell 1 HCl	2/29/00	1815.4	34.3	229.2	395.2	7851.7	714.0	158	2463.5	118.6	268.7
Cell 1A HCl	2/29/00	636.6	168.9	3.9	330.0	368.8	370.7	16518	240.7	38.8	1890.0
Cell 1B HCl	2/29/00	280.3	13.2	457.5	396.7	7854.2	145.4	18194	830.4	126.9	81.2
Cell 2A HCl	2/29/00	1186.7	54.9	513.4	678.9	8435.1	1243.4	15020	4171.1	4.7	1085.3
Cell 2B2 HCl	3/1/00	663.1	63.1	386.5	305.1	25669.1	1132.9	61630	1049.5	30.5	242.7
Cell 2C2 HCl	3/1/00	757.3	454.4	2027.1	1883.4	25339.2	1395.9	17553	9104.6	21.4	2549.5
Outlet HCl	3/1/00	1223.9	81.6	934.4	2434.6	10778.0	1016.0	14594	10824.1	75.0	8019.7

Appendix A continued

Site ID	Sampling Date	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Si	Sr	Zn
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
SUMMER												
Augusta Lake												
Pond PC2 Ox	9/28/00	0.0	0.0	0.0	41080	30.6	40.6	95.5	13.1	1551.6	0	0.0
SAPS Ox	9/28/00	0.0	1.7	34.5	58390	8.6	110.5	38.0	31.8	215.9	3	12.1
Mix zone Ox	9/28/00	1292.7	0.0	110.3	81490	33.8	344.1	251.5	62.2	842.7	9	112.5
PondPC2 HCl	9/19/00	35.5	2.1	940.1	320	41.8	198.5	6.3	4.0	29.2	19	6.3
SAPS HCl	9/28/00	36.4	0.0	364.2	1020	31.0	145.7	3.6	14.9	18.2	0	0.0
Mix zone HCl	9/28/00	275.5	0.0	1038.3	2755	38.1	205.5	53.0	18.4	182.2	30	44.5
Friar Tuck												
Feeder Ox	9/22/00	0.0	0.0	0.0	53954	39.8	0.0	595.7	43.0	0.0	0	0.0
AMD Ox	9/22/00	745.8	31.3	759.2	100257	1719.3	355.0	60.3	346.3	261.2	36	129.5
Mix zone Ox	9/22/00	0.0	10.9	0.0	95854	1763.4	298.0	60.1	243.3	432.0	5	0.0
Weir Ox	9/22/00	330.3	0.0	0.0	26239	89.2	451.3	139.5	33.4	560.1	0	0.0
Feeder HCl	9/22/00	102.7	22.3	40283.3	4243	35.3	634.2	4470.5	44.7	424.3	56	24.6
AMD HCl	9/22/00	132.0	4.6	45.5	2800	304.2	195.8	4.6	15.7	113.8	9	2.3
Mix zone HCl	9/22/00	251.5	16.4	300.7	1072	78.2	27.3	43.7	6.6	196.8	44	27.3
Weir HCl	9/22/00	242.1	10.3	8021.4	886	71.4	359.0	24.6	16.8	178.5	16	12.3
Tecumseh												
Cell 2 Ox	9/19/00	241.7	0.0	0.0	52291	54.7	410.7	526.3	121.6	8258.1	0	0.0
Cell 4A Ox	9/19/00	0.0	0.0	0.0	108015	405.6	0.0	16.0	118.0	0.0	0	0.0
Cell 4B Ox	9/19/00	0.0	0.0	0.0	66809	179.4	238.1	11.3	156.4	160.9	0	0.0
Cell 5 Ox	9/19/00	399.0	0.0	0.0	40835	21.0	617.2	1558.6	149.8	918.0	0	0.0
Cell 2 HCl	9/19/00	111.9	4.4	127.1	1394	14.5	175.8	72.6	17.1	45.0	9	2.9
Cell 4A HCl	9/19/00	19.0	1.9	512.5	4252	916.2	38.0	3.8	78.8	102.5	9	3.8
Cell 4B HCl	9/19/00	1.8	0.0	233.5	749	8.9	160.6	7.1	12.7	28.5	20	0.0
Cell 5 HCl	9/19/00	1.6	13.0	3655.4	2334	1.6	32.4	81.1	29.3	3.2	24	0.0
Midwestern												
Cell 1A Ox	9/19/00	0.0	9.0	74.9	36641	45.7	385.0	1295.8	41.8	2636.5	7	25.5
Cell 2A Ox	9/19/00	1590.4	10.1	0.0	14478	88.9	680.7	129.7	33.4	954.2	4	16.2
Cell 2B Ox	9/19/00	2295.8	6.5	43.4	12226	4.3	267.2	834.0	61.7	1248.9	4	45.6
Cell 2C2 Ox	9/19/00	2493.0	21.4	0.0	19228	77.0	413.4	7008.6	65.0	1628.7	4	49.9
Outlet Ox	9/19/00	1232.8	8.1	0.0	12937	97.9	562.6	544.3	39.2	426.5	2	67.0
Cell 1A HCl	9/19/00	726.5	15.0	3819.9	1092	25.5	31.5	269.6	15.3	46.4	6	6.0
Cell 2A HCl	9/19/00	679.4	7.9	3595.6	2569	56.8	216.5	39.7	22.4	401.3	12	11.9
Cell 2B HCl	9/19/00	81.4	5.4	1276.0	407	61.1	13.6	54.3	26.3	19.0	8	10.9
Cell 2C2 HCl	9/19/00	205.4	12.7	2607.0	1654	1.8	181.8	621.8	36.7	36.4	25	12.7
Outlet HCl	9/19/00	639.8	7.7	13022.9	2088	41.8	605.4	208.8	36.4	224.1	48	21.1

Appendix A continued.

Site ID	As µg/L	Be µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Se µg/L	V µg/L
<i>SUMMER</i>										
Augusta Lake										
Pond PC2 Ox	488.1	389.1	1503.8	407.9	344.4	453.8	23226	446.1	41.1	739.3
SAPS Ox	252.8	25.0	18.3	337.3	773.2	500.3	14645	75.3	38.9	715.8
Mix zone Ox	14.8	454.7	418.7	306.2	307.5	3.8	41429	11.0	68.0	781.6
PondPC2 HCl	135.1	10.4	187.4	157.0	1066.9	45.3	11364	279.1	36.2	12.5
SAPS HCl	62.4	9.1	15.6	114.8	193.2	4.7	8359	115.2	6.9	9.1
Mix zone HCl	35.2	346.0	458.6	857.6	1290.9	404.9	13731	617.1	25.2	1113.5
Friar Tuck										
Feeder Ox	344.9	433.9	12.0	364.6	598.3	29.2	39828	98.4	48.5	2275.3
AMD Ox	200.2	138.8	52.9	3679.8	565.4	13.5	21592	2471.8	56.5	72524.6
Mix zone Ox	593.3	173.5	623.9	4021.7	1283.3	112.8	24141	3398.4	93.6	65889.4
Weir Ox	906.8	533.8	29.9	10196.0	430.2	43.6	5395	3210.6	22.9	12128.5
Feeder HCl	458.9	280.0	802.1	364.4	2014.8	27.6	18065	2387.1	42.5	53.2
AMD HCl	107.1	30.3	29.0	688.0	445.1	1.1	10632	810.3	79.0	1039.5
Mix zone HCl	53.6	13.7	347.8	868.3	2865.2	46.2	13342	3854.9	105.0	622.5
Weir HCl	1285.7	58.1	148.3	1230.1	3856.8	179.6	2175	3446.5	102.2	494.8
Tecumseh										
Cell 2 Ox	653.2	323.7	45.3	626.4	255.5	1083.0	21572	1018.0	20.3	3724.3
Cell 4A Ox	9.9	28.0	7.9	53.9	142.6	65.7	19168	9.9	9.9	573.7
Cell 4B Ox	118.3	44.2	23.0	255.5	515.3	575.2	14784	388.7	33.1	1846.8
Cell 5 Ox	1311.6	577.5	24.2	2860.0	576.2	600.2	20215	3377.5	35.4	10978.8
Cell 2 HCl	243.7	27.7	91.9	289.2	3335.2	163.9	8193	2536.2	109.8	137.2
Cell 4A HCl	26.9	44.8	72.4	290.6	36.4	9.5	11198	604.9	9.5	218.1
Cell 4B HCl	27.7	0.0	59.8	185.4	817.3	23.3	12720	432.1	18.3	8.9
Cell 5 HCl	1185.3	56.8	149.1	1048.3	5835.6	666.6	20344	8177.9	118.4	922.5
Midwestern										
Cell 1A Ox	284.5	136.9	26.5	347.2	7.5	155.6	22320	326.1	10.6	447.2
Cell 2A Ox	2058.4	506.5	146.2	4041.9	464.4	1003.9	27128	7253.1	25.6	11823.7
Cell 2B Ox	188.3	1089.0	184.4	420.7	121.8	185.7	23588	825.4	39.6	301.5
Cell 2C2 Ox	571.1	1280.2	155.7	543.9	1393.5	336.1	34482	431.8	57.6	892.8
Outlet Ox	995.0	847.9	169.2	7792.9	584.7	263.0	42732	7116.6	25.9	9425.9
Cell 1A HCl	181.7	7.5	258.4	136.4	652.1	24.3	10082	849.8	7.5	7.5
Cell 2A HCl	1694.5	89.8	925.5	3128.7	6974.6	3520.1	17422	6495.9	934.1	2942.0
Cell 2B HCl	206.9	47.4	516.9	172.6	1532.0	248.2	67004	815.3	82.8	13.6
Cell 2C2 HCl	186.9	94.3	1898.0	412.9	1365.1	124.4	13599	2218.0	101.3	0.0
Outlet HCl	2540.2	226.4	1359.6	4239.4	10260.5	996.2	24042	13563.2	354.4	2666.7

APPENDIX B: Distribution of metals between extracts as a percentage.

Sample	Sampling Date	Al	Ba	Ca	Fe	K	Na	Mg	Mn	Si°	Sr	Zn
Augusta Lake Wetland												
SAPSOX	03/07/00	97	0	83	89	66	68	92	0	3	99	75
SAPSHCl	03/07/00	3	100	17	11	33	32	8	0	97	1	25
LakeOX	03/07/00	67	38	85	87	54	66	87	24	2	99	0
LakeHCl	03/07/00	33	62	15	13	46	44	13	76	98	1	100
Friar Tuck Wetland												
FT02XOX	02/29/00	29	0	81	81	6	0	85	0	3	100	0
FT02XHCl	02/29/00	71	100	19	19	94	100	15	0	97	0	100
FT07OX	02/29/00	59	75	92	89	56	0	83	0	1	99	76
FT07HCl	02/29/00	41	25	8	11	44	100	17	0	99	1	24
FT03OX	02/29/00	39	65	1	90	71	71	68	74	0	99	50
FT03HCl	02/29/00	60	35	99	10	29	29	32	26	100	1	50
Tecumseh Wetland												
Tec01OX	03/01/00	87	0	0	96	78	96	94	0	18	99	0
Tec01HCl	03/01/00	13	100	100	4	22	4	6	0	82	1	100
Tec02Ox	03/01/00	86	63	47	98	88	82	98	0	8	100	0
Tec02HCl	03/01/00	14	37	53	2	12	18	2	100	92	0	100
Tec04AOx	03/01/00	0	0	84	89	73	64	89	0	14	0	0
Tec04AHCl	03/01/00	100	100	16	11	27	36	11	0	86	0	100
Tec04BOx	03/01/00	59	29	0	96	69	79	98	100	1	99	79
Tec04BHCl	03/01/00	41	71	100	4	31	21	2	0	99	1	21
Tec05Ox	03/01/00	65	99	1	89	70	80	58	64	2	5	19
Tec05HCl	03/01/00	35	1	99	11	30	20	42	36	98	95	81
Midwestern Wetland												
C1AinOX	03/01/00	83	25	1	98	77	0	100	38	2	100	10
C1AinHCl	03/01/00	17	75	99	2	23	100	0	62	98	0	90
C1AoutOx	03/01/00	99	15	22	80	77	0	77	100	1	0	0
C1AouHCl	03/01/00	1	85	78	20	23	100	23	0	99	100	100
Cell1BOX	03/01/00	98	55	0	84	91	0	88	44	0	0	0
Cell1BHCl	03/01/00	2	45	100	16	9	100	12	56	100	100	100
C2B2OX	03/01/00	79	39	0	63	89	86	54	48	1	99	0
C2B2HCl	03/01/00	21	61	100	37	11	14	46	52	99	1	100
C2B3OX	03/01/00	88	38	0	87	90	84	90	45	0	100	89
C2B3HCl	03/01/00	12	62	100	13	10	16	10	55	100	0	11
C12C2OX	03/01/00	71	35	0	91	95	71	67	71	1	100	68
C12C2HCl	03/01/00	29	65	100	9	5	29	33	29	99	0	32
OutletOX	03/01/00	44	55	0	82	59	44	54	74	0	99	65
OutletHCl	03/01/00	56	45	100	18	41	56	46	26	100	1	35

Appendix B continued

Sample	Sampling Date	As	Be	Cd	Cr	Cu	Mo	Ni	Pb	Se	V
Augusta Lake Wetland											
SAPSOX	03/07/00	63	100	54	68	51	36	43	26	100	69
SAPSHCl	03/07/00	37	0	46	32	49	64	57	74	0	31
LakeOX	03/07/00	61	89	31	66	4	49	22	6	67	86
LakeHCl	03/07/00	39	11	69	33	96	51	78	94	33	14
Friar Tuck Wetland											
FT02XOX	02/29/00	28	62	67	63	45	45	60	0	55	6
FT02XHCl	02/29/00	72	38	33	37	55	55	40	100	45	94
FT07OX	02/29/00	21	80	69	74	13	35	23	29	7	86
FT07HCl	02/29/00	79	20	31	26	87	65	77	71	93	14
FT03OX	02/29/00	66	87	17	69	4	42	0	5	0	81
FT03HCl	02/29/00	33	13	83	31	96	58	0	95	0	19
Tecumseh Wetland											
Tec01OX	03/01/00	87	100	26	20	14	94	76	10	42	81
Tec01HCl	03/01/00	13	0	74	80	86	6	24	90	58	19
Tec02Ox	03/01/00	90	100	40	68	34	89	75	35	50	82
Tec02HCl	03/01/00	10	0	60	32	66	11	25	65	50	18
Tec04AOx	03/01/00	75	0	16	1	33	85	63	38	61	68
Tec04AHCl	03/01/00	25	0	84	99	67	15	37	62	39	32
Tec04BOx	03/01/00	71	100	87	44	10	85	47	12	64	84
Tec04BHCl	03/01/00	29	0	13	56	90	15	53	88	36	16
Tec05Ox	03/01/00	54	93	22	59	4	68	52	10	100	76
Tec05HCl	03/01/00	46	7	78	41	96	32	48	90	0	24
Midwestern Wetland											
C1AinOX	03/01/00	71	99	93	75	5	79	99	2	21	82
C1AinHCl	03/01/00	29	1	7	25	95	21	1	98	39	18
C1AoutOx	03/01/00	10	30	0	92	0	99	48	9	15	14
C1AouHCl	03/01/00	90	70	0	8	100	1	52	91	85	86
Cell1BOX	03/01/00	79	100	10	1	0	10	69	0	15	87
Cell1BHCl	03/01/00	21	0	90	99	100	90	31	100	85	13
C2B2OX	03/01/00	61	86	11	76	2	43	31	4	100	34
C2B2HCl	03/01/00	39	14	89	24	98	57	69	96	0	66
C2B3OX	03/01/00	55	94	32	79	2	21	39	17	65	43
C2B3HCl	03/01/00	45	6	68	21	98	79	61	83	35	57
C12C2OX	03/01/00	80	88	8	74	16	57	76	1	74	55
C12C2HCl	03/01/00	20	12	92	26	84	43	24	99	26	45
OutletOX	03/01/00	81	88	10	60	15	54	61	2	18	18
OutletHCl	03/01/00	19	12	90	30	85	46	39	98	82	82

Appendix B continued

Sample	Sampling	Al	Ba	Ca	Fe	K	Na	Mg	Mn	Si ^o	Sr	Zn
Augusta Lake Wetland												
PC2 OX	09/28/00	0	0	0	99	42	77	17	94	98	0	0
PC2HCl	09/28/00	100	100	100	1	58	23	83	6	2	100	100
SAPSOX	09/28/00	0	100	9	98	22	68	43	91	92	100	100
SAPSHCl	09/28/00	100	0	91	2	78	32	57	9	8	0	0
Lake OX	09/28/00	82	0	10	97	47	77	63	83	82	23	72
LakeHCl	09/28/00	18	0	90	3	53	23	37	17	18	77	28
Friar Tuck Wetland												
FeederOX	09/22/00	0	0	0	93	53	49	0	12	0	0	0
Feeder HCl	09/22/00	100	100	100	7	47	51	100	88	100	100	100
AMDOX	09/22/00	85	87	94	97	85	96	64	93	70	80	98
AMDHCl	09/22/00	15	13	6	3	15	4	36	7	30	20	2
Mixed OX	09/22/00	0	40	0	99	96	97	92	58	69	11	0
Mixed HCl	09/22/00	100	60	100	1	4	3	8	42	31	89	100
Weir OX	09/22/00	58	0	0	97	56	67	56	85	76	0	0
Weir HCl	09/22/00	42	100	100	3	44	33	44	15	24	100	100
Tecumseh Wetland												
Cell2 OX	09/19/00	68	0	0	97	79	88	70	88	99	0	0
Cell2 HCl	09/19/00	32	100	100	3	21	12	30	12	1	100	100
Cell4A OX	09/19/00	0	0	0	96	31	60	0	81	0	0	0
Cell4A HCl	09/19/00	100	100	100	4	69	40	100	19	100	100	100
Cell4B OX	09/19/00	0	0	0	99	95	93	60	61	85	0	0
Cell4BHCl	09/19/00	100	0	100	1	5	7	40	39	15	100	0
Outlet OX	09/19/00	100	0	0	95	93	84	95	95	100	0	0
Outlet HCl	09/19/00	0	100	100	5	7	16	5	5	0	100	0
Midwestern Wetland												
M1AOx	09/19/00	0	38	2	97	64	73	92	83	98	56	81
M1AHCl	09/19/00	100	63	98	3	36	27	8	17	2	44	19
M2AOx	09/19/00	70	56	0	85	61	60	76	77	70	25	58
M2AHCl	09/19/00	30	44	100	15	39	40	24	23	30	75	42
M2BOx	09/19/00	97	55	3	97	7	70	95	94	99	35	81
M2BHCl	09/19/00	3	45	97	3	93	30	5	6	1	65	19
M2C4Ox	09/19/00	92	63	0	92	98	64	69	92	98	12	80
M02C4HCl	09/19/00	8	37	100	8	2	36	31	8	2	88	20
Outlet OX	09/19/00	66	51	0	86	70	52	48	72	66	4	76
Outlet HCl	09/19/00	34	49	100	14	30	48	52	28	34	96	24

Appendix B continued.

Sample	Sampling Date	As	Be	Cd	Cr	Cu	Mo	Ni	Pb	Se	V
Augusta Lake Wetland											
PC2 OX	09/28/00	78	97	89	72	24	91	67	62	53	98
PC2HCl	09/28/00	22	3	11	28	76	9	33	38	47	2
SAPSOX	09/28/00	80	73	54	75	80	99	64	40	85	99
SAPSHCl	09/28/00	20	27	46	25	20	1	36	60	15	1
Lake OX	09/28/00	30	57	48	26	19	1	75	2	73	41
LakeHCl	09/28/00	70	43	52	74	81	99	25	98	27	59
Friar Tuck Wetland											
FeederOX	09/22/00	43	61	1	50	23	51	69	4	53	98
Feeder HCl	09/22/00	57	39	99	50	77	49	31	96	47	2
AMDOX	09/22/00	65	82	65	84	56	92	67	75	42	99
AMDHCl	09/22/00	35	18	35	16	44	8	33	25	58	1
Mixed OX	09/22/00	92	93	64	82	31	71	64	47	47	99
Mixed HCl	09/22/00	8	7	36	18	69	29	36	53	53	1
Weir OX	09/22/00	41	90	17	89	10	20	71	48	18	96
Weir HCl	09/22/00	59	10	83	11	90	80	29	52	82	4
Tecumseh Wetland											
Cell2 OX	09/19/00	73	92	33	68	7	87	72	29	16	96
Cell2 HCl	09/19/00	27	8	67	32	93	13	28	71	84	4
Cell4A OX	09/19/00	27	38	10	16	80	87	63	2	51	72
Cell4A HCl	09/19/00	73	62	90	84	20	13	37	98	49	28
Cell4B OX	09/19/00	81	100	28	58	39	96	54	47	64	100
Cell4BHCl	09/19/00	19	0	72	42	61	4	46	53	36	0
Outlet OX	09/19/00	53	91	14	73	9	47	50	29	23	92
Outlet HCl	09/19/00	47	9	86	27	91	53	50	71	77	8
Midwestern Wetland											
M1AOx	09/19/00	61	95	9	72	1	87	69	28	59	98
M1AHCl	09/19/00	39	5	91	28	99	13	31	72	41	2
M2AOx	09/19/00	55	85	14	56	6	22	61	53	3	80
M2AHCl	09/19/00	45	15	86	44	94	78	39	47	97	20
M2BOx	09/19/00	48	96	26	71	7	43	26	50	32	96
M2BHCl	09/19/00	52	4	74	29	93	57	74	50	68	4
M2C4Ox	09/19/00	75	93	8	57	51	73	72	16	36	100
M02C4HCl	09/19/00	25	7	92	43	49	27	28	84	64	0
Outlet OX	09/19/00	28	79	11	65	5	21	64	34	7	78
Outlet HCl	09/19/00	72	21	89	35	95	79	36	66	93	22

