# Ameliorative Designs to Improve the Efficiency of Constructed Wetlands Treating High Metal Load Acid Mine Drainage in the Rock Creek Watershed

## Final Report

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# PROJECT SUMMARY

The Rock Creek watershed was identified in the 1992 nonpoint source priority assessment performed under section 319 of the Clean Water Act as being impaired due to low pH and high levels of metals, sulfates, and sediment discharged by acid mine drainage (AMD) which was released from underground mines in the area. Deteriorated water quality deriving from past mining activities has resulted in several documented fish kills and degradation of aesthetic values in Rock Creek. The influence of AMD not only seriously limits both consumptive and nonconsumptive water uses, but also adversely effects recreational activities in the area. Jones Branch is one of the Rock Creek tributaries which significantly impairs the water quality in the watershed. The point at which Jones Branch empties into Rock Creek signifies the location where the protected and relatively pristine Kentucky Wild River is transformed into a AMD polluted stream that periodically displays signs of stressed biological activity.

In an attempt to improve water quality and protect aquatic habitat, the U.S. Forest Service constructed an artificial wetland to treat the Jones Branch drainage in the spring of 1989. The project was a cooperative effort between the Kentucky Division of Abandoned Lands, U.S. Office of Surface Mining, USDA Forest Service Northeastern Forest Experimental Station, and the Daniel Boone National Forest. The original surface flow wetland substantially reduced metal concentrations and acidity of AMD during the first

year of treatment. During the following three years, however, and during periods of high flow rate (> 40 lpm) the efficiency of the wetland was drastically reduced due to insufficient size of treatment area forced by topographic limitations, metal overloading, and inadequate design, which limits residence time, effluent-substrate contact, and full utilization of redox chemical reactions. Several other AMD treatment wetlands constructed in the Appalachian region have been confronted with similar limitations. Unfortunately, little information exists on how to ameliorate problems associated with these passive treatment systems, especially for those operating under high metal load conditions.

There is a critical need to improve wetland design parameters and use more efficient approaches that could adequately suppress acidity and Fe levels in high metal load acid mine effluents to the extent that they meet acceptable discharge parameters. Therefore, a project to improve the performance of the AMD treatment system at the Jones Branch wetland was implemented. The objectives of the project were: 1) to modify the design parameters of the existing constructed wetland by introducing an anaerobic/alkaline pretreatment system and by developing a substrate drainage system for enhanced utilization of wetland cells; 2) to monitor influent, internal and effluent acid mine water quality at different stages of treatment before and after design modifications; 3) to use monitoring data to evaluate design and operating efficiency of the constructed wetland ; and 4) to evaluate metal attenuation processes by the renovated design through characterization of substrate samples.

The following thesis is organized into two chapters. Chapter one summarizes the Jones Branch wetland renovation and presents results of the water quality and performance data. Chapter two details the metal attenuation processes within the wetland system and differentiates the nature of abiotic and biotic treatment functions.

# *CHAPTER ONE*

## INTRODUCTION

The exposure and oxidation of iron sulfide materials as a consequence of coal mining activities has resulted in acid mine drainage (AMD), a serious water pollution problem for the Appalachia region. Acid mine drainage, a low pH, iron and sulfate rich water with high acidity is formed upon exposure of pyrite to the atmosphere. Pyrite ($FeS_2$), the most common sulfide in the bituminuos coal fields, undergoes oxidation to form a variety of soluble iron sulfates which hydrolyze and produce AMD. As AMD enters natural waters, chemical and biological processes aid in the oxidation of iron from ferrous ($Fe^{2+}$) to the ferric ($Fe^{3+}$) state and the formation of ferric hydroxide precipitates commonly referred to as "yellow boy". The accumulation of ferric hydroxide precipitates on stream bottoms results in the formation of sediment layers which smother biological activity and contribute to further surface and groundwater contamination. The U.S. Bureau of Mines has estimated that approximately 20,000 km of streams and rivers are impacted by AMD in the United States and nearly 90% of these streams receive AMD from abandoned surface and deep mines (Kleinmann, 1989; Skousen et al., 1995).

The Surface Mine Control and Reclamation Act (SMACRA) of 1977 and the Clean Water Act of 1972 require coal mine operators to meet established state or federal

AMD discharge water quality standards. Current standards for active mines require a pH of 6.0 - 9.0, average monthly total Fe of 3.5 mg $L^{-1}$, and average monthly total Mn of 2.0 mg $L^{-1}$ (Code of Federal Regulations, 1996). Conventional practices for the treatment of AMD requires the addition of highly alkaline chemicals such as sodium hydroxide ($NaOH$), calcium hydroxide ($Ca(OH)_2$), calcium oxide ($CaO$), sodium carbonate ($Na_2CO_3$), or ammonia ($NH_3$) (Skousen et al., 1990; Narin et al., 1992). These reagents efficiently promote metal removal (via precipitation) and acidity neutralization; however, this type of chemical treatment can be very expensive and potentially dangerous to both humans and the environment when handled improperly (Hedin et al, 1994). In addition, chemical treatment is a long-term endeavor which requires continual support for reagents, labor and maintenance. In recent years, however, several low-cost passive treatment technologies have been developed that utilize natural chemical and biological processes to clean contaminated mine waters without the burdens of chemical addition. Constructed wetlands and anoxic limestone drains (ALD) are two such technologies that offer a potential solution to the AMD problem.

### *Pyrite Chemistry*

Drainage from coal mines is characteristically acidic and high in concentrations of sulfate, iron, manganese, aluminum, calcium, magnesium and zinc. This acidic drainage is formed when pyrite from the geologic strata immediately above or below a coal seam is disturbed by mining activities and subjected to the oxidizing forces of air and water. The chemical reactions for the oxidation of $FeS_2$ and subsequent production of acidity ($H^+$) are as follows:

$$2FeS_{2(s)} + 7O_2 + 2H_2O \leftrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad [1]$$

$$Fe^{2+} + 1/4O_2 + H^+ \leftrightarrow Fe^{3+} + 1/2H_2O \qquad [2]$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3H^+ \qquad [3]$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \leftrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad [4]$$

(Stumm and Morgan, 1981 and references therein). Reaction [1] shows that two moles of $FeS_{2(s)}$ produces four moles of acidity and two moles of ferrous iron. The $Fe^{2+}$ is oxidized to $Fe^{3+}$ in reaction [2] and undergoes hydrolysis to produce an additional three moles of $H^+$ (reaction [3]). Once the reaction has started, excess $Fe^{3+}$ in solution can act as an oxidant upon $FeS_{2(s)}$ which promotes further hydrolysis and the production of 16 additional moles of $H^+$ (reaction [4]) (Stumm and Morgan, 1981). Thus, the oxidation of pyrite will continue as long as ferric iron is being generated.

The oxidation of $Fe^{2+}$ to $Fe^{3+}$ (reaction [2]) was determined by Singer and Stumm (1970) to be the rate determining step in the generation of AMD. Further, these researchers showed that the oxidation of $Fe^{2+}$ is pH dependent and is extremely slow at $pH \approx 3$. However, certain chemosynthetic iron bacteria were found to act as catalysts and accelerate the chemical reaction at low (<4) pH levels (Nordstrom, 1982 and references therein). Singer and Stumm (1970) demonstrated that the rate of $Fe^{2+}$ oxidation in an untreated mine water sample was $10^6$ times higher than that observed in a sterilized sample. According to the EPA (1971), bacteria in AMD which catalyze the oxidation reaction are *Thiobacillus thiooxidans*, a sulfur-oxidizing bacteria; and *Thiobacillus ferrooxidans*, a bacterium that oxidizes $Fe^{2+}$ to $Fe^{3+}$. A direct contact mechanism for iron and sulfur oxidation by autotrophic bacteria may be described by the reactions:

$$Fe^{2+} + \textit{Thiobacillus ferrooxidans} \rightarrow Fe^{3+} + e^{-}, \text{ and} \qquad [5]$$

$$2S^{0} + 3O_2 + 2H_2O + \textit{Thiobacillus thiooxidans} \rightarrow 2SO_4^{2-} + 4H^{+} \qquad [6]$$

(Arkesteyn, 1979). Therefore, the oxidation of pyrite can be described as both a chemical and biological phenomenon in which $O_2$, $Fe^{3+}$, and bacteria act individually or together, depending upon pH conditions, to breakdown the mineral and initiate the acid forming process (Kleinmann et al., 1981; Nordstrom, 1982; Evangelou, 1995).

### *Constructed Wetland Treatment of AMD*

The discharge of wastewater into natural wetlands has occurred in the U.S. throughout the last century, however, only recently was the water quality purification potential of wetlands realized (Kadlec and Knight, 1996). The reduction of sediments, organic compounds, nutrients, heavy metals and microorganisms has been documented as water passes through natural wetlands (Mitsch et al., 1986; Hammer, 1989). Research conducted during the last twenty years has also demonstrated that biological and chemical processes occurring in natural wetlands aid in the reduction of AMD contaminants. Researchers from Wright State University and West Virginia University noted amelioration of AMD from abandoned mine lands after passing through natural *Sphagnum* moss wetlands (Huntsmann et al., 1978; Wieder and Lang, 1982). The purifying potential of wetlands posed a viable alternative to conventional AMD treatments, however, federal regulations established for natural wetland preservation and protection nullified this procedure. Constructed wetlands, on the other hand, are not considered "waters of the U.S.", which removed them from federal entanglements and allowed for research and development of these man-made treatment systems. Since their inception, over 400 wetlands that receive AMD from active and abandoned mines have been constructed in the bituminous coal region of the U.S. (Wieder, 1994).

Constructed wetlands, according to Hammer and Bastian (1989), are a designed and man-made complex of saturated substrates, emergent and submergent vegetation, animal life, and water that simulates natural wetlands for human use and benefits. These systems have been successfully used to treat municipal wastewater, septic tank effluent, agricultural wastewater and industrial discharge (Moshiri, 1993). In addition, treatment by constructed wetlands has been found to reduce the levels of metals (Fe, Mn, Al, Ni, Cu, Zn) present in mine water (Nawrot and Yaich, 1982; Wieder, 1988; Eger and Lapakko, 1989; Fennessy and Mitsch, 1989; Kleinmann et al., 1991). Examples of studies that have investigated passive AMD treatment systems are presented in Table 1.1. Pollutant removal processes implicated in constructed wetlands include several physical, chemical and biological mechanisms, such as plant uptake; exchange on adsorption sites; reduction and formation of metal sulfides; organic complexation; oxidation and formation of metal oxides/hydroxides. Wetland substrates also aid in the treatment process through physical entrapment of suspended solids; generation of alkalinity through microbial mineralization of organic matter, microbial dissimilatory sulfate reduction, and chemical dissolution of

Table 1.1. Examples of previous studies using passive treatment technology for acid mine drainage amelioration.

| Site | Treatment technology† | Time period | Flow (lpm) | % Reduction | | | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | | Fe | Mn | Al | Acidity | |
| Keister | aerobic CW | 36 mo. | 17 | 62 | 11 | 52 | 76 | Faulkner and Skousen, 1994 |
| WCF19 | aerobic CW | | 492 | 82 | 15 | | | Brodie, 1993 |
| Z & F | staged CW | 36 mo. | 30 | 77 | | 63 | 67 | Faulkner and Skousen, 1994 |
| REM | anaerobic CW | 12 mo. | | 72 | | | 6 | Kepler and McCleary, 1994 |
| Howe | ALD | 17 mo. | | <1 | <1 | <1 | 23 | Hedin et al., 1994 |
| Morison | ALD | 31 mo. | 6.8 | 24 | <1 | <1 | 77 | Hedin et al., 1994 |
| IMP4 | ALD/CW | | 34 | 87 | 83 | | 88 | Brodie et al., 1993 |
| Howe | SAPS | 19 mo. | | 48 | | | 71 | Kepler and McCleary, 1994 |
| REM | SAPS | 12 mo. | | 85 | | | 49 | Kepler and McCleary, 1994 |

†CW = constructed wetland; ALD = anoxic limestone drain; SAPS = successive alkalinity producing system.

carbonates; and by providing a habitat suitable for both microbial and vegetative growth (Faulkner and Richardson, 1989; Guntenspergen et al., 1989; Portier and Palmer, 1989; McIntire and Edenborn, 1990; Kelpler and McCleary, 1994).

The types of constructed wetlands for AMD treatment are usually divided into two general categories: 1) surface flow or "aerobic" wetlands in which water flows through emergent vegetation and above the surface of a relatively shallow sediment layer composed of clay or in *situ* soil, and 2) subsurface flow or "anaerobic" wetlands in which water flows through a relatively deep permeable sediment forcing the contact of drainage with plant roots and substrate materials. Substrates in "anaerobic" systems may be comprised of soil, peat moss, spent mushroom compost, sawdust, hay/manure compost, hay/straw bales, limestone and gravel, either alone or in various combinations. In general, aerobic wetlands treat AMD by promoting metal precipitation through oxidation/hydrolysis reactions and retention of the precipitate by physical entrapment. However, successful treatment by these systems is dependent upon initial pH and metal concentration (Brodie, 1993). Even though iron is removed from solution by hydrolysis, protons produced during the reaction may lower pH to levels suitable for causing plant stress or even death and resolubilization of retained metals (Gilbin, 1985; Watzlaf, 1988). Unfortunately aerobic wetlands do not produce adequate alkalinity to buffer acidity from hydrolysis, thus, treatment of net acidic and moderate (20-75 mg/L Fe) to high (>75 mg/L Fe) metal content AMD by these systems alone has not been very successful (Wieder, 1989; Brodie et al., 1993). However, aerobic wetlands used in conjunction with an alkalinity generating system such as anaerobic wetlands or ALD's have displayed favorable results.

Anaerobic wetlands also rely on oxidation/hydrolysis reactions near the surface, but primarily depend on chemical and microbial reduction processes within the substrate. High oxygen demand of organic matter in the substrate creates anoxic conditions which are favorable for the formation of metal sulfides and alkalinity from bacterially mediated sulfate reduction according to the reaction:

$$CH_2O + SO_4^{2-} \leftrightarrow H_2S + 2HCO_3^- \qquad [7]$$

(McIntire and Edenborn, 1990). Simple organic compounds such as lactate, pyruvate, ethanol or acetate ($CH_2O$) react with sulfate to form hydrogen sulfide and bicarbonate. If $H_2S$ does not degas, it can dissociate to $HS^-$ and react with dissolved metals to form solid metal sulfide precipitates. Dissolved $Fe^{2+}$ may precipitate to FeS by the reactions:

$$H_2S \leftrightarrow H^+ + HS^- \qquad [8]$$

$$Fe^{2+} + HS^- \leftrightarrow FeS + H^+. \qquad [9]$$

The bicarbonate ion produced from sulfate reduction and limestone dissolution acts as a buffer to neutralize proton acidity released from metal hydrolysis and raise pH (McIntire and Edenborn, 1990; Hedin et al., 1994). Sulfate reduction and metal sulfide precipitation has been observed in field and laboratory studies (McIntire and Edenborn, 1990; Staub and Cohen, 1992; Eger, 1992), but relatively high seasonal variations have prevented long term efficiency documentation. In addition, uncertainties concerning substrate permeability and clogging with precipitates may limit the use of this configuration in moderate to high metal load AMD (Wildeman, 1991; Wieder, 1992).

### *Anoxic Limestone Drains*

The addition of alkalinity is necessary for successful treatment of AMD. Constructed wetlands can passively generate alkalinity through sulfate and organic carbon reduction, but factors such as climate, season, organic matter inputs, and nutrient availability may limit these processes and necessitate additional alkaline inputs, particularly in high metal load systems (Faulkner and Skousen, 1994). The most inexpensive alkaline source in coal mining regions is limestone (Table 1.2); however, limestone has been rarely utilized to treat AMD because it has a low solubility under atmospheric conditions, and it tends to become armored with ferric hydroxides (USEPA, 1983; Nairn et al., 1992; Hedin et al., 1994). In oxidized environments, limestone dissolves upon contact with AMD. The dissolution results in a pH increase to circumneutral levels (pH 6-8) and oxidation of ferrous iron contained in the drainage. Ferric iron hydrolyzes to $Fe(OH)_3$ which quickly coats the limestone and inhibits further dissolution and alkalinity production. Thus, the dissolution of limestone in oxidized environments creates conditions that render it useless in AMD treatments (Nairn et al., 1992). Turner and McCoy (1990) discovered that buried beds of limestone, now referred to as anoxic limestone drains (ALD), can be useful in AMD treatment. In an anaerobic environment, ALD can raise pH to circumneutral levels and produce bicarbonate alkalinity without inducing precipitation of metal hydroxides and associated armoring. The alkaline water generated in the ALD builds up enough buffering

Table 1.2. Comparative cost of alkaline chemicals used in the treatment of acid mine drainage.

| Material | Chemical composition | Cost to neutralize one metric ton of acidity as $CaCO_3$ equivalent† |
|---|---|---|
| Limestone | $CaCO_3$ | $ 21 |
| Hydrated lime | $Ca(OH)_2$ | $ 49 |
| Ammonia | $NH_3$ | $ 102 |
| Soda ash | $NaCO_3$ | $ 269 |
| Caustic soda | NaOH | $ 475 |

†Chemical costs from Skousen (1995 b).

capacity so that when it is exposed to aerobic conditions it can withstand hydrolysis and precipitation processes without dropping the pH level significantly (Brodie et al., 1990).

Generation of alkalinity in an ALD is dependent upon maintenance of low dissolved oxygen and high carbon dioxide levels. The dissolution of limestone can be described by the following reactions:

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3 \qquad [10]$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2 \qquad [11]$$

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad [12],$$

where $H_2CO_3$ includes both $CO_{2(aq)}$ and carbonic acid (Stumm and Morgan, 1981). In acidic waters limestone deteriorates to dissolved calcium and dissolved carbon dioxide (reaction [10]). The dissolved carbon dioxide acts as a weak acid and further dissolves the limestone producing more calcium and bicarbonate alkalinity (reaction [12]). Limestone dissolution and alkalinity production rates increase as the partial pressure of carbon dioxide ($pCO_2$) increases (Stumm and Morgan, 1981). Thus, the elevation of $pCO_2$ in a closed system (ALD) results in further limestone dissolution and bicarbonate alkalinity generation (Figure 1.1).

Several researchers have documented alkalinity increases by ALD's (Turner and McCoy, 1990; Brodie et al., 1991; Faulkner and Skousen, 1994; Hedin and Watzlaf, 1994; Hedin et al., 1994); but, large variation exists in the amount of alkalinity generated and the fate of metals as AMD passes through ALD. Low dissolved oxygen (DO) (<2.0 mg/L), ferric iron (<25 mg/L) and aluminum (<25 mg/L) concentration in influent water represent

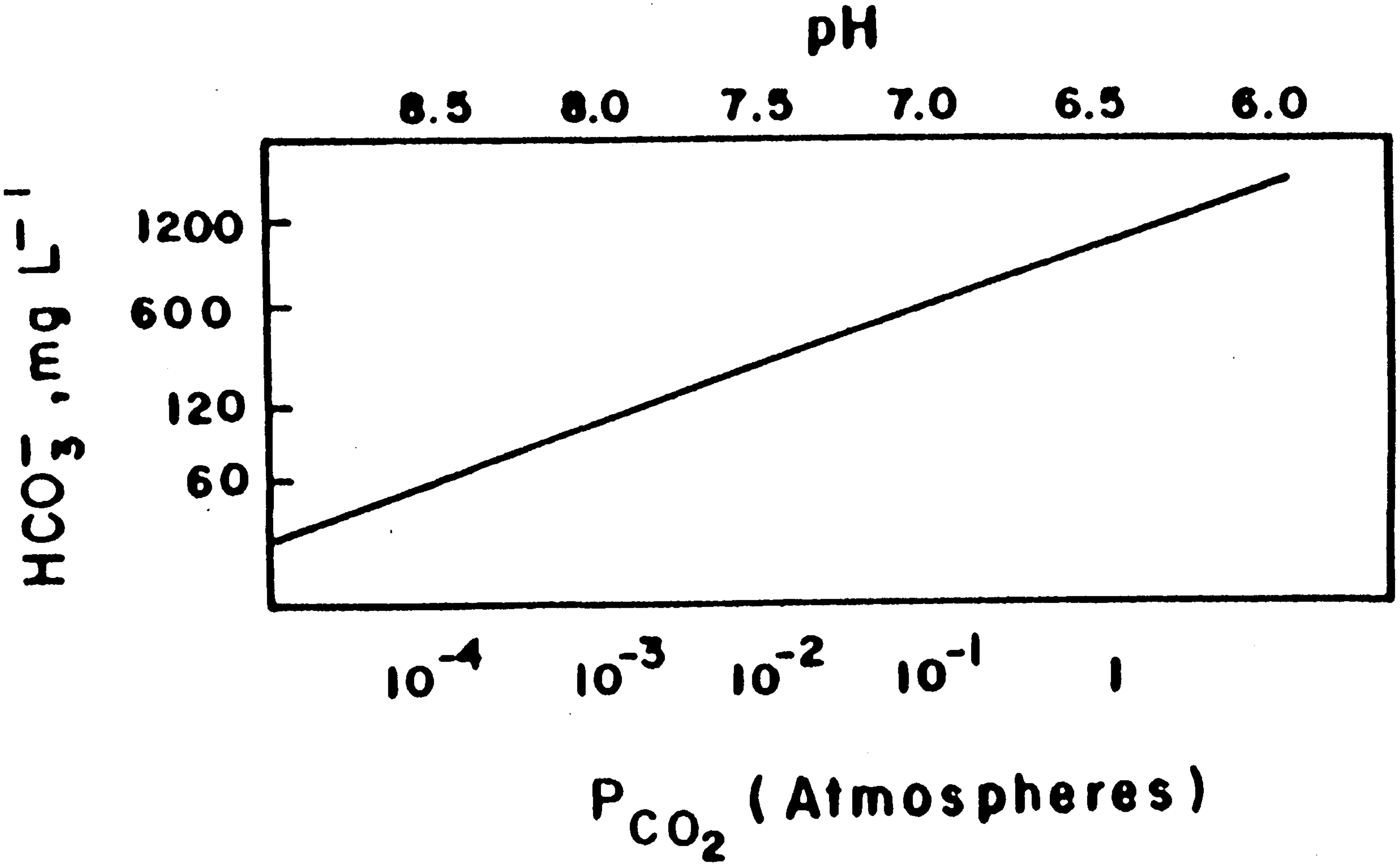

Figure 1.1. Concentration of $HCO_3^-$ at varying $pCO_2$ and pH levels.
(From Evangelou, 1995)

the few recommendations for implementation of ALD's. However, complications have arisen due to fluctuations in AMD chemical composition, chemical interactions, mineral precipitation, physical clogging and improper retention within the system (Skousen, 1991; Hedin and Watzlaf, 1994; Evangelou, 1995). The formation of precipitates within the drain poses the greatest problem in ALD efficiency. The solubility of hydroxides decreases with an increase in pH; thus, precipitation of ferric hydroxide at pH 3 to 4 (especially if the drain is not entirely anoxic) and aluminum hydroxide at pH 4 to 5 may occur as limestone dissolves (Hedin and Watzlaf, 1994). Bicarbonate production from the dissolution may also react with $Fe^{2+}$ and $Mn^{2+}$ to form siderite ($FeCO_3$) and rhodocrocite ($MnCO_3$). In moderate to high metal content AMD, alkalinity release may be controlled by the solubility of $FeCO_3$ or $MnCO_3$, if present, which have lower solubility and alkalinity generation rates than $CaCO_3$ (Evangelou, 1995). In addition, calcium released during limestone dissolution is capable of forming gypsum ($CaSO_4$) within the drain, especially in systems with long retention times (Nairn et al., 1992). Physical characteristics of precipitates within the drain may differ (form amorphous gels) from those found in highly oxidized environments, hence, removal of substances clogging the drain could possibly be performed by agitation or flushing.

### *Other Alkalinity Producing Systems*

Recently, several systems have been developed which utilize the processes of anoxic alkalinity production found in ALD and anaerobic wetlands. Kepler and McCleary (1994) developed a successive alkalinity-producing system (SAPS) which promotes vertical flow of AMD through organic substrates and limestone beds. High biological oxygen demand in the organic substrate promotes sulfate reduction and reduces iron to its ferrous state before entry into a limestone layer which functions as a submerged ALD. Although the limestone layer does not represent a closed system, $pCO_2$ levels increase in waterlogged conditions and facilitate the dissolution process. Apparently, atmospheric $pCO_2$ (0.0003 atm) is much lower than that observed in flooded or waterlogged soils (0.05 - 0.3 atm) because diffusion of gasses is much slower through water than air (Lindsay, 1979). Perforated pipes below the limestone move highly buffered drainage to an aerobic settling pond where precipitation takes place. This system has the potential to neutralize large amounts of acidity and decrease treatment area requirements (Kepler and McCleary, 1994). Similar systems have been described by Skousen et al. (1995) in which anoxic or oxic AMD seeps flow upward through a pond filled with limestone or compost overlain by limestone, respectively, to add alkalinity before being discharged into a precipitation basin. A diagram illustrating various passive treatment technologies is presented in Figure 1.2.

### *The Jones Branch Constructed Wetland*

Underground coal mining in the Rock Creek watershed began in the early 1900's and continued until the mid 1960's (Pomerene, 1964). The Stearns number 2 coal seam and overlying geologic strata found in this area contain high sulfur and pyrite quantities which generate low pH and high metal content AMD. Jones Branch, a tributary of White Oak Creek, joins Rock Creek and eventually flows to the Big South Fork of the Cumberland River in McCreary Co. Kentucky ($36^0$ 42.64 N, $84^0$ 36.92 W) (Figure 1.3).

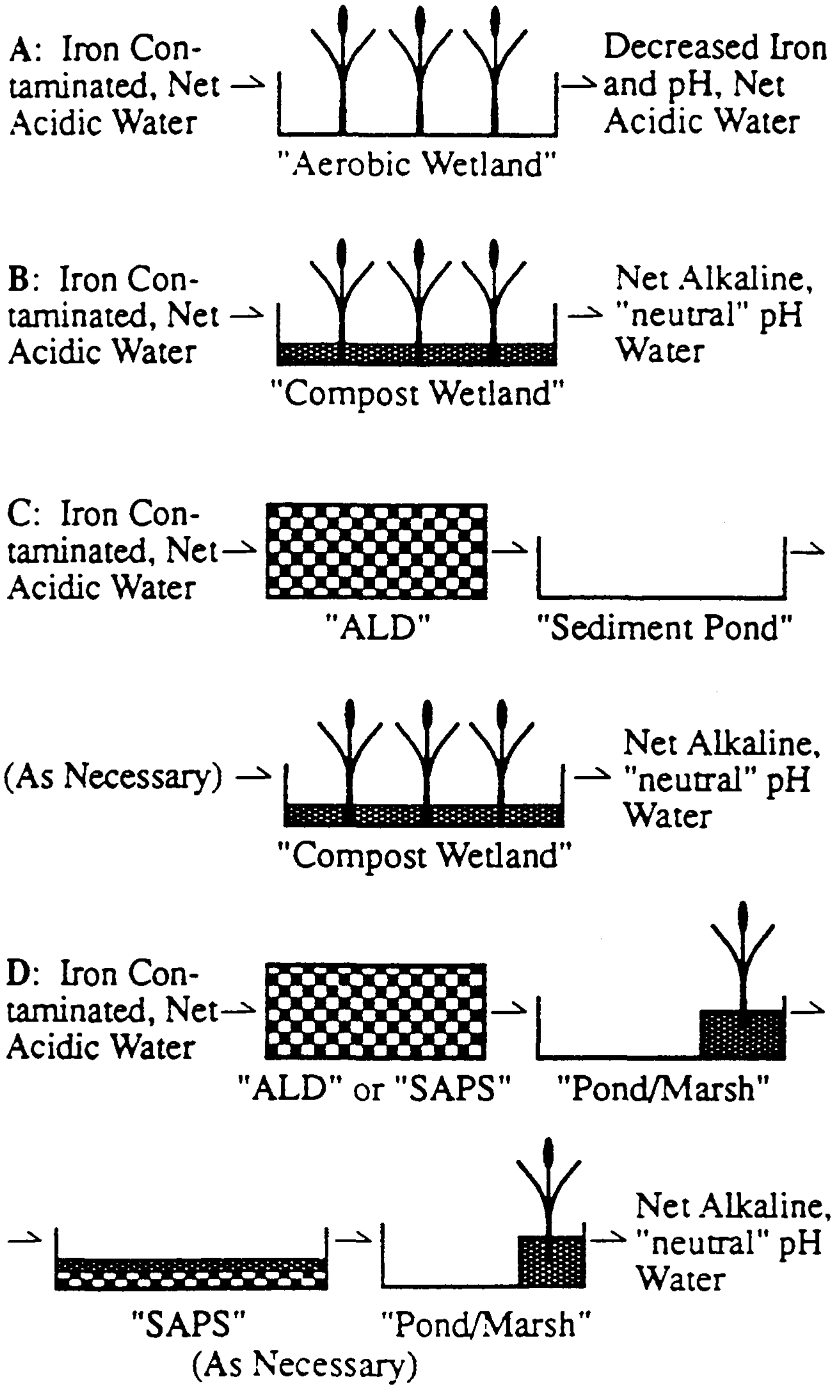

Figure 1.2. Evolution of passive AMD treatment technologies. (From Kepler and McCleary, 1994)

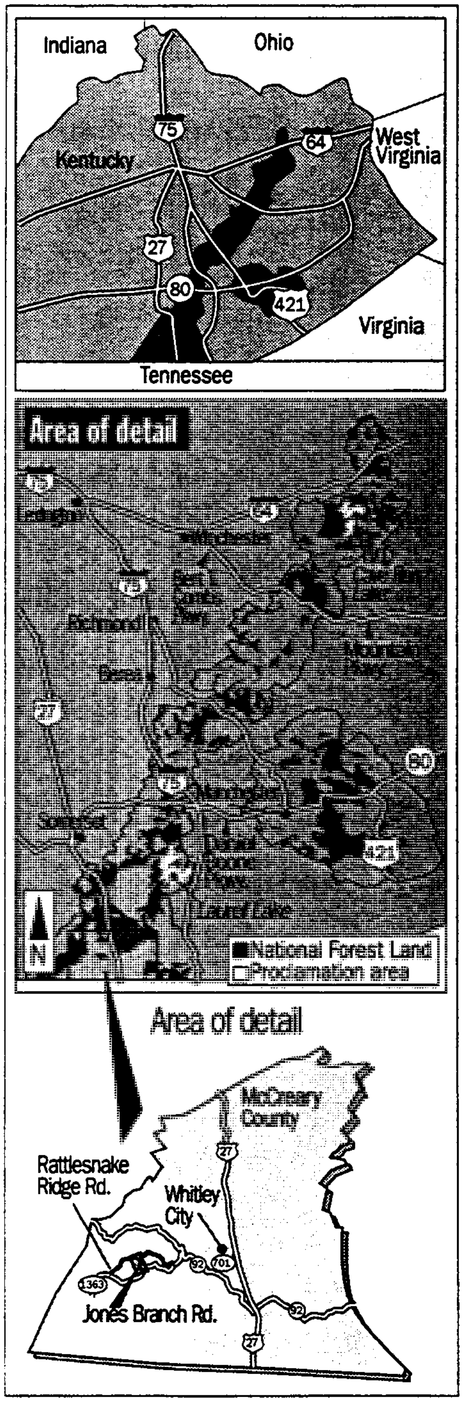

Figure 1.3. Location of the Jones Branch wetland: McCreary County, Kentucky.

Acid mine drainage from several abandoned underground mines and approximately six hectares of pyritic coal waste piles has since degraded water quality and impaired aquatic biota in Jones Branch (Halverson and Wade, 1988; Ramey et al., 1992). In an effort to restore water quality, a constructed wetland was designed to receive and ameliorate AMD from two collapsed portals to a 91 hectare mine located approximately 2.25 stream kilometers above the confluence of Jones Branch and White Oak Creek. The U.S. Forest Service's Daniel Boone National Forest supervised construction of the artificial wetland and access road to the site during the summer of 1989.

The original wetland designed at Jones Branch consisted of two sequential ponds with 15 and 10 cells, respectively, providing 1022 $m^2$ of treatment area. Each cell consisted of 23 cm crushed limestone over a compacted floor treated with bentonite clay. A 46 cm layer of spent mushroom compost was placed over the limestone to serve as an organic substrate. The substrate was topped with 19 kg per 100 $m^3$ hydrated lime, 3.4 kg of superphosphate, and 4.5 kg of 10-10-10 fertilizer. Cattails (*Typha latifolia*) were transplanted in the substrate on a three foot center pattern and gradually introduced to the AMD.

From the mine seeps, AMD was collected in a settling basin then flumed into the first wetland field where it flowed in a serpentine fashion through fifteen cells to a second flume that led to the second wetland field. After flowing through ten cells in the second field, treated water exited the wetland and flowed into Jones Branch. The design provided approximately 14 to 46 $m^2$ of surface area per liter inflow per minute at a flow rate of 200 to 100 lpm. The surface flow orientation of the wetland allowed for a flow path of 200 linear meters which resulted in a residence time of approximately two hours. H-flumes at the settling basin and at the outlet of each wetland field were used to monitor flow. Post-construction monitoring and chemical analyses were performed by the Northeastern Forest Experimental Station from June, 1989 to June, 1992.

Initial drainage had an average pH of 3.0, 1250 mg/L Fe, 21.5 mg/L Mn, 18 mg/L Al, and 4000 mg/L $SO_4^{2-}$ (Chalfant, 1993). Metal concentrations and acidity were reduced substantially during the first six months of treatment, however, the system failed thereafter due to insufficient utilization of treatment area, inadequate alkalinity production and metal overloading. In an attempt to improve the treatment system, a two phase renovation project began in 1995 that incorporated the use of anoxic limestone drains and a series of anaerobic subsurface drains which promote vertical flow through limestone beds overlain by organic compost (Figure 1.4).

## MATERIALS AND METHODS

### *Wetland Design Renovation Criteria*

Limitations in topography at the site prevented expansion, so design modifications were selected that could maximize available surface area, decrease retention time, regulate flow and facilitate alkalinity production. Drainage from the mine seeps contained low dissolved oxygen (<1.0 mg/L) and ferric iron (<25 mg/L) concentrations which made it suitable for ALD treatment. However, the steep mountainous terrain and the presence of a

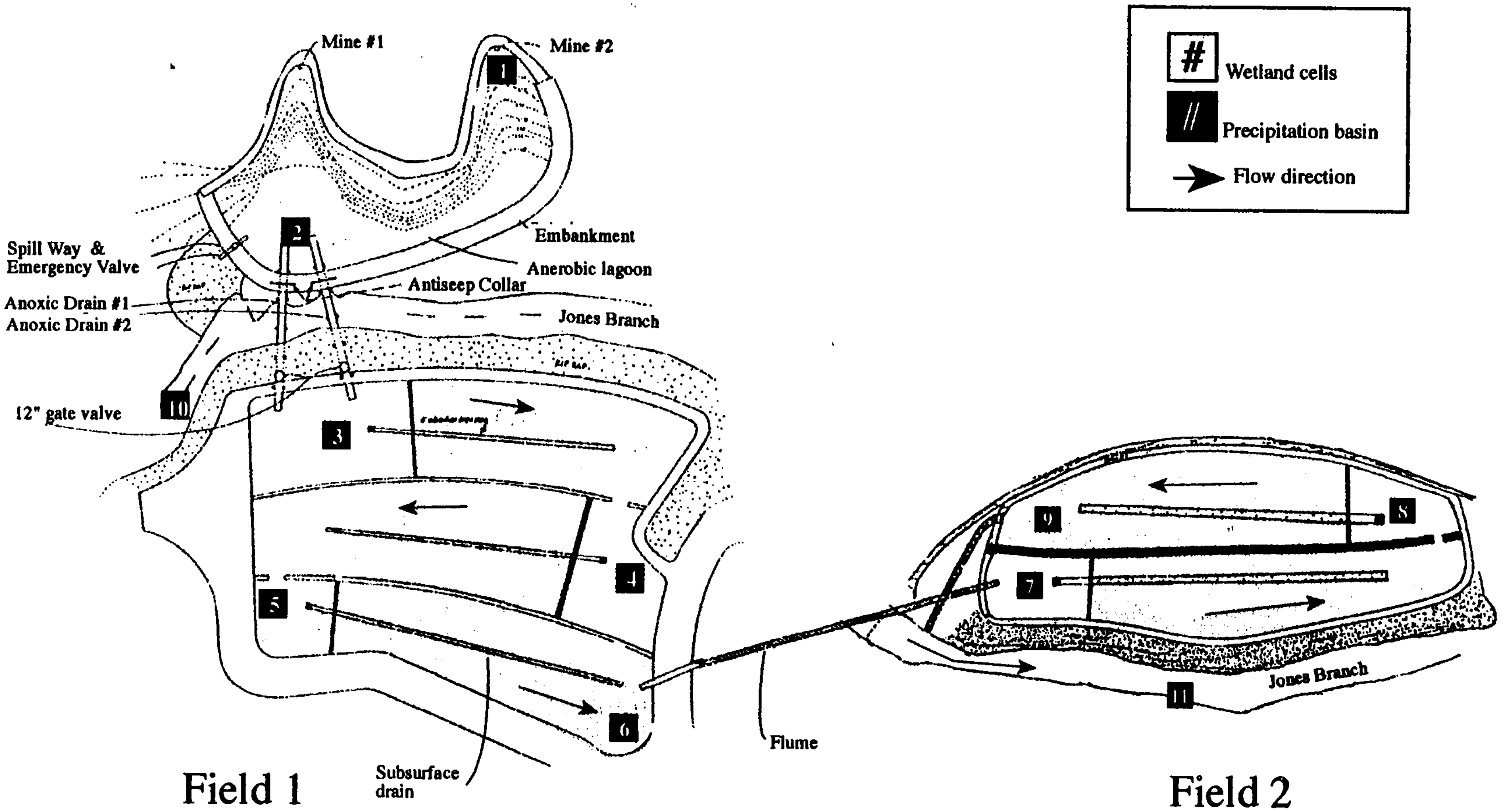

Figure 1.4. Site plan for the Jones Branch wetland. Sample points 2 and 9 represent influent and effluent respectively.

creek through the site prevented excavation of the traditional trench to install the ALD system. Instead, large PVC pipes filled with limestone and equipped with gate valves, to control flow, were expanded across the creek and into the existing wetland (Figures 1.5 and 1.6). A modified SAPS design was also created to force more interaction of AMD with the substrate (limestone/compost) and enhance alkalinity production processes and greater retention of drainage within the system. Aerobic precipitation basins follow each subsurface wetland to promote hydrolysis and metal precipitation (Figure 1.7).

Anaerobic AMD from a collection lagoon was diverted to a precipitation basin through two ALD's. Both ends of the drain were submerged in five feet of water to maintain an anoxic state. The acidic environment in the drain is expected to dissolve some of the limestone, thus raising the pH of AMD to circumneutral levels through production of bicarbonate alkalinity. Precipitation of metal hydroxides in the drain should be deterred because the iron is in its reduced state; thus, armoring of limestone should be prevented. From the ALD's, the drainage enters an aerobic basin where iron oxidation and hydrolysis reactions are expected to occur. Drainage then passes through perforated subsurface pipes into a wetland cell. The perforated pipe is overlain with ≈ 30 cm of limestone and ≈ 50 cm of hay/manure compost that supports emergent vegetation. This compost substrate was chosen for its characteristically high permeability (Wieder, 1993), low cost (transport) and capacity to remove metals from AMD (Mitchell and Karathanasis, 1995). Cattails *Typha latifolia* were selected as the vegetation species for their tolerance to high acidity and metal content, and ability to transport oxygen via aerenchyma tissue from the atmosphere

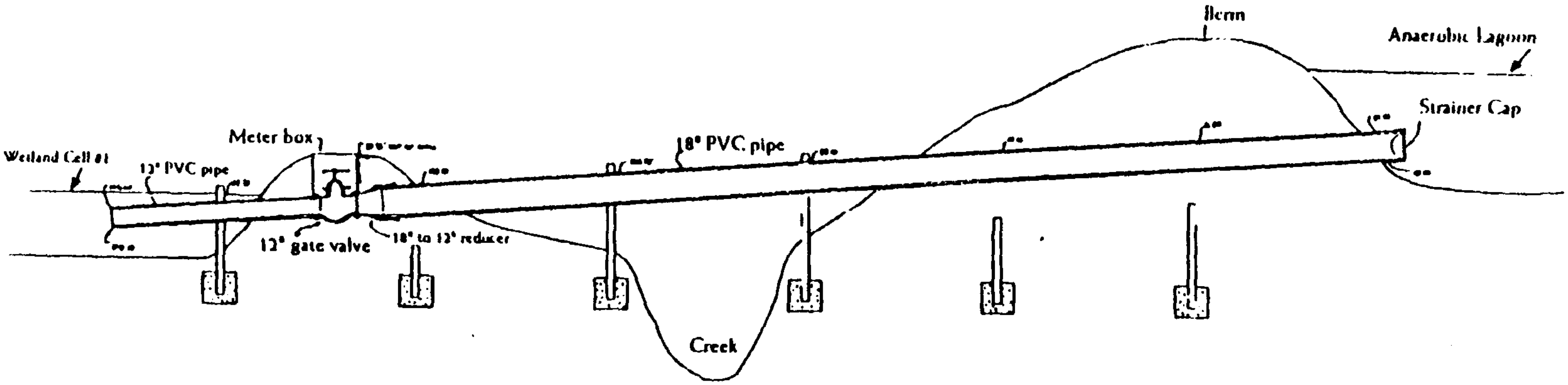

Figure 1.5. Construction design of the anoxic limestone drains at the Jones Branch wetland.

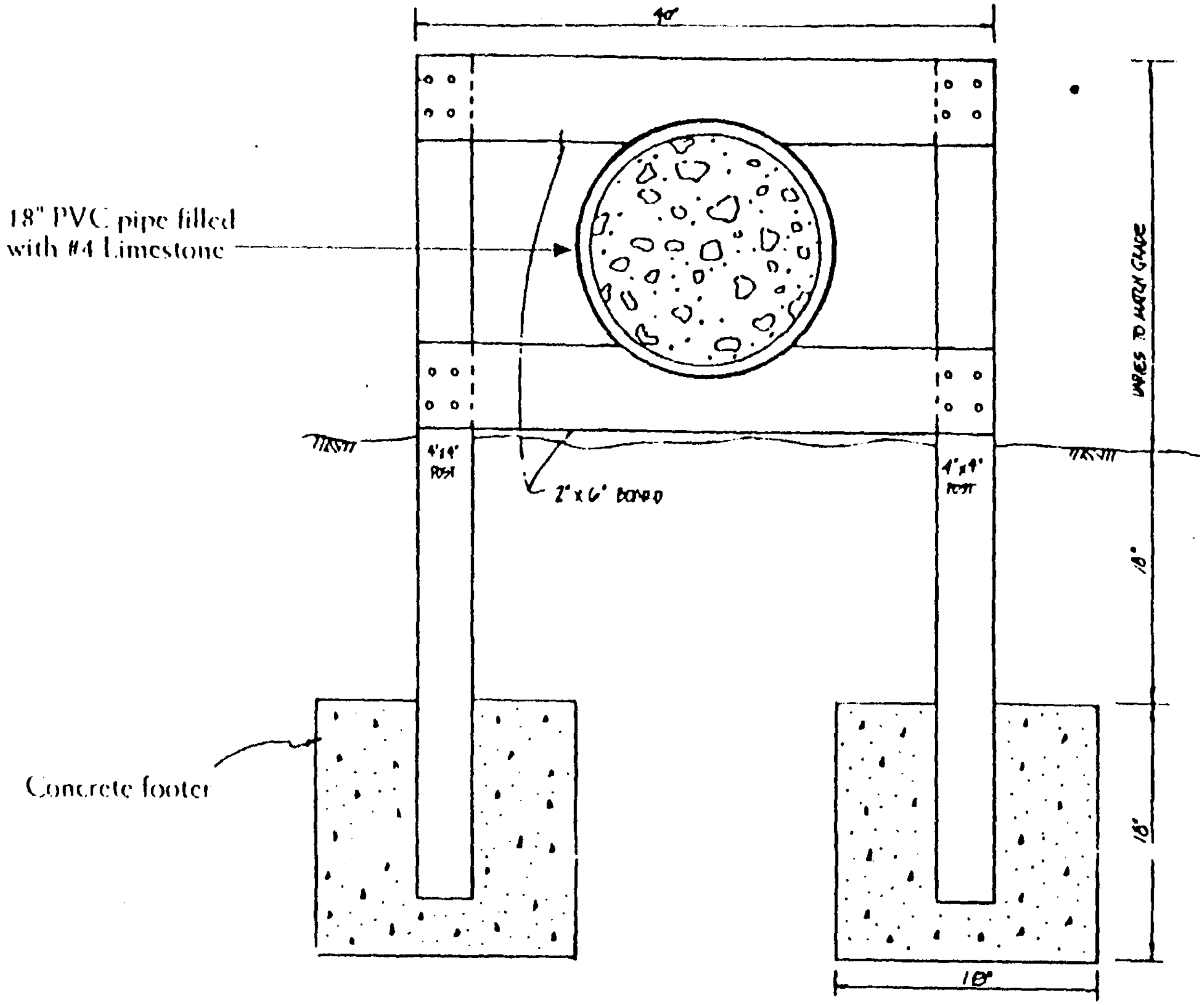

Figure 1.6. Anoxic limestone drain cross section.

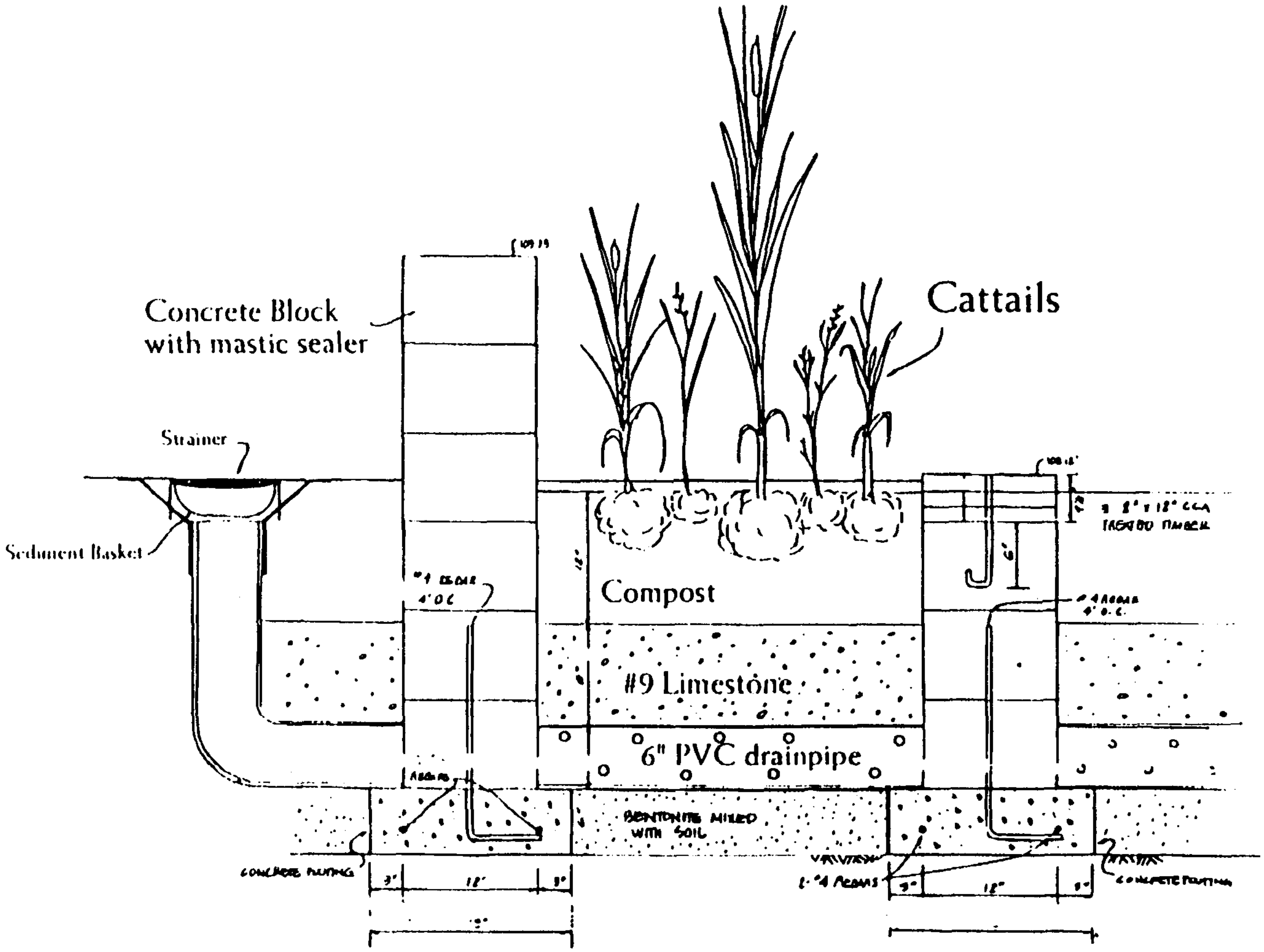

Figure 1.7. Detail of the subsurface flow system and wetland cell cross section at the Jones Branch wetland.

through the plant root and into adjacent soil (Sencindiver and Bhumbla, 1988; Mendelssohn, 1993). As AMD flows through the subsurface, the redox potential should be lowered by the oxygen demand of organic matter resulting in alkalinity generation through dissolution of limestone and bacterially mediated sulfate reduction. Mixing of substrate components was encouraged during placement to readily reduce any ferric iron that enters the drainpipes. From the end of the first wetland cell, drainage enters another aerobic basin where further oxidation and hydrolysis reactions occur and additional metals are precipitated. This treatment process is repeated so that drainage passes through a series of three aerobic/anaerobic treatment sequences in the first wetland field, then proceeds through a flume to a second field with two more treatment sequences.

The treatment principle of the new design was to generate enough alkalinity in the ALD's and anaerobic wetland cells to promote metal precipitation while compensating for acidity produced during hydrolysis in aerobic zones. With each subsequent treatment series, the amount of alkalinity produced is expected to increase as the concentration of metals decreases such that the final effluent is net alkaline. In addition, the system is also expected to provide supplementary treatment through organic complexation of metals, adsorption to exchange sites, physical entrapment of solids, uptake by plants, and precipitation of metal carbonates.

### *Wetland Renovation Plan Implementation*

The renovation project for the Jones Branch Wetland utilizing new design technology for the treatment of AMD began in May, 1995. The renovation stages involved: removal of preexisting substrate; installation of anoxic limestone drains; converting the original surface flow design to a subsurface flow system with a modified SAPS (Kelpler and McCleary, 1994) design; and addition of a new substrate (Figure 1.4). The original organic compost was excavated from the wetland, taken to a refuse area and deposited over 15 cm graded limestone. Armoring of limestone in the original wetland was not evident and efforts were made to retain as much as possible. An anaerobic lagoon was constructed by creating a berm that surrounds the portals and pools AMD from the seeps. The berm is approximately two meters high and is lined with a high density polyethylene sheet. The lagoon is equipped with an emergency spillway for periods of high flow or malfunction of the ALD's. After completion, floating bags filled with compost were placed in the lagoon to reduce surface aeration and oxidation of $Fe^{2+}$.

Anaerobic AMD is diverted from the subsurface of the lagoon through two 0.5 meter diameter by 12.2 meter long PVC pipes (Figure 1.5). The pipes are filled with #4 (2.5-7.5 cm) crushed limestone and wrapped with pipe insulation (Figure 1.6). The inlets of the drains are covered with a screening cap to keep large debris from entering the ALD's. A 30 cm gate valve was installed at the outlet of each ALD to regulate flow through the drain and into the 1022 $m^2$ wetland. The gate valves are also used to control the quantity of water within the anaerobic lagoon.

In the wetland fields, AMD flows through a series of five alternating abiotic/biotic treatment zones (Figure 1.4). AMD collected in a precipitation basin with no organic substrate or plants flows into the subsurface of a wetland cell through a perforated 15 cm diameter PVC pipe. The AMD percolates through holes in the pipe into a substrate composed of 30 cm of crushed limestone (≈ 350 tons) overlain by 50 cm of hay/manure compost in which cattails (*Typha latifolia*) were planted (Figure 1.7). Drainage flows through three treatment zones in the first field and proceeds through a flume into the second field and two more treatment zones before being discharged into Jones Branch. H-flumes at the outlet of each wetland field are used to measure flow.

Pre-renovation monitoring of the wetland system began in July of 1994. Construction of the anaerobic lagoon, anoxic limestone drains and renovation of wetland field 1 (Phase I) began in May 1995 and was completed in June 1995. Renovation of wetland field 2 (Phase II) began and was completed during the last week of September 1995. Mean post renovation analyses describes data from July 1995 through the end of October 1996.

### *Sample Collection*

Water samples were taken after renovation on a bimonthly basis from June, 1995 through the end of October 1996. Eleven water sampling stations were located within the project site, including the mine seep; anaerobic lagoon; precipitation basins 1,2,3,4 and 5; wetland cells 3 and 5; upstream and downstream (Figure 1.4). Three water samples were collected at each station. One sample was preserved with $HNO_3$ to $pH < 2.0$ for total iron, manganese, magnesium and calcium analyses. A second sample was preserved with $2N$ zinc acetate and NaOH to $pH > 9$ for sulfide analysis. The third sample was used as sampled for the determination of acidity, alkalinity, sulfate, aluminum, total suspended solids, total solids and ferrous iron. Water pH, dissolved oxygen, conductivity, temperature and redox potential were measured in *situ* at each sampling station. Samples were transported with ice in coolers and stored at $4^0$ C prior to analysis.

***Solution Analysis***

Surface waters were analyzed for total Fe, Mn, Mg and Ca using a IL S11 atomic absorption spectrophotometer. Aluminum and ferrous iron were determined colorimetrically and measured with a Bio-Tek Instruments spectrophotometer microplate autoreader. Ferrous iron was analyzed using the phenanthroline method; and total Al by the eriochrome cyanine-R method. Acidity, alkalinity and sulfide were analyzed by titrimetric procedures using a Metrohm 665 Dosimat. Sulfate was determined turbidimetrically using the barium chloride method. Total and suspended solids were determined gravimetrically. All solution characterization procedures followed guidelines of the *Standard Methods for the Examination of Water and Wastewater* (APHA, 1989) manual or other approved U.S. EPA methods. Duplicate analyses were performed for 5% of the samples with ≤ 10% analytical error. Table 1.3 summarizes the methodology and instrumentation used in the study. Geochemical modeling of aqueous-phase speciation equilibria was performed with the MINTEQA2 computer program (Allison et al., 1990). Measured pH and Eh values were used as model inputs in the computer simulation.

***Maintenance Activities***

In an effort to optimize treatment efficiency and operational performance, several maintenance procedures were implemented. To prevent sediment clogging or precipitation

Table 1.3. Analytical methods and instruments used for water quality analyses at the Jones Branch wetland.

| Parameter | Analytical Instrument | Analytical Method |
|---|---|---|
| pH (field) | Oakton pH meter | electrometric |
| Conductivity (field) | Hanna 8033 conductivity meter | electrometric |
| Redox potential (field) | Oakton ORP meter | electrometric |
| Dissolved Oxygen (field) | GS 1000W DO meter | electrometric |
| Total Solids | Sartorius analytical balance | gravimetric |
| Total Suspended Solids | Sartorius analytical balance | filtration |
| Alkalinity | Metrohm 665 Dosimat | titrimetric |
| Acidity | Metrohm 665 Dosimat | titrimetric |
| Sulfate | Turbidimeter | turbidimetric |
| Sulfide | Titration glassware | titration |
| Al | Bio-Tek spectrophotometer | colorimetric |
| $Fe^{2+}$ | Bio-Tek spectrophotometer | colorimetric |
| $Fe_{(total)}$ | IL S11 AA | atomic absorption |
| Mn | IL S11 AA | atomic absorption |
| Mg | IL S11 AA | atomic absorption |
| Ca | IL S11 AA | atomic absorption |

build-up in the ALD's, gate valves were periodically opened and flushed with drainage from the lagoon. Subsurface drains were cleaned twice during the study period by inserting the intake hose of a 7.5 cm trash pump into the drainpipe and removing obstructions by vacuum. Strainer caps covering the intake of the subsurface drains were removed and cleaned at each sampling event. Site inspections were also performed at each sampling event to determine additional maintenance needs. Problems associated with cattail stands, leaks, clogging or hot spots were identified and remediated upon observation.

## RESULTS AND DISCUSSION

### *Water Quality*

Influent water quality data from the Jones Branch wetland showed much higher acidity, iron and sulfate, but slightly lower manganese and aluminum concentrations than average levels observed in other AMD treatment wetlands throughout the eastern U.S. (Table 1.4). The original wetland design proved to be sufficient at reducing metal levels and acidity during the first six months of operation, but failed thereafter (Table 1.5). Average pH levels rose from an influent level of 3.05 to 7.20 in the effluent during the first year, however, effluent pH levels consistently remained below influent levels in subsequent years (Chalfant, 1993). Apparently, hydrated lime which was topdressed on the substrate efficiently promoted metal precipitation and buffered acidity produced during metal hydrolysis, but neutralization ceased as the carbonate source was exhausted (Chalfant,

Table 1.4 **Comparison of Jones Branch Wetland influent chemistry to the mean influent chemistry from a survey of other constructed wetlands.***

| Parameters† | Jones Branch Wetland Post Renovation‡ | Wetland Survey§ |
|---|---|---|
| Acidity | 2244 ± 337 (26) | 257 ± 40 (107) |
| Alkalinity | 0 (26) | 55.6 ± 7.5 (101) |
| Total Iron | 787 ± 121 (26) | 61 ± 7 (137) |
| Total Manganese | 10.9 ± 2.1 (26) | 38 ± 3.5 (136) |
| Total Aluminum | 12.6 ± 4.1 (26) | 21 ± 6 (20) |
| Sulfate | 3034 ± 569 (26) | 1194 ± 93 (122) |

* Numbers are average ± standard deviation (number of samples).

† Parameters are in mg/L except for acidity and alkalinity which are in mg $CaCO_3$/L.

‡ For period July, 1995 through October, 1996.

§ From Wieder (1989). Numbers in parentheses indicate number of wetlands evaluated.

Table 1.5. Comparison of inflow and outflow water quality data prior to renovation at the Jones Branch wetland.†

**Influent**

| Date‡ | n* | pH | | | Fe | | | Mn | | | Al | | | $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Min | Ave | Max | Min | Ave | Max | Min | Ave | Max | Min | Ave | Max | Min | Ave | Max |
| 1989 | 8 | 2.89 | 3.05 | 3.33 | 960 | 1256 | 1420 | 15.8 | 22.2 | 37.3 | 8.1 | 12.4 | 20.6 | 3490 | 4311 | 5290 |
| 1990 | 10 | 2.83 | 3.19 | 3.61 | 560 | 937 | 1218 | 10.4 | 17.3 | 22.8 | 6.8 | 10.4 | 14.3 | 2700 | 3725 | 4600 |
| 1991 | 11 | 2.94 | 3.15 | 3.69 | 475 | 1017 | 1322 | 8.5 | 19.1 | 47.0 | 3.9 | 17.2 | 38.8 | 2000 | 3655 | 4800 |
| 1992 | 9 | 2.68 | 3.30 | 3.85 | 888 | 1229 | 1440 | 16.3 | 18.1 | 20.2 | 25.4 | 35.9 | 42.8 | 4100 | 4363 | 4600 |
| 94/95 | 5 | 3.24 | 3.47 | 3.87 | 225 | 739 | 1149 | 4.2 | 8.4 | 16.6 | 9.1 | 15.0 | 26.7 | 1098 | 2559 | 5385 |

**Effluent**

| Date‡ | n* | pH | | | Fe | | | Mn | | | Al | | | $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Min | Ave | Max | Min | Ave | Max | Min | Ave | Max | Min | Ave | Max | Min | Ave | Max |
| 1989 | 8 | 6.10 | 7.20 | 7.92 | 0.11 | 33.6 | 231 | 0.29 | 4.18 | 13.7 | 0.2 | 0.5 | 0.7 | 12.0 | 763 | 2460 |
| 1990 | 10 | 2.49 | 2.98 | 5.33 | 145 | 452 | 768 | 7.7 | 14.4 | 20.3 | 0.5 | 8.2 | 12.3 | 1550 | 3028 | 3800 |
| 1991 | 11 | 2.48 | 2.59 | 2.77 | 223 | 467 | 856 | 7.8 | 15.8 | 38.8 | 4.1 | 12.0 | 25.9 | 1650 | 2661 | 3900 |
| 1992 | 9 | 2.74 | 2.79 | 2.82 | 558 | 848 | 1038 | 13.1 | 15.4 | 17.8 | 26.5 | 33.8 | 39.7 | 3100 | 3880 | 4500 |
| 94/95 | 5 | 2.37 | 2.53 | 2.72 | 193 | 452 | 755 | 6.1 | 9.3 | 19.4 | 4.0 | 44.5 | 18.5 | 1572 | 2665 | 5010 |

† Values in mg $L^{-1}$ except for pH which is in standard units.

‡ Analysis from 1989-1992 performed by U.S. Forest Service Northeastern Experimental Station. Analysis for 1994-1995 performed by researcher.

* n = number of samples.

1993). Elevated pH levels decreased the solubility of metal hydroxides which led to > 95% reductions in iron and aluminum. Manganese and sulfate levels also displayed a reduction of ≈ 80% during this time period. However, increased acidity in subsequent years most likely curtailed metal hydroxide precipitation of Mn and Al.

Several studies have suggested that adsorption and complexation of metals in organic substrates occurs only in the initial few months of AMD exposure before becoming saturated (Henrot and Wieder, 1990; Kleinmann et al., 1991; Wieder, 1993). During the 1990-1992 period a reduction of only ≈ 20% Mn and Al was observed which indicates that many of the metal retention processes had ceased. With continued age, however, increased Mn levels were observed as drainage passed through the wetland resulting in effluent concentrations that exceeded those of the influent. Apparently, the wetland substrate had become saturated with accumulated metals and resolubilization of precipitated Mn was occurring (Watzlaf, 1988). In addition, reduction of sulfate declined with each passing year indicating lowered microorganism metabolism rates or inadequate infiltration and retention of AMD within the substrate zone (McIntire and Edenborn, 1990). A ≈ 30% reduction in iron concentration continued from 1990 through 1995, evident by low pH levels in effluent waters and the accumulation of a ≈ 10 cm layer of yellowboy above the substrate. Water quality parameters had significantly deteriorated by 1995, such that effluent water quality was equal to or worse than water coming into the system. Aesthetic qualities had also deteriorated and suggested failure of the system through mass vegetation die-off and precipitate accumulation throughout.

Analytical results from post-renovation water quality monitoring are very encouraging. Bi-weekly performance data reveals dramatic changes in water quality and indicates good consistency in treatment efficiency. During the first 15 months after renovation, mean iron concentrations have decreased from 787 to 37 mg $L^{-1}$, pH increased from 3.38 to 6.46 and acidity has been reduced from 2244 to 199 mg $CaCO_3$ $L^{-1}$ (Tables 1.6 and 1.7). Renovation has resulted in the retention of 98% Al, 95% Fe, 94% acidity, 55% $SO_4^{2-}$, and 49% Mn within the wetland. Each of the water quality parameters investigated in the study will be discussed in detail forthcoming. Complete water quality data for the study period are presented in the Appendix.

### *pH*

Prior to renovation, influent drainage pH (pH=3.24) was consistently higher than that observed at the flume (between wetland fields 1 and 2) and in effluent waters (pH=2.57) (Figure 1.8). The lowering of pH as drainage passed through the wetlands indicates that hydrolysis reactions dominated, while the buffering capacity of the wetland was exhausted. Inhibition of microbial processes due to high acidity and armoring of some limestone within the substrate probably contributed to the lack of alkalinity generation. Under these low pH conditions, resolubilization of previously retained metals could have acted as a secondary source of water contamination (Watzlaf, 1988). With the completion of Phase I renovation, influent pH levels rose from 3.1 to 6.44 at the flume then dropped to 5.31 in field 2. This trend remained constant until Phase II renovation was completed, which suggest that the old substrate was acting as a sink and contributing contaminants to

Table 1.6. Post renovation influent water quality and flow data from July 1995 to October 1996 for the Jones Branch wetland.

| Parameter | Units | Average | Min | Max | SD† | n=‡ |
|---|---|---|---|---|---|---|
| pH | std. | 3.38 | 2.70 | 4.41 | 0.45 | 26 |
| EC | µS | 2909 | 2020 | 3820 | 450 | 26 |
| Eh | mv | 260.6 | 146.6 | 374.0 | 63.2 | 25 |
| DO | mg/L | 1.5 | 0.3 | 4.8 | 0.9 | 25 |
| $Fe^{2+}$ | mg/L | 787 | 550 | 1007 | 109 | 26 |
| Total Fe | mg/L | 787 | 430 | 1031 | 121 | 26 |
| Mn | mg/L | 10.9 | 6.6 | 14.1 | 2.1 | 26 |
| Al | mg/L | 12.6 | 4.8 | 22.3 | 4.1 | 26 |
| Mg | mg/L | 102 | 28 | 152 | 28 | 26 |
| Ca | mg/L | 261 | 157 | 337 | 47 | 26 |
| Sulfate | mg/L | 3034 | 1944 | 4245 | 569 | 26 |
| Sulfide | mg/L | 1.2 | 0 | 6.4 | 1.8 | 26 |
| TSS | mg/L | 48 | 0 | 312 | 61 | 26 |
| TS | mg/L | 4834 | 2834 | 5670 | 645 | 25 |
| Alkalinity | mg $CaCO_3$/L | 0 | 0 | 0 | 0 | 26 |
| Acidity | mg $CaCO_3$/L | 2244 | 1281 | 2883 | 337 | 26 |
| Flow | lpm | 37.1 | 10.6 | 57.2 | 14.4 | 26 |

† Standard deviation of the mean.

‡ Number of samples.

Table 1.7. Post renovation effluent water quality and flow data from July 1995 to October 1996 for the Jones Branch wetland.

| Parameter | Units | Average | Min | Max | SD† | n=‡ |
|---|---|---|---|---|---|---|
| pH | std. | 6.46 | 4.39 | 8.35 | 0.99 | 26 |
| EC | µS | 1974 | 875 | 4550 | 1014 | 26 |
| Eh | mv | 159.3 | -43.2 | 417.0 | 109.6 | 25 |
| DO | mg/L | 3.8 | 0.6 | 6.6 | 1.7 | 25 |
| $Fe^{2+}$ | mg/L | 19.5 | 0.1 | 275 | 55.5 | 26 |
| Total Fe | mg/L | 37.3 | 0.2 | 331 | 75.2 | 26 |
| Mn | mg/L | 5.6 | 0.6 | 13.0 | 3.1 | 26 |
| Al | mg/L | 0.2 | 0 | 0.7 | 0.2 | 26 |
| Mg | mg/L | 74 | 9 | 207 | 48 | 26 |
| Ca | mg/L | 264 | 76 | 613 | 128 | 26 |
| Sulfate | mg/L | 1352 | 312 | 3390 | 730 | 26 |
| Sulfide | mg/L | 1.2 | 0 | 4.8 | 1.6 | 26 |
| TSS | mg/L | 43 | 0 | 202 | 52 | 26 |
| TS | mg/L | 2247 | 612 | 4744 | 1111 | 25 |
| Alkalinity | mg $CaCO_3$/L | 141 | 0 | 295 | 90 | 26 |
| Acidity | mg $CaCO_3$/L | 119 | 4 | 915 | 206 | 26 |
| Flow | lpm | 26.1 | 1.1 | 57.2 | 18.7 | 26 |

† Standard deviation of the mean.

‡ Number of samples.

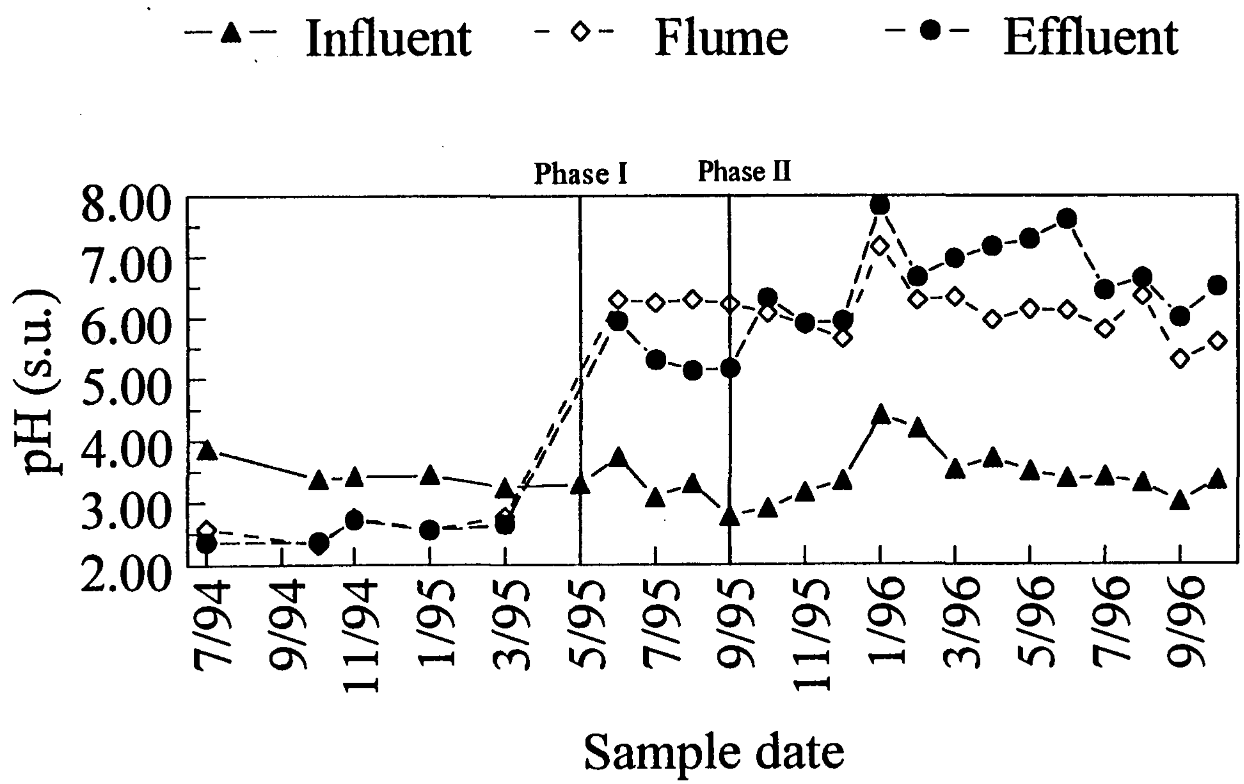

Figure 1.08. Performance data for pH at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

the Phase I partially treated mine water. Effluent pH levels increased to 6.46 and remained higher than flume pH levels for all sampling events that occurred after Phase II had been completed.

The pH of the water within the wetland is very important because it influences the solubility of metal hydroxide precipitates; the kinetics of metal oxidation and hydrolysis; and the viability of iron catalyzing and sulfate reducing bacteria. Autooxidation of ferrous iron in abiotic systems predominates above pH 5 (Singer and Stumm, 1970), while chemolithotrophic microbial iron oxidation occurs at lower pH levels (1-4). Aluminum hydrolysis occurs at pH $\approx$ 5 (Stumm and Morgan, 1981), and microbially catalyzed Mn oxidation occurs at pH > 6 (Wildeman, 1991). Silver (1989) also noted that a pH >5 is necessary for sulfate reduction in AMD systems. Therefore, reaching and maintaining a pH $\approx$ 6 in the treatment system is necessary for the adequate treatment of AMD and the prevention of secondary contaminantions through metal resolubilization.

Post renovation influent and flume pH values remained relatively constant except for an increase that occurred during January 1996 which may have been caused by freezing conditions and ice formation within the system. Post renovation effluent pH values, however, showed a gradual increase from 5.3 to 7.6 during the first nine months, followed by a drop to 6.4 where it remained for the rest of the study period. Flume and effluent pH values indicate that conditions were favorable for precipitation of metal hydroxides. The increased pH levels also suggest that a sufficient amount of alkalinity was generated to neutralize the acidity produced from hydrolysis. The slight decline in pH during the last four months may indicate that some of the limestone neutralizing potential associated with the finer particles may be exhausted and the buffering reached a steady state condition. Examination of alkalinity levels may be used to further explain the behavior of effluent pH. The observed pH conditions should also be examined with regard to the redox state of samples in order to evaluate the stability of metal oxides/hydroxides within the wetland system.

### *Eh and Dissolved Oxygen*

The ability to analyze the redox state of elements is important for characterization of chemical stability and biochemical cycles. Field Eh measurements are often used to evaluate the oxidative state of soil and wetland environments. Patrick and Mahapatra (1968) suggested five redox conditions in soils at pH 7: oxidized (>400 mv); moderately reduced (100 to 400 mv); reduced (100 to -100); and highly reduced soils (< -100 mv). Alternatively, the $Fe^{2+}$ to $Fe^{3+}$ redox couple is sometimes used as an arbitrary boundary between oxidizing and reducing conditions. It has been suggested that an Eh of 150-250 mv is representative of conditions necessary for $Fe^{3+}$ reduction (Bohn, 1971; Kadlec and Knight, 1996).

Post renovation Eh values at the Jones Branch wetland suggest that both oxidizing and reducing conditions occurred within the system. Influent surface water samples display a moderately reduced redox potential (260 mv), which increased as drainage was exposed to oxygen in the first precipitation basin (Table 1.8). The drainage then moves through a series of anaerobic to aerobic zones of treatment. In the biotic wetland cells, Eh

Table 1.8. Mean† Eh and pH values from surface and subsurface water samples in the Jones Branch wetland.‡

Surface Water

| | Lagoon | B1 | B2 | B3 | B4 | B5 | C1 | C2 | C3 | C4 | C5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Eh (mv) | 260.6 | 294.8 | 345.4 | 246.8 | 169.1 | 264.3 | | | 83.8 | | 159.3 |
| pH | 3.38 | 3.20 | 3.19 | 4.62 | 5.69 | 4.83 | | | 6.07 | | 6.46 |

Subsurface water

| | Lagoon | B1 | B2 | B3 | B4 | B5 | C1 | C2 | C3 | C4 | C5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Eh (mv) | 269.1 | 176.6 | 67.8 | -10.06 | 48.2 | 97.9 | 13.2 | -14.3 | 6.7 | -28.1 | -72.5 |
| pH | 3.51 | 3.93 | 5.53 | 6.20 | 6.04 | 5.36 | 5.76 | 6.35 | 6.63 | 7.16 | 7.72 |

†Standard deviations for the mean are presented in the Appendix.

‡ Sample sites are indicated as, B# = abiotic precipitation basin; C# = biotic wetland cell.

values were greatly reduced due to low oxygen diffusion rates and high oxygen demand by the organic compost. However, the Eh increased as the drainage left the wetland cell and moved into the abiotic basin due to surface aeration and a decreased biochemical oxygen demand. Redox conditions were highest at the second precipitation basin (345 mv), then gradually decreased toward the last basin where values rebounded. This rebound to more oxidized conditions may be attributed to the lack of vegetation in wetland cell 4. The lack of vegetation in cell 4 was the result of a flooding event and is discussed further in the Hydrology section of this chapter. Since vegetation was not established in cell 4, attachment of microorganisms that would normally create a high biochemical oxygen demand were absent in the substrate. Moreover, water levels above the substrate in cell 4 were high due to lower evapotranspiration rates and loss of some of the substrate, thus, the potential for turbulence, surface aeration and subsequent increases in dissolved oxygen levels were high. In general, surface water samples displayed higher Eh levels than subsurface waters, and abiotic basins showed higher Eh values than biotic wetland cells. Therefore, metal speciation and solubility control are expected to vary between these zones of differing oxidation.

The comparison of Eh and pH values from the post renovation period suggests that influent samples were operating under reduced conditions with soluble ferrous ($Fe^{2+}$) iron as the probable dominant iron species. Effluent samples, on the other hand, exhibited lower Eh values than influent waters, but the increase in pH may have shifted iron stability to the ferric ($Fe^{3+}$) form with insoluble $Fe(OH)_3$ as the dominant species. The relationship between Eh and iron redox chemistry is of great consequence to alkalinity production since $Fe(OH)_3$ has the capability to coat and armor limestone rendering it less effective or useless. Influent/effluent Eh-pH values indicated that $Fe^{2+}$ oxidation occurred within the system, but provide little information as to the conditions within the substrate and ALD's.

Subsurface water samples were collected from within the limestone substrate zone and subjected to on-site Eh and pH determination. Results indicated that the subsurface water displayed a higher pH than surface waters, but also exhibited much lower Eh conditions (Table 1.8). In the biotic wetland cell substrates, Eh values ranged from 13.2 to -72.5 which implies highly reduced conditions and the prevalence of ferrous iron. Unfortunately, subsurface samples could not be taken within the ALD's, so a submersible dissolved oxygen (DO) probe was used at the inlet and outlet of the pipes to evaluate redox conditions. Dissolved oxygen levels below 2 mg $L^{-1}$ will maintain iron in its reduced state, which is a necessary requirement for long term treatment by ALD (Skousen, 1991). Results indicated that DO levels were lower than 2 mg $L^{-1}$ throughout the post renovation period. Thus, the armoring of limestone should be prevented in both ALD and substrate environments based upon the prevailing redox conditions.

### *Alkalinity*

Pre-renovation samples at all locations and all influent samples throughout the study contained no titratable alkalinity (Figure 1.9). Pre-renovation samples reveal that the system had zero buffering capacity to combat acidity produced during hydrolysis, thus, pH levels dropped as drainage proceeded through the system (Figure 1.8). At the restart of

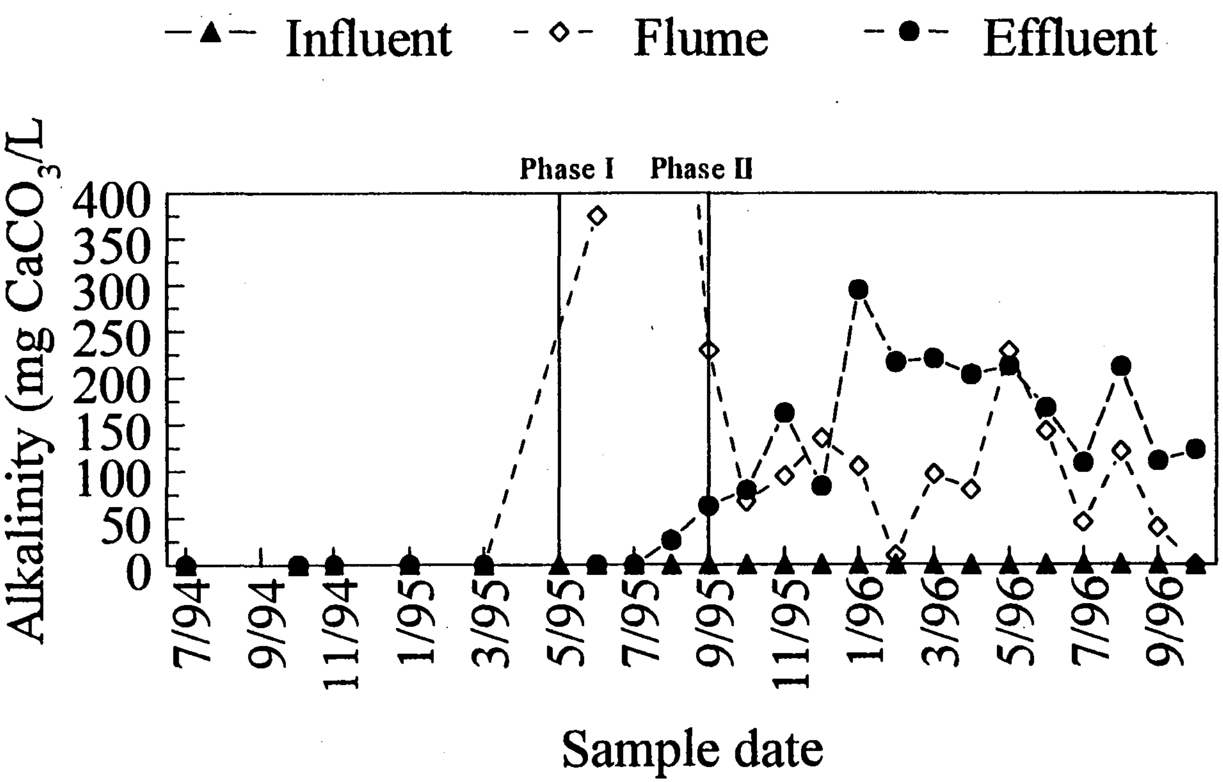

Figure 1.09. Performance data for alkalinity at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

the system following renovation, alkalinity levels at the flume displayed a tremendous increase to 1268 mg $CaCO_3$ $L^{-1}$. Dissolution of limestone dust and fines accumulated in the system during the renovation probably elicited this response. Alkalinity generation in flume samples after renovation was erratic with values ranging from zero to 238 mg $CaCO_3$ $L^{-1}$. Post renovation wetland effluent samples, on the other hand, displayed an increase from zero to ≈ 200 mg $CaCO_3$ $L^{-1}$ during the first nine months then fell to ≈ 100 mg $CaCO_3$ $L^{-1}$ during the last few months of the study. Apparently, either limestone dissolution or sulfate reduction processes, or both, peaked during the first nine months and possibly moved toward a steady state afterward. Alternatively, this reduction may be an indication that some iron coating of limestone particles may have taken place in the substrate.

### *Iron*

Total influent iron concentrations prior to renovation showed erratic levels and limited retention within the wetland system (< 30%) (Figure 1.10). Pre-renovation influent fluctuations in metal content, and other parameters, may have been the result of several seeps which appeared at the site toward the end of the 1994 summer. Much of the drainage which had been flowing into the wetland was bypassing the system and flowing directly into Jones Branch. These seeps were eventually contained by the construction of the lagoon during the renovation and influent levels have remained relatively constant since. Post renovation analysis displayed a drastic reduction in iron levels. Mean influent total Fe levels dropped from 787 to 110 and 37 mg $L^{-1}$ at the flume and effluent,

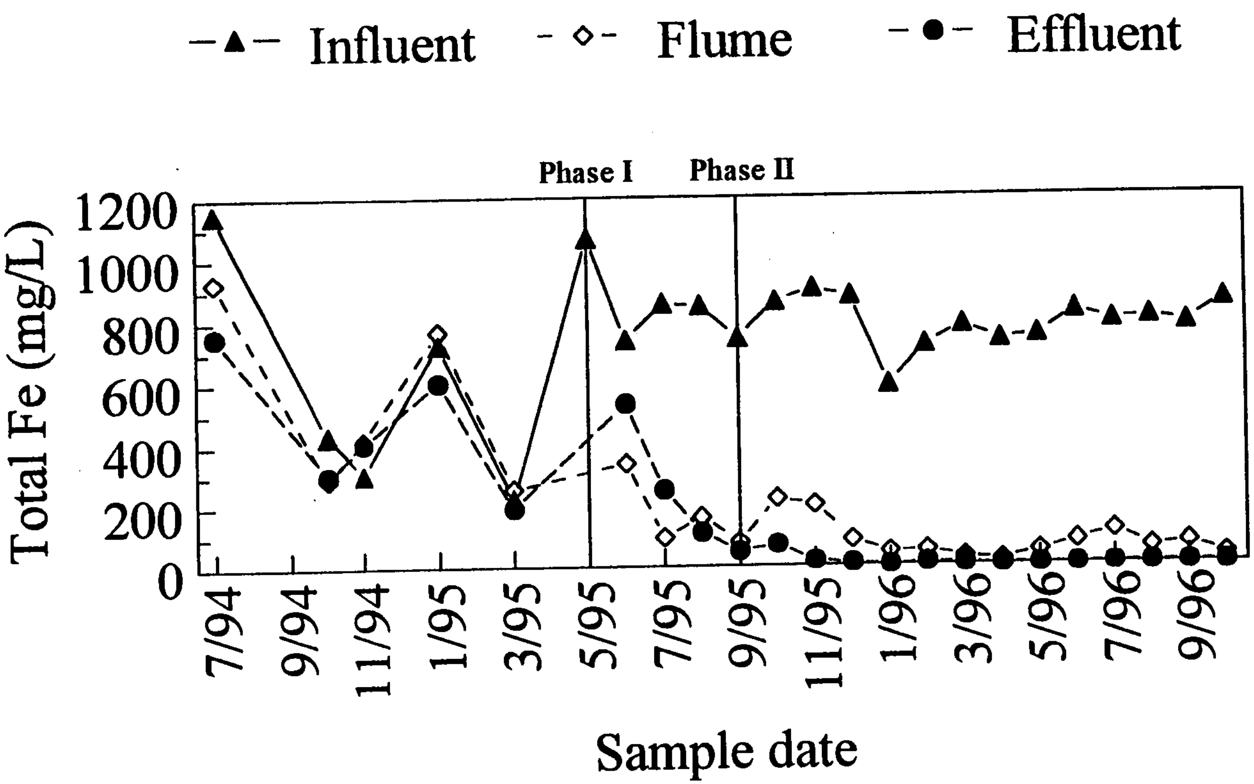

Figure 1.10. Performance data for total iron at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

respectively. This accounted for an 86% Fe reduction in field 1 and a total reduction of 95% for the entire system. Mean effluent Fe levels did not meet OSM discharge guidelines for the entire post construction period, however, samples from 11/95 through the end of the study period contained an average of 3.3 ± 2.5 mg $L^{-1}$ Fe which would satisfy the discharge criteria.

Iron retention in the wetland system was the result of several precipitation and/or adsorption processes at the surface and within the substrate. The formation of insoluble oxyhydroxide, carbonate, and sulfide precipitates within AMD treating wetland systems have been suggested to be responsible for the observed reduction of iron in effluent samples. The hydrolysis of ferric iron or microbial oxidation of ferrous iron usually accounts for 40 to 70% of the total iron removed from AMD by wetlands (Henrot and Wieder, 1990; Wieder, 1993), while nearly 30% of the iron retained may be an iron sulfide form (McIntire and Edenborn, 1990; Wieder, 1993). Limestone dissolution and high $pCO_2$ concentrations in the wetland substrates may also provide the conditions necessary for iron carbonate precipitation.

Sequential extractions of substrate samples revealed that nearly 70% of the iron within the Jones Branch wetland was in the oxyhydroxide form. Sequential extractions also indicated the potential for crystalline iron sulfide precipitation, however, AMD samples indicated undersaturation with pyrite. Based on the high $pCO_2$ levels usually encountered in waterlogged soils, wetland substrates may favor siderite precipitation. Therefore, the remaining ≈ 30% of iron retained in the wetland may be attributed to siderite precipitation, adsorption to exchange sites, and/or organic complexation. Even though the solution data suggest that pyrite formation is not favored under the current conditions, future precipitation with solution chemistry shifts is possible.

Characterizations of surface waters and abiotic zones within the treatment system suggested the presence of crystalline Fe oxyhydroxide minerals such as hematite, lepidocrocite, goethite, and jarosite. Biotic wetland cell substrate characterization suggested the presence of amorphous iron minerals such as ferrihydrite and $Fe(OH)_3$. Apparently high $Fe^{3+}$ activity and low oxygen diffusion rates in the lower biotic subsurface environment inhibited the kinetics of crystalline iron precipitation. Instead, amorphous ferrihydrite appeared to dominate the wetland compost area. Some goethite, lepidocrocite and hematite, however, were observed near the surface in wetland cells and were most likely attributable to increased oxygen levels from surface aeration and/or oxygen transport by plant roots. A detailed summary of iron retention processes is presented in Chapter two. The fate of acidity corresponds almost identically to that of Fe (Figure 1.11), which implies that much of the acidity produced originates from dissolved iron and can be treated by its removal (Hedin and Nairn, 1993). Moreover, iron oxidation and hydrolysis reactions are strongly influenced by the solution pH such that high levels of acidity may result in low metal removal rates. It has been shown that rate constants for the formation of iron precipitates increases from minutes and hours at circumneutral pH values, to months and years as pH falls below 4 (Stumm and Morgan, 1970). Therefore, the

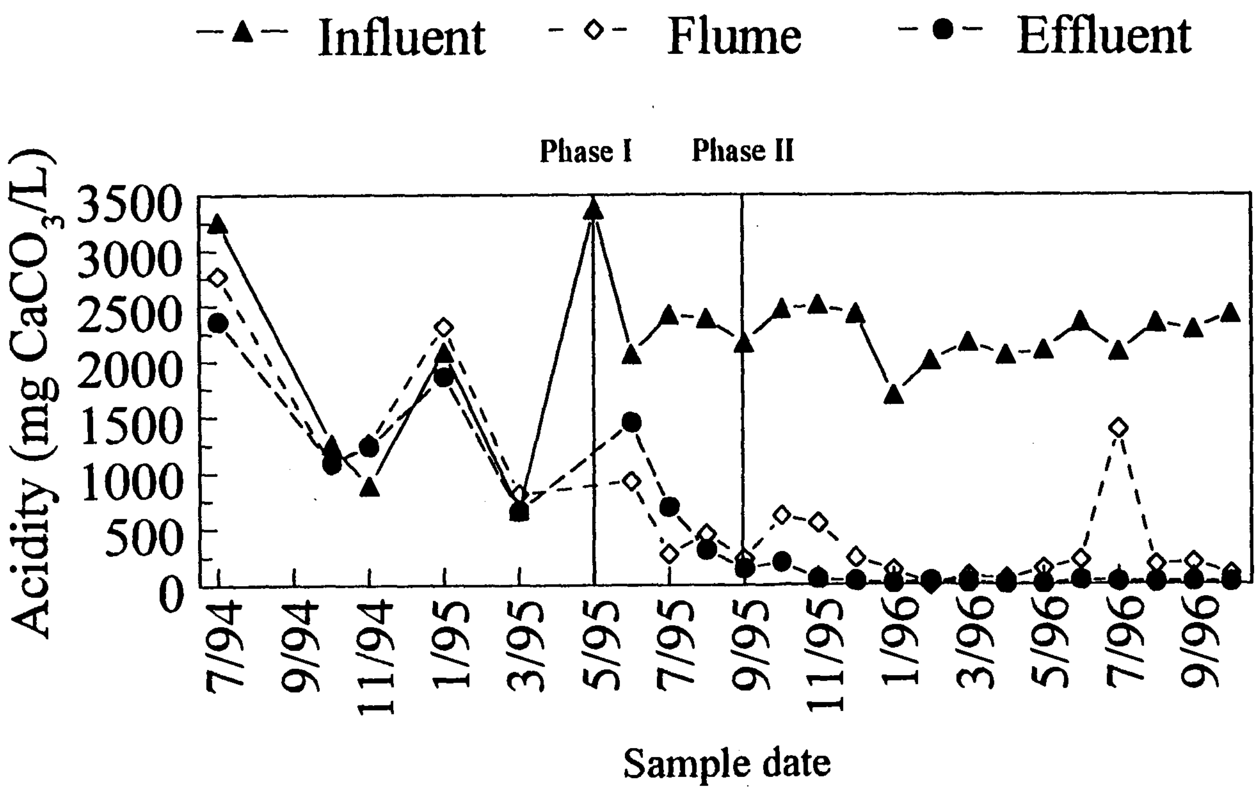

Figure 1.11. Performance data for acidity at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

maintenance of high alkalinity levels is necessary for continued metal removal within the wetland system.

### *Aluminum and Manganese*

Aluminum concentrations were reduced by 98% through the wetland after renovation and low levels (< 0.7 mg $L^{-1}$) were observed in the effluent throughout the post renovation period (Figure 1.12). This reduction may be attributed to the solubility of Al which is pH dependent and forms aluminum hydroxide precipitates at pH ≈ 5.0 (Stumm and Morgan, 1981). Interstitial solution analysis reveals that a pH of 5.76 is achieved in the subsurface of the first wetland cell and maintained at or above this level in subsequent substrate zones (see Chapter two).

Manganese concentrations, on the other hand, displayed a moderate 48.6% reduction through the wetland system and showed variable efficiency rates. Several researchers have reported similar results for Mn in wetland treatment systems (Wieder, 1989; Fennessy and Mitsch, 1989; Brodie, 1990; Brodie et al., 1993; Dietz and Stindinger, 1996; Sikora et al., 1996), and attribute low efficiency rates to several biogeochemical interactions and slow kinetic processes of $Mn^{2+}$ oxidation (Stumm and Morgan, 1981). A pH of 8 to 10 is generally accepted as the level needed for uncatalyzed Mn oxide precipitation (Stumm and Morgan, 1981; Brezonik, 1994), which, unfortunately, is infrequently reached in AMD treatment environments. Manganese oxide precipitation can occur at lower pH levels (6-8) by coprecipitation with Fe oxyhydroxides (Watzlaf, 1988), catalysis via microorganisms (Bender et al., 1994), or sorption onto other solids (Watzlaf,

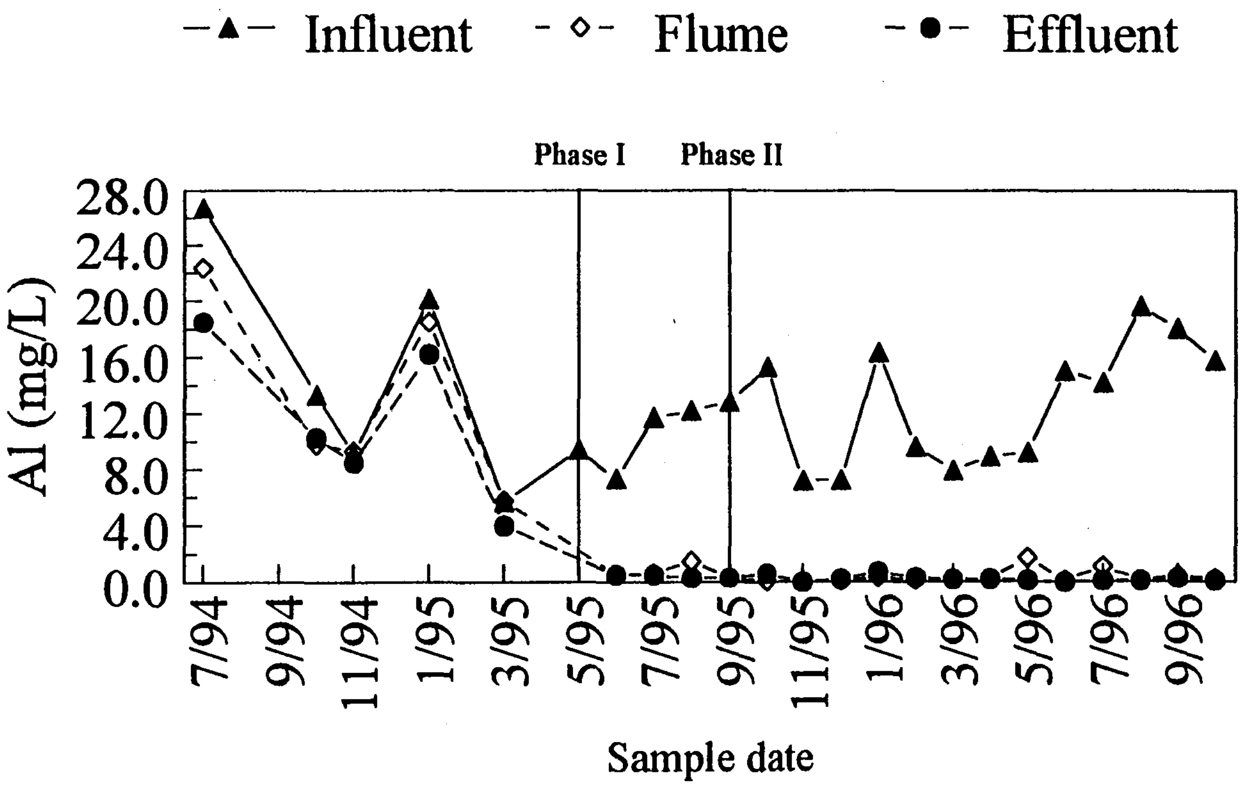

Figure 1.12. Performance data for aluminum at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

1988; Davies and Morgan, 1989). However, ferrous iron may control Mn oxidation rates in reduced environments by contributing electrons to previously precipitated Mn oxides and producing soluble $Mn^{2+}$ (Burdige et al., 1992; Hedin et al., 1994 b). Manganese retention in the Jones Branch wetland appears to be influenced by all of these factors.

Flume Mn concentrations displayed an initial four month reduction from influent levels after Phase I renovation, then returned to levels equal with the influent (Figure 1.13). The completion of Phase II resulted in an initial three-month reduction of effluent Mn concentrations while flume values remained consistent with influent concentrations. By November 1995, flume and effluent Mn concentrations remained relatively equal and displayed reductions from 30 to 90%. The reduction of Mn during the first four months of Phase I, when field 2 was not contributing to treatment, and the first three months of Phase II, when field 1 did not contribute to Mn treatment, may be attributed to sorption processes. In the initial months of AMD treatment by compost wetlands, sorption sites on organic matter and limestone are plentiful (Kleinmann et al., 1991; Wieder, 1993; Wildemann et al., 1994). Sorption of Mn onto carboxyl and hydroxyl functional groups in fresh compost occurs upon exposure, but can soon become saturated (Henrot and Wieder, 1990). Sorption of Mn onto limestone may also occur by displacement of soluble $Ca^{2+}$ for $Mn^{2+}$ and formation of a solid phase $MnCO_3$ at the surface (Evangelou, 1995).

The concentration of Mn in the flume and effluent, after November 1995, appears to be influenced by loading rates and $Fe^{2+}$ concentrations. After Phase II renovation, flume and effluent Mn levels gradually dropped during the first eight months, then increased in

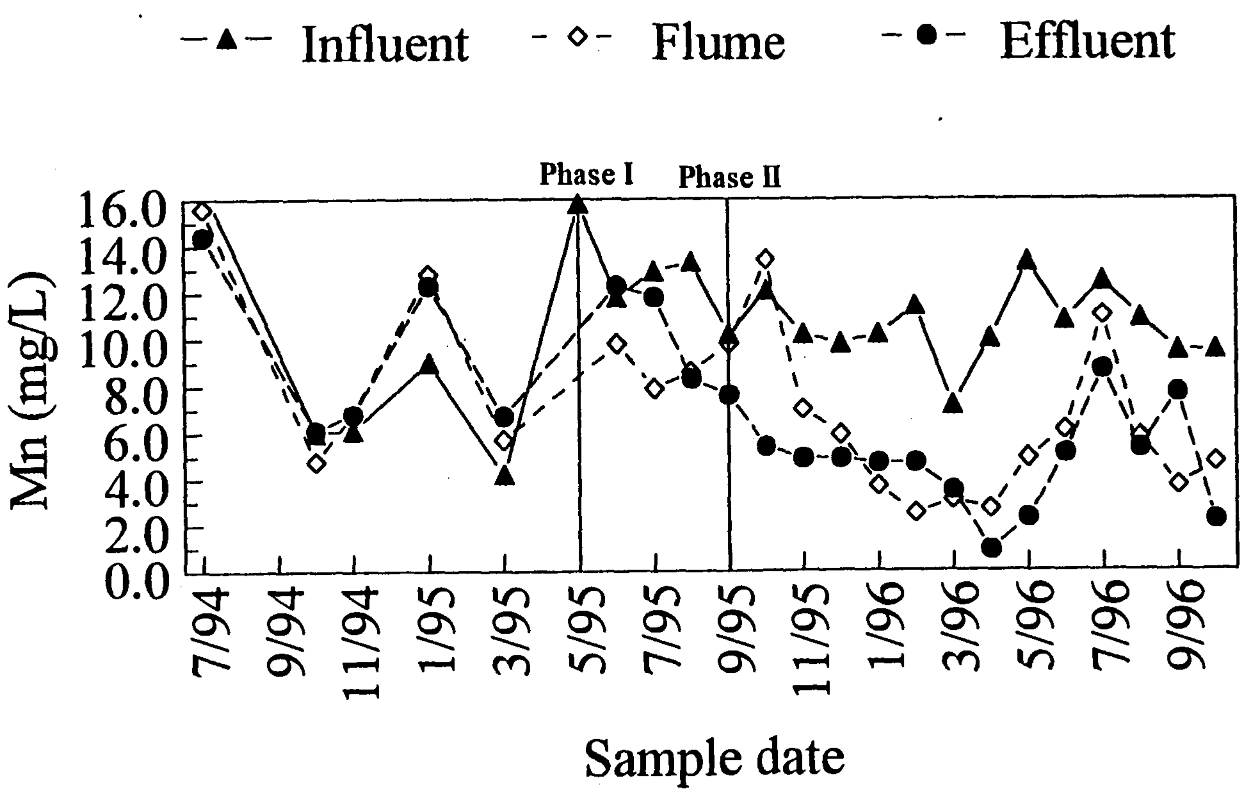

Figure 1.13. Performance data for manganese at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

the following four months before falling again toward the end of the study (Figure 1.13). This trend was consistent with influent loading rates during the post construction period. With the exception of one sampling event (2/96), the mean Mn loading rate of the first eight months was 318 ± 107 g day$^{-1}$, while the following four months displayed a mean of 645 ± 107 g day$^{-1}$ (Figure 1.14). However, the difference in Mn retention between these time periods was not significant and two of the higher reduction rates actually occurred during the later four month period. Thus, loading rates may have influenced the final Mn concentration, but removal rates were governed by other processes. Figure 1.13 reveals that most of the Mn treatment occurred in field 1. Upon observation of analytical data for flume waters, a relationship between total Mn and $Fe^{2+}$ was discovered. Apparently, Mn oxidation was inhibited by the presence of ferrous iron within the system (Figure 1.15). High $Fe^{2+}$ concentrations at the flume may have inhibited Mn oxidation and resolubilize oxides that had previously precipitated. This relationship can then be used to explain the variable Mn treatment rates. Areas displaying low $Fe^{2+}$ concentrations exhibited high Mn retention, while high $Fe^{2+}$ content corresponded with low Mn treatment efficiency.

The lack of Mn treatment in field 2 may be linked to a flooding event that occurred soon after Phase II renovation which led to poor vegetation establishment. After the sorptive capacity of the compost was fulfilled during the initial months of AMD exposure, additional removal of Mn may have occurred through coprecipitation with other oxides, uptake by plants and biota, or oxidation via microbial catalysis. Unfortunately, vegetation was not available in field 2 to provide the oxygenated root zone needed for these reactions

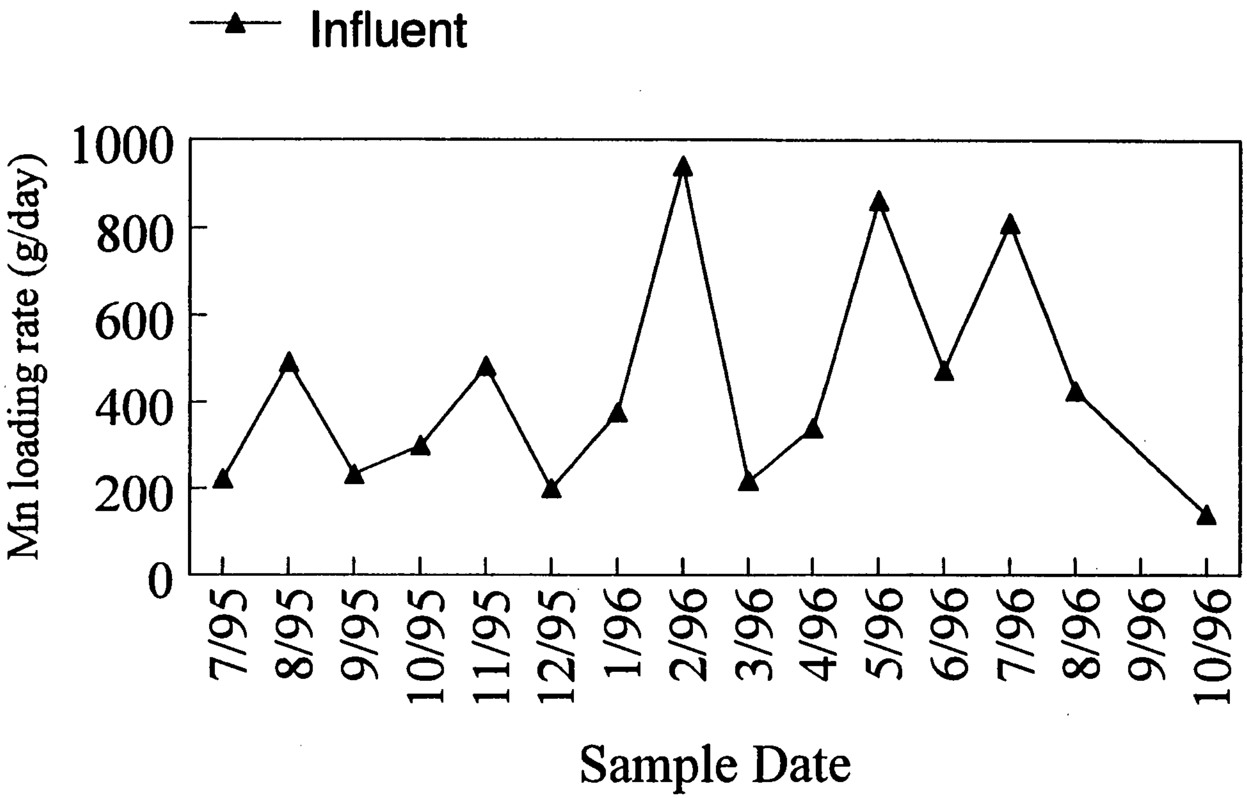

Figure 1.14. Influent manganese loading rates for the post renovation period at the Jones Branch constructed wetland.

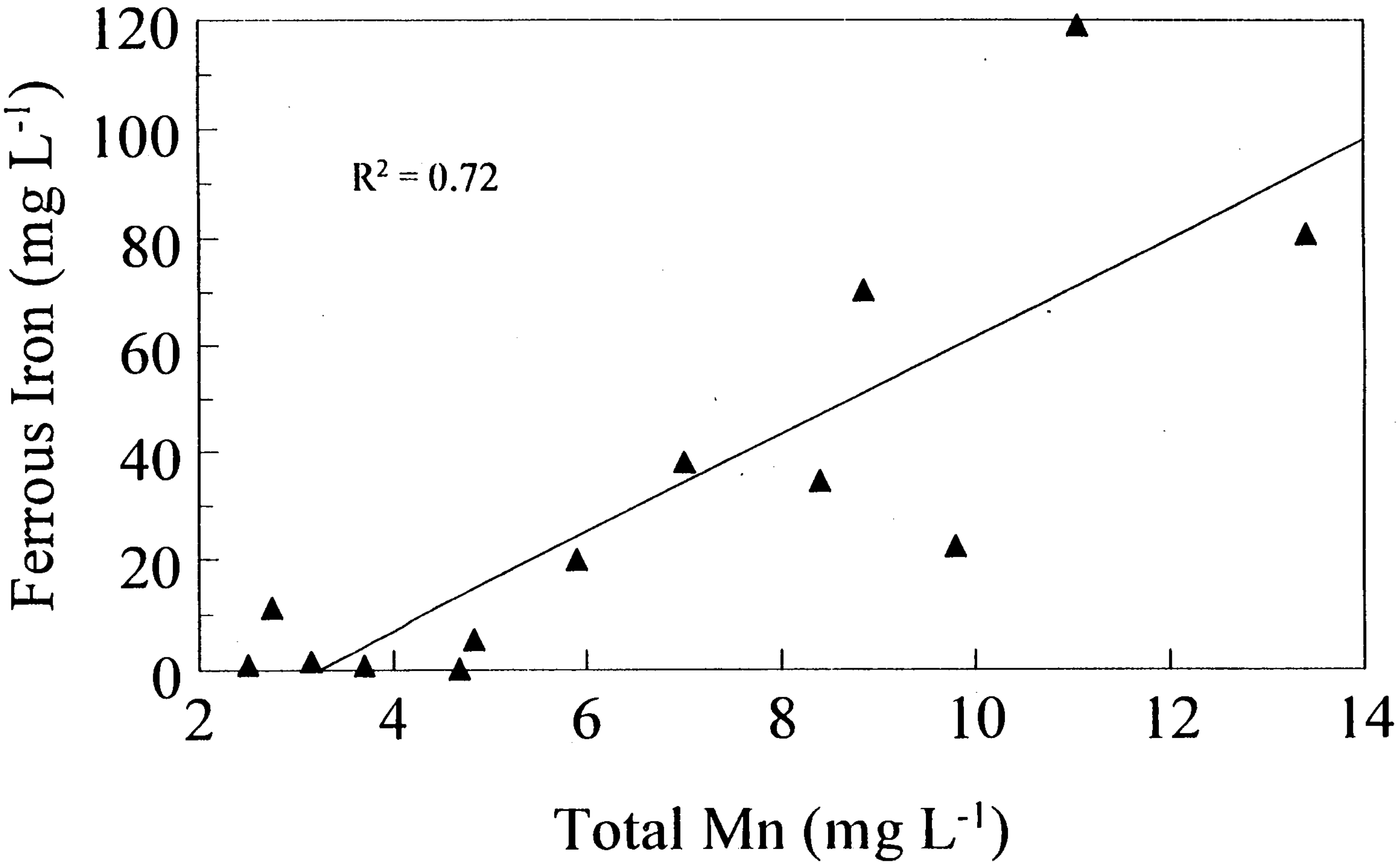

Figure 1.15. Influence of ferrous iron concentration on total manganese at the flume sampling point in surface water samples from the Jones Branch wetland.

to occur. In addition, Mn removal through coprecipitation was limited in field 2 since 86% of the total iron had been removed in field 1. Future re-establishment of field 2 vegetation should contribute to further Mn retention.

### *Sulfate*

The concentration of sulfate in the drainage was reduced by 53.4% as it passed through the wetland. Flume and effluent levels varied little during the post renovation period (Figure 1.16). On several occasions flume $SO_4^{2-}$ concentrations were lower than those observed in the effluent, which indicated lower redox conditions and higher $H_2S$ production in field 1. As with Mn, treatment processes appeared to diminish in field 2. In contrast to the Mn system, sulfate removal may have been hindered by the presence of adequate levels of oxygen in the upper water column and the high solubility of sulfate salts.

As drainage splashed off the flume and into the fourth precipitation basin, dissolved oxygen and redox values increased. Sulfate reduction depends upon fermenting bacteria to break down complex organic substrates (glucose and cellulose) into simple organic compounds (lactate and acetate) which can then be utilized by sulfate reducing bacteria (SRB) (Chapelle, 1993). An oxygen free environment is necessary for sulfate reduction because aerobic bacteria may deplete the supply of simple organic compounds to levels that are too low for utilization by SRB (Brock et al., 1994). Dissimilatory iron reducing bacteria (IRB) may also have influenced sulfate reduction in field 2. IRB use soluble carbon as an energy source and solid ferric oxyhydroxide as an electron acceptor

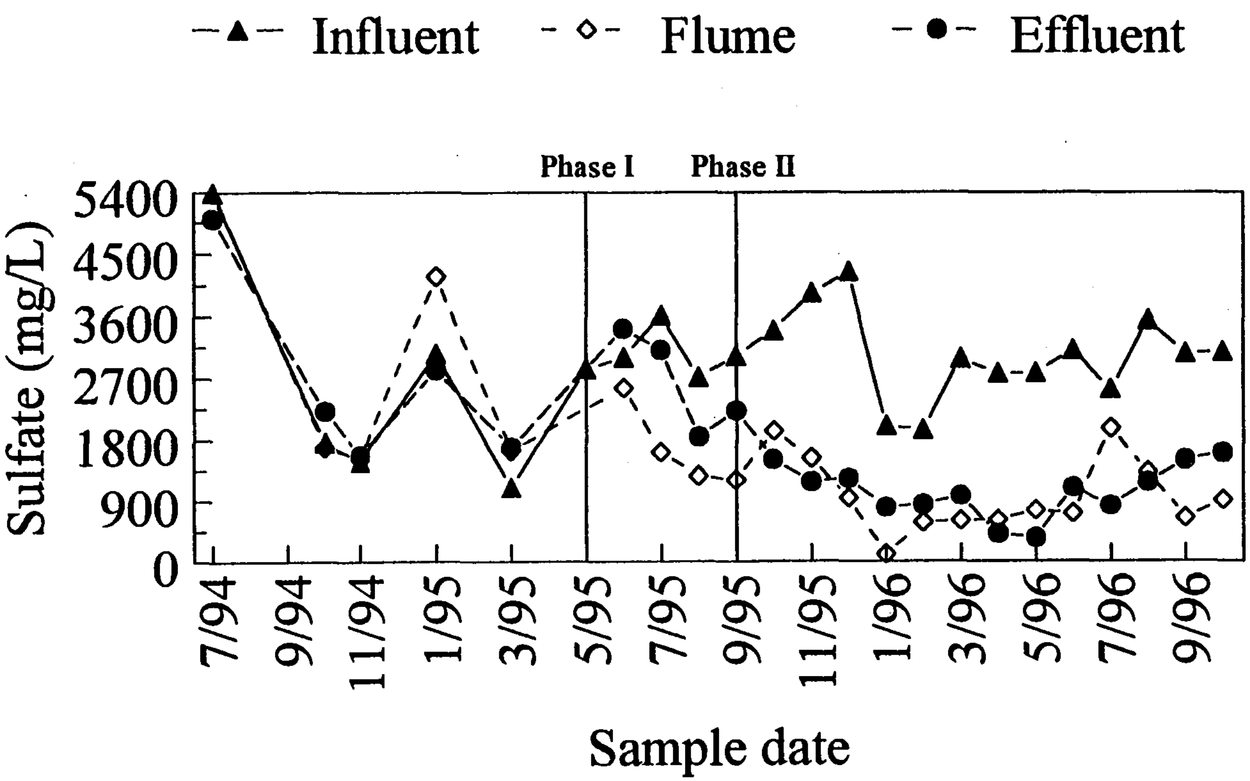

Figure 1.16. Performance data for sulfate at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

to produce soluble ferrous iron (Lovely, 1993). If SRB and IRB compete for the same carbon source, in the presence of excess sulfate and FeOOH, IRB have the potential to competitively exclude SRB as the dominant microbe in the substrate (Chapelle and Lovely, 1992). However, definitive conclusions on the role of bacteria in both Mn and sulfate systems cannot be made from information available at this time. Comparisons of current research to those generated after establishment of vegetation in field 2 might indicate a biological link to the treatment process. Moreover, biological treatment variations attributable to climate cannot be determined at this time due to the limited data base and the small number of seasons examined. Future research to isolate and identify microbial populations within the wetland would be beneficial.

Bacterially mediated sulfate reduction may be occurring at a much lower rate than initially anticipated. Sulfate retention within the wetland may actually be attributed to the precipitation of gypsum. According to Lindsay (1979), gypsum is too soluble to persist in soils unless $SO_4^{2-}$ activity approaches $10^{-2}$ *M*, which happens to be the approximate level currently found at Jones Branch. Geochemical modeling suggested that the system was at or near saturation with respect to gypsum in both surface and interstitial solutions. To verify this precipitation event, the fate of calcium was examined.

### *Calcium*

The dissolution of limestone and subsequent increase in calcium and carbonate species is expected as AMD passes through the wetland. The completion of Phase I and II renovation corresponded to an initial increase in effluent $Ca^{2+}$ concentration (Figure 1.17).

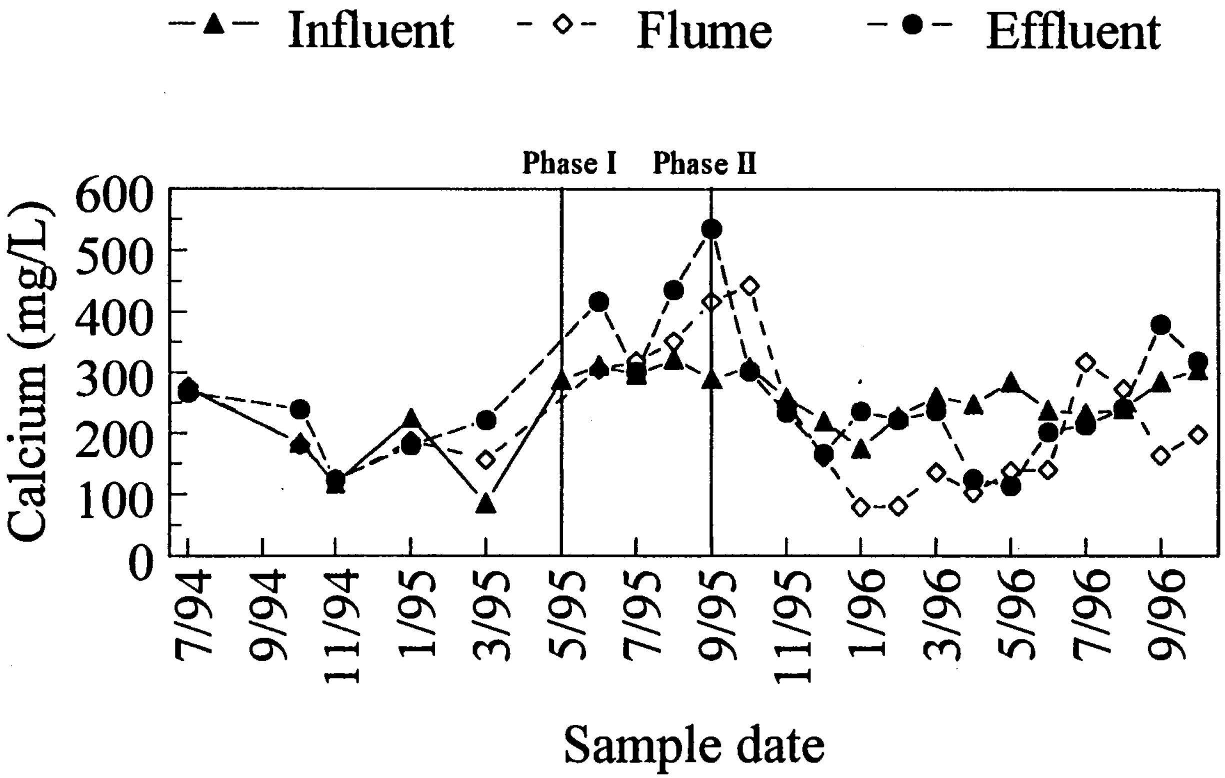

Figure 1.17. Performance data for calcium at the influent, flume and effluent sampling points in the Jones Branch constructed wetland.

However, flume and effluent waters displayed reductions in $Ca^{2+}$ concentration after the November 1995 sampling period. Interestingly, flume samples usually contained less $Ca^{2+}$ than effluent samples. The initial increase in $Ca^{2+}$ may be attributed to fines and dust from placement of limestone in the ALD's and substrate. By November 1995 calcium levels had dropped below influent levels which indicates that precipitation or sorption processes were exceeding dissolution. Since $Ca^{2+}$ levels were lowest in flume samples, precipitation of gypsum most likely occurred to a greater degree in field 1. Trends for the retention of $Ca^{2+}$ in field 1 are similar to those observed in the $SO_4^{2-}$ system. After drainage entered field 2, either limestone dissolution was promoted or gypsum precipitation was inhibited which resulted in the increase of observed $Ca^{2+}$ levels. Based on sulfate results, gypsum precipitation was probably inhibited in field 2 while limestone continued to dissolve. Moreover, sampling events in which flume $SO_4^{2-}$ levels exceeded effluent concentrations corresponded to flume $Ca^{2+}$ levels that exceeded those observed in the effluent. The actual amount of gypsum precipitated within the system was hard to assess because we could not quantify the amount of limestone dissolution that took place before it was precipitated. Therefore, determinations on the contribution of sulfate reduction vs. gypsum precipitation toward the fate of sulfur within the wetland system were difficult to make.

### *Hydrology*

The 1022 $m^2$ original wetland constructed at Jones Branch was limited by surface area, due to topography, and high metal loading. In addition, high flow rates and low retention time curtailed exposure of AMD to substrate components used in the treatment process. The wetland was only large enough to meet the U.S. Bureau of Mines minimum hydraulic load design requirements eighty percent of the time (Chalfant, 1993) without consideration of the metal or acidity loading. Based on the acid load, a ≈ 16,000 $m^2$ wetland is needed to sufficiently treat AMD at Jones Branch. Unfortunately, alterations to increase the size of the wetland were not possible, so designs were selected for renovation that would adequately regulate the flow into and within the system, and increase retention time. The average flow rate of AMD into the wetland prior to renovation was 87 lpm. Two 30 cm gate valves were installed at the outlets of the ALD's to reduce the flow rate and provide a method to control water levels within the system. Average influent flow rates after renovation were lowered to 37.1 lpm, but variability in monthly flow still existed (Figure 1.18). An attempt to keep flow rates at ≈ 20 lpm during the first year, for plant establishment, saw some success, however, we discovered that regulating flow from two 30 cm valves into one 15 cm subsurface pipe was extremely difficult.

Average effluent flow rates were 26.1 lpm for the post construction period. The decrease in mean effluent levels may be attributed to evapotranspiration, especially during the summer months. The influence of rainfall on effluent flow rates was difficult to determine since continuous flow measurements were not performed. However, two sampling events (10/95 and 10/96) did reveal increased flow in the effluent which indicated the retention of water from a rainfall event. The subsurface flow system was installed to increase retention time and promote flow through the substrate. Prior to renovation, retention of drainage within the system was estimated to be ≈ 2 hours. A

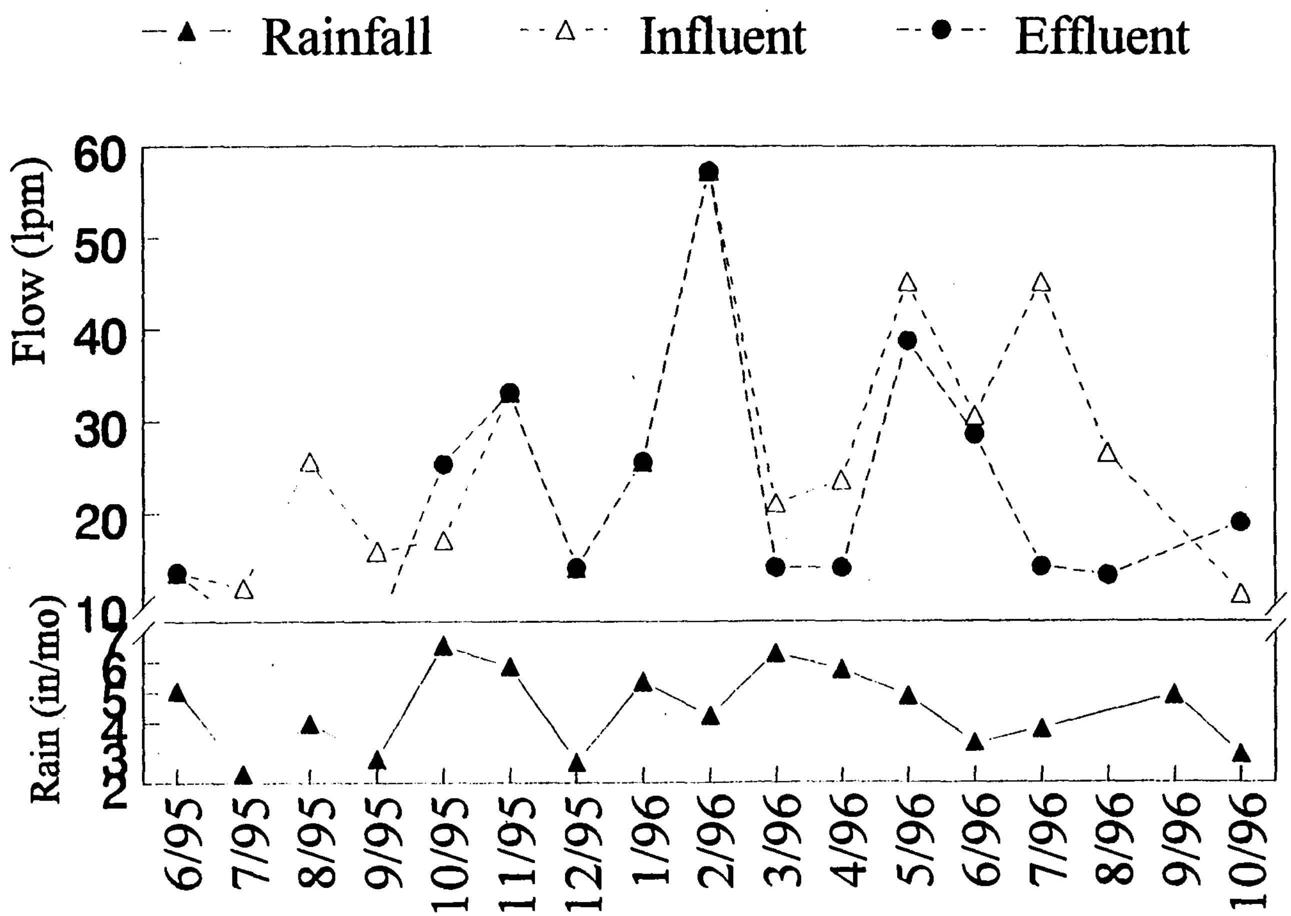

Figure 1.18. Influent and effluent flow data; and monthly rainfall accumulation during the post renovation period at Jones Branch wetland.

tracer study similar to the one performed by Hellier (1996) was conducted to determine retention time in the renovated system. An increased residence within the system to nearly 94 hours was determined by the study. Thus, the goal of increasing contact time between AMD and the substrate was achieved, however, problems associated with increased water depth after rainfall were created. Even though rainfall dilutes the AMD and lessens the amount of chemical stress to vegetation and bacteria, water levels that are too high can have profound effects on early plant development as well as oxygen and nutrient availability to wetland substrates and microorganisms (Guntenspergen et al., 1989). Retention of a 12.7 cm rainfall event in October, 1995 (Figure 1.18) caused substrate expansion in field 2 and subsequent uprooting of recently transplanted cattails. Because of the systems delay in remove excess water, vegetation was not established in field 2 and treatment efficiencies may have suffered.

### *Loading Rates and Treatment Efficiency*

Evaluations on the performance of AMD wetland treatment systems are often based on treatment efficiencies, where effluent concentrations are compared to influent concentrations. However, efficiency alone is not very informative because the influence of flow on performance is withheld (Wieder, 1988). Loading rates represent the mass of a contaminant entering and leaving the wetland system. These rates can be produced from flow measurements and efficiency data by the equation:

$$\text{loading (kg day}^{-1}\text{)} = \text{lpm} \times \text{mg L}^{-1} \times 0.00144$$

(Stark et al., 1990). Post renovation influent Fe loading rates ranged from 16.5 to 59.3 kg $day^{-1}$, and averaged 42.0 kg $day^{-1}$ (Figure 1.19). Post renovation effluent Fe loading rates ranged from 10.5 to 0.03 kg $day^{-1}$, and averaged 1.4 kg $day^{-1}$. Based on these values, the wetland retained 18676 kg (18.7 metric tons) of iron during the post renovation period. The average acid load input was 120 kg $day^{-1}$, while output levels were reduced to 4.47 kg $day^{-1}$ (Figure 1.20). Thus, 53144 kg (53.1 metric tons) of acid were neutralized during the post renovation period. On a yearly basis the wetland system removed 14.8 metric tons of iron and neutralized 42.2 tons of acid. It was also estimated that the wetland removed an average of 0.37 kg Mn $day^{-1}$, and 170 kg of Mn over the entire study period.

Loading rates are also used to determine the optimal size for wetlands treating AMD. The design maximum for Fe and Mn removal by surface flow wetlands ranges from 10 to 20 and 0.5 to 1.0 gram per day per square meter (GDM), respectively (Hedin et al., 1994). Dietz and Stindinger (1996) suggest a design criteria for Fe at 10 GDM, and 25 GDM for acidity in subsurface flow wetland systems. During the post construction period, removal rates for Fe, Mn and acidity were 39.7, 0.37 and 113 GDM, respectively. From these results, the Jones Branch wetland system appears to have exceeded design limits for Fe and acidity removal, but fell short for Mn. Based on OSM design requirements (0.5-1.0 GDM), the Jones Branch system should be adequately treating Mn but instead appears to be somewhat inhibited. Research has shown that Fe oxidation/hydrolysis reactions can overwhelm and suppress other wetland system mechanisms (Brodie, 1993). In addition,

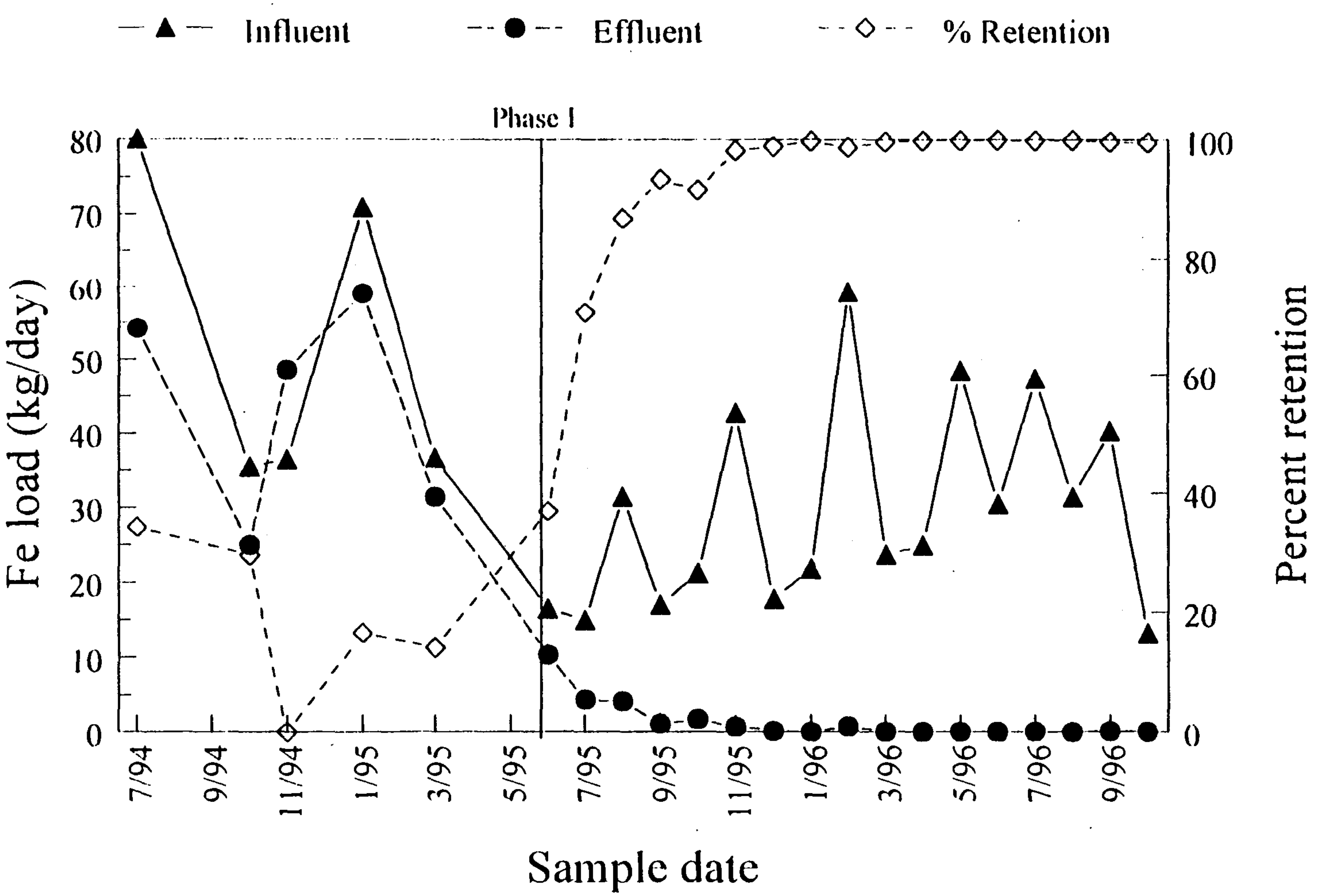

Figure 1.19. Loading rates and percent retention of total iron within the Jones Branch constructed wetland.

several problems associated with water depth, vegetation and microbial activity may have contributed to the inadequate Mn treatment.

Findings from this study suggest that the surface area requirements for high Fe and acidity AMD may be lowered by utilizing designs implemented in the renovation of the Jones Branch system. Retention rates, based on loading, reveal that nearly 100% of the Fe and acidity are removed from surface waters by the treatment system (Figures 1.19 and 1.20). Moreover, these retention rates were sustained during high load periods and have been maintained throughout the post renovation period. However, there also exists a chance that the high loading rates could overload the wetland and eventually reduce the life expectancy of the system.

### *Trends at Different Stages of Treatment*

Treatment of AMD by constructed wetlands involves numerous physical, chemical and biological reactions and interactions. In an effort to better understand some of these processes, examination of mean water quality as AMD passes through individual units of the treatment system was performed. High standard deviations of the mean are inherent in all of the following results due to the open nature of the wetland environment. Factors such as variable mine water chemistry, rainfall, evapotranspiration, temperature and flow contribute to the contaminant removal rates and fluctuations in daily water quality. However, the illustrative purpose of comparing means is valid as long as error bars are thought to represent minimum and maximum conditions, such that, a high or low influent concentration represents a similar condition at each sample point throughout the

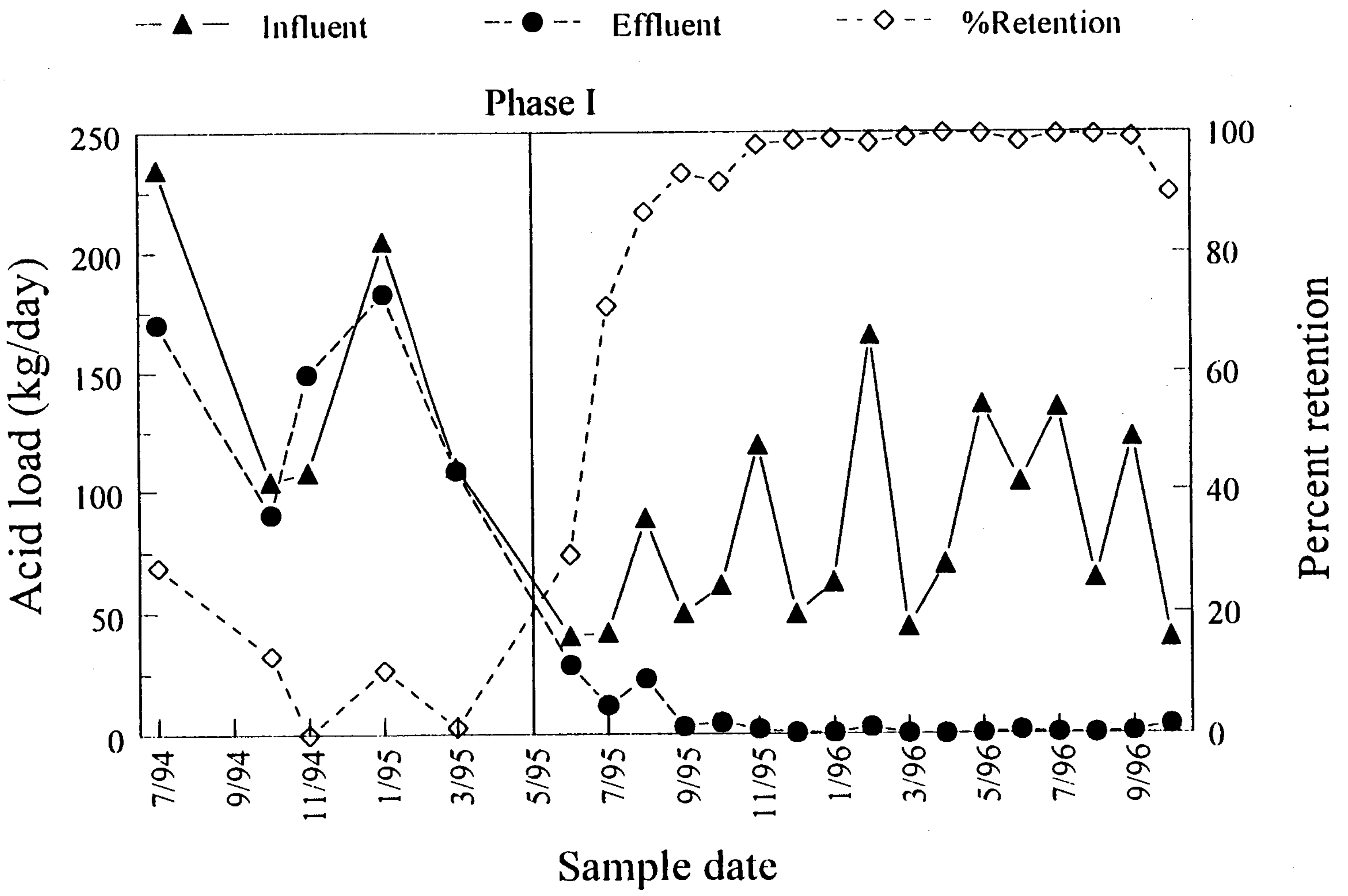

Figure 1.20. Loading rates and percent retention of acidity within the Jones Branch constructed wetland.

treatment system. Infrequently, did a high influent concentration result in an effluent that was lower than the average.

For all average post renovation figures, sample points 2 and 9 represent influent and effluent, respectively, while points 3,4,5,7, and 8 represent precipitation basins 1-5. Average post renovation results indicate that iron, aluminum and acidity are greatly reduced in the first wetland cell (Figures 1.21 and 1.22), then gradually drop through each successive stage of treatment. The average pH falls from 3.38 in the influent to 3.19 at the second precipitation basin before increasing to 4.62 in the third basin. This suggests that the alkalinity generated by the ALD or the first wetland substrate is not enough to compensate for the shock of the first hydrolysis and acidity generation. It took the extra buffering generated by the second wetland cell substrate before it balanced out. From the third basin, pH showed a gradual rise to 6.46 in the effluent. As Fe levels were lowered and acidity production curtailed, pH levels displayed a corresponding rise. This rise may be attributed to alkalinity generation from sulfate reduction and/or carbonate dissolution (Figure 1.22c). It is anticipated that metal concentrations will increase and pH levels decrease in a sequential manner toward the effluent as the system ages and becomes saturated. At some point in time the treatment capacity of the wetland cells will be exhausted and the renovation process will need to be renewed.

Several parameters (Fe, Mn, $SO_4^{2-}$, acidity, total solids, and conductivity) displayed higher concentrations in the first precipitation basin than observed in the influent drainage (Figures 1.21, 1.22, and 1.23). This may be a response to changing Eh and pH

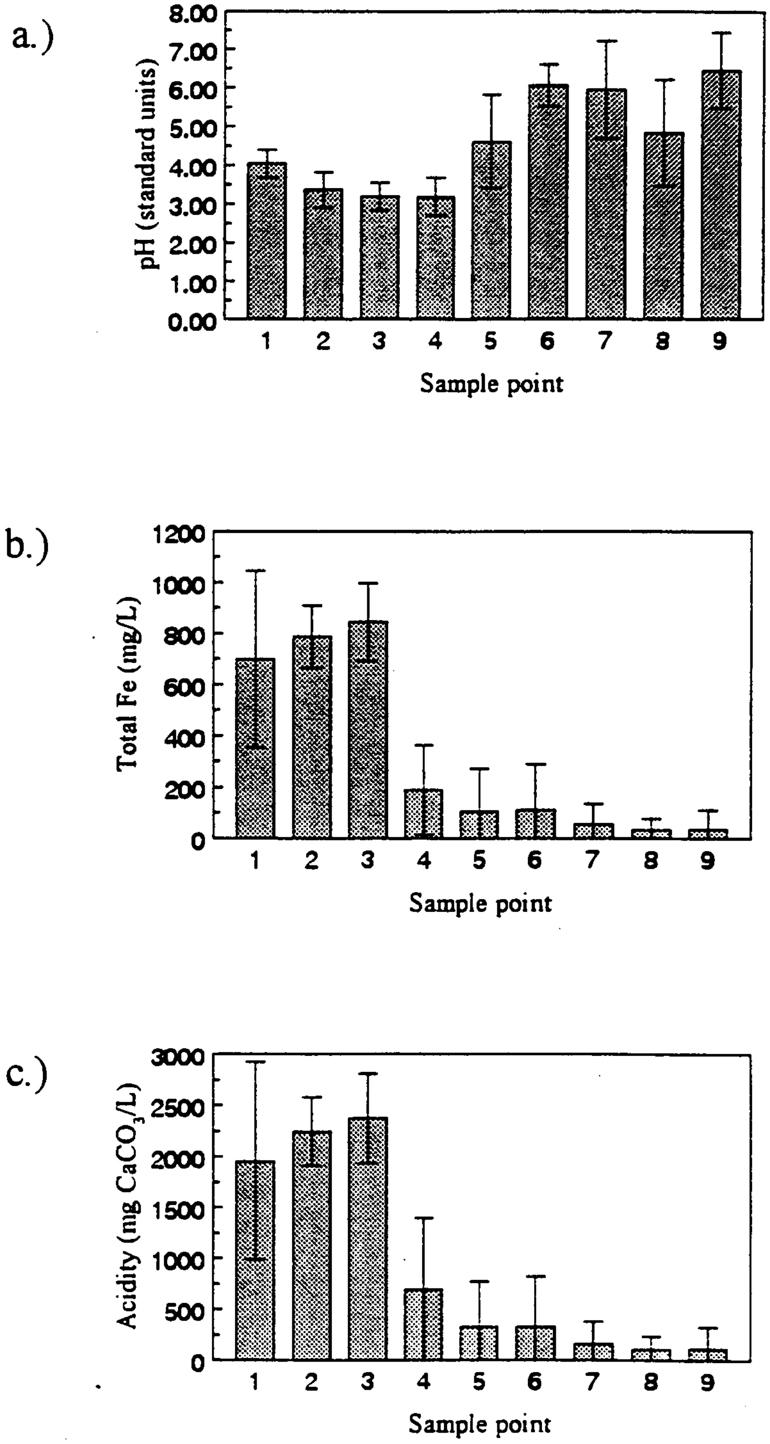

Figure 1.21. Mean post construction performance of a.) pH, b.) total iron, and c.) acidity at the Jones Branch wetland for the period July 1995 through October 1996.

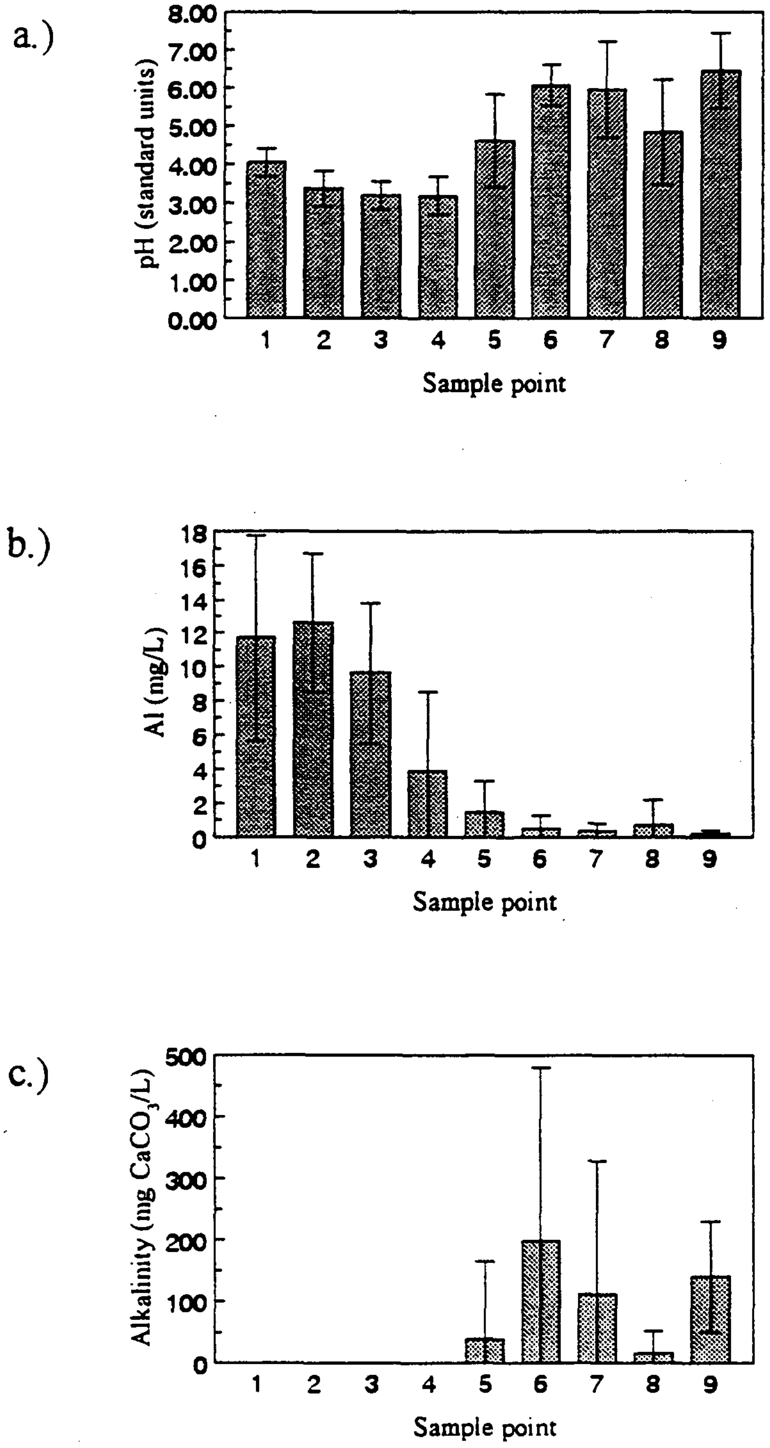

Figure 1.22. Mean post construction performance of a.) pH, b.) aluminum, and c.) alkalinity at the Jones Branch wetland for the period July 1995 through October 1996.

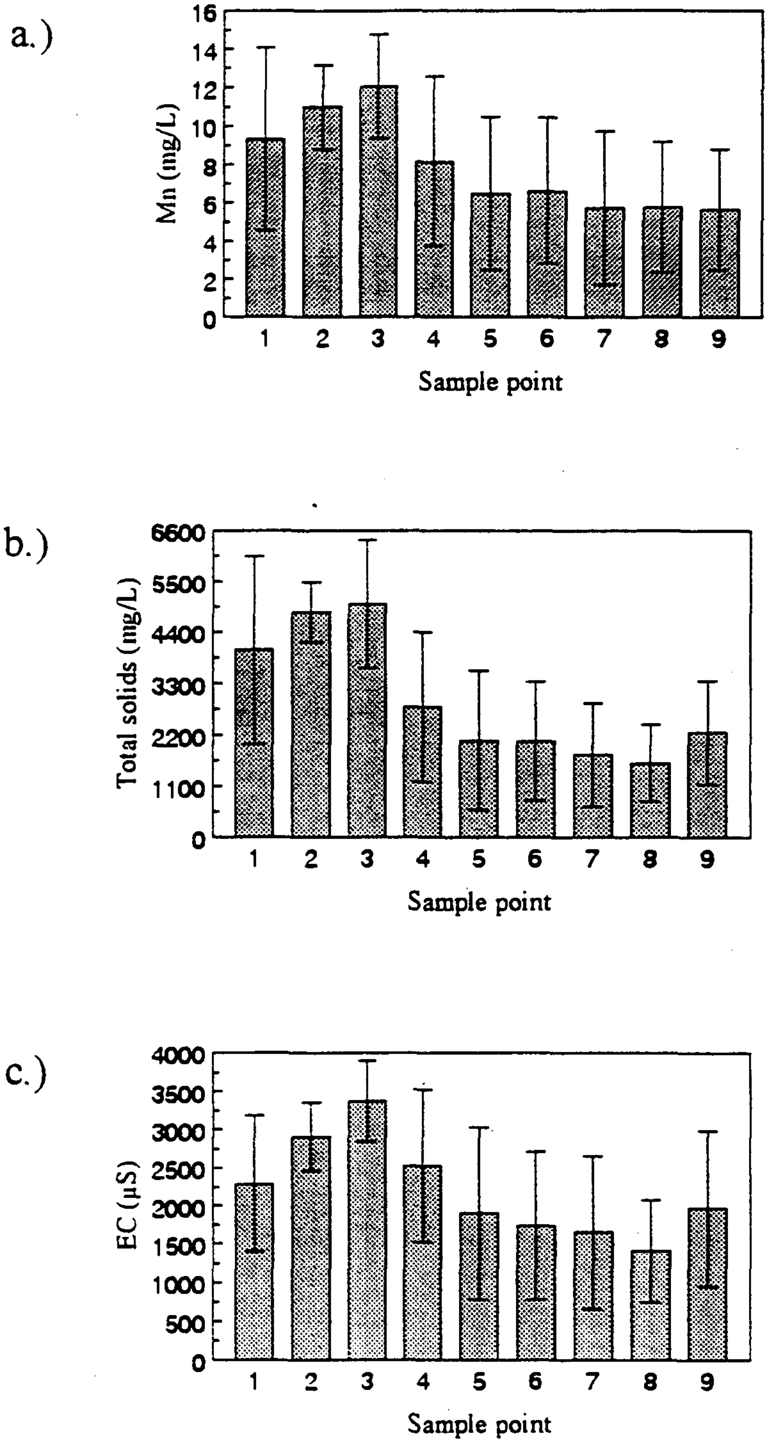

Figure 1.23. Mean post construction performance of a.) manganese, b.) total solids, and c.) conductivity at the Jones Branch wetland for the period July 1995 through October 1996.

conditions which promoted the formation of colloidal precipitates that remained suspended in the basin. Total solids and conductivity data confirmed the presence of this colloid phase. Acidification of the sample for metal analysis may have resulted in the solubilization of these particles and resulted in the observed increase, or low pH levels produced during hydrolysis may have increased the solubility of previously precipitated metals.

The anoxic limestone drains are located between sample points 2 and 3. Average iron and manganese concentrations did not display reductions through the drains, which suggested that precipitation of these metals was inhibited (Figures 1.21b and 1.23a). Aluminum, on the other hand, showed a reduction of 2.91 mg $L^{-1}$ as drainage passed through the ALD's (Figure 1.22b). Apparently, the pH inside the ALD's reached levels sufficient for aluminum hydroxide precipitation. Based on average influent flow rates, ≈ 72 kg of Al may have precipitated within the drains during the post renovation period. Continued Al accumulation could present a potential plugging problem (Nairn et al., 1992; Brodie et al., 1993; Hedin and Watzlaf, 1994). It has been suggested that $Al(OH)_3$ occurs in a gelatinous form within ALD and does not armor limestone as $Fe^{3+}$ does (Karathanasis, 1994; Kepler and McCleary, 1995), therefore, removal by flushing the system may be possible. Calcium and magnesium display increased concentrations as drainage flows through the ALD's which indicates dissolution of limestone within (Figure 1.24 a,b).

Influent/effluent comparisons do not indicate an increase in calcium concentration which may suggest limited limestone dissolution, however, several sampling points display

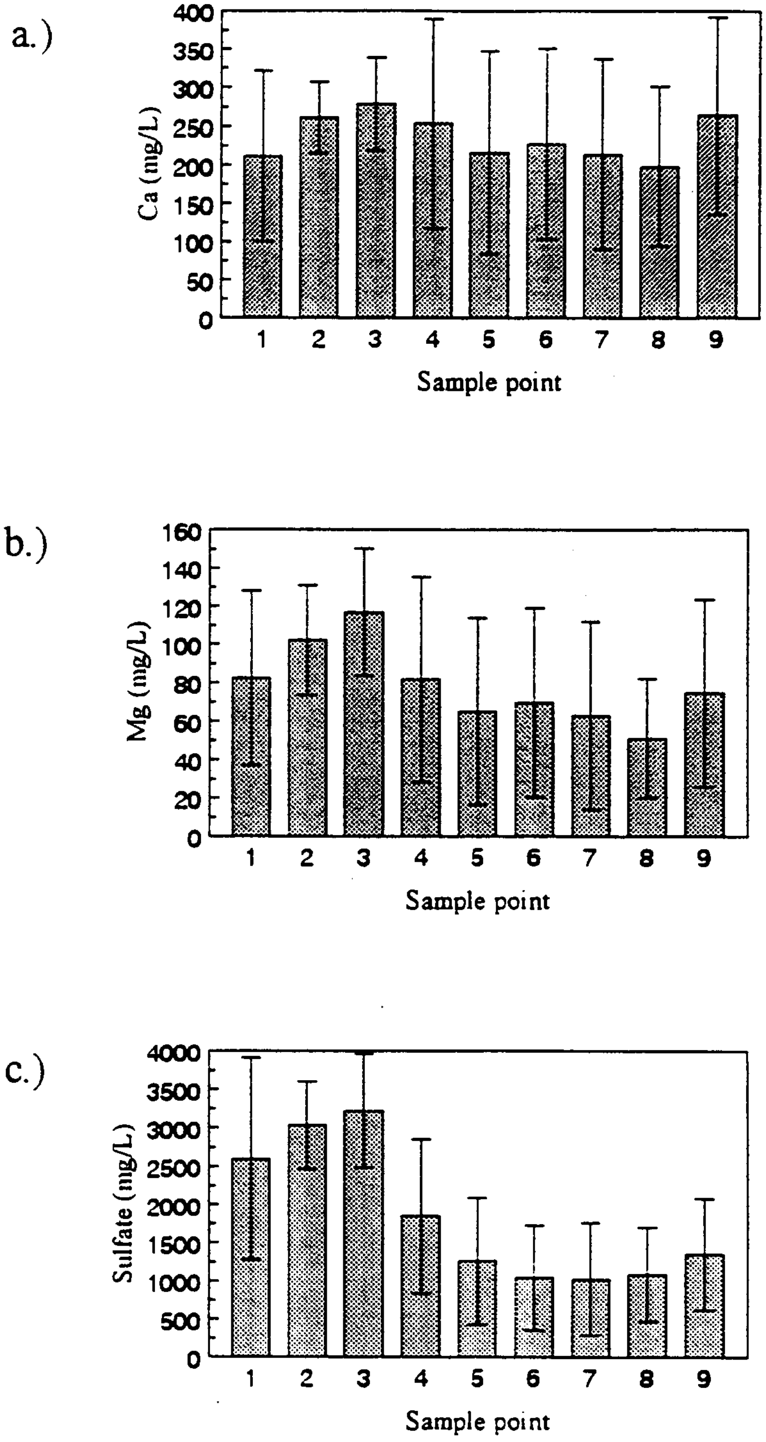

Figure 1.24. Mean post construction performance of a.) calcium, b.) magnesium, and c.) sulfate at the Jones Branch wetland for the period July 1995 through October 1996.

error bars that are higher than the maximum influent concentration (Figure 1.24 a). Apparently, calcium was being released through limestone dissolution then removed by some other physicochemical process. Earlier discussion on the possibility of gypsum precipitation is supported by the similar trends in $Ca^{2+}$ and $SO_4^{2-}$ reduction displayed in Figure 1.24 and the positive identification of gypsum precipitates within the wetland (see Chapter Two). Sulfide and alkalinity data were also consistent with gypsum precipitation (Figures 1.25 c and 1.22 c). The presence of sulfide as an indicator of sulfate reduction did not prove to be an effective measurement. Surface aeration of water samples most likely resulted in the evolution of $H_2S$ gas, thus , very little sulfide was observed. Total alkalinity was present in the last five sampling points and reflects the high pH conditions observed there. Alkalinity concentrations did not appear to reflect their mode of generation, but rather seemed to indicate the neutralization of acidity within the system. Therefore, alkalinity measurements cannot be used to distinguish the amount of limestone dissolution or sulfate reduction within the wetland system. However, sample point 6 displayed the highest concentrations of alkalinity and sulfides. Examination of dissolved oxygen and Eh values also revealed that this point exhibitedthe most reduced conditions in surface water samples (Figure 1.25). Given that Eh and dissolved oxygen levels decreased below the water-sediment interface (Stumm and Morgan, 1981), associated increases in alkalinity and sulfide concentrations within the substrate should be anticipated.

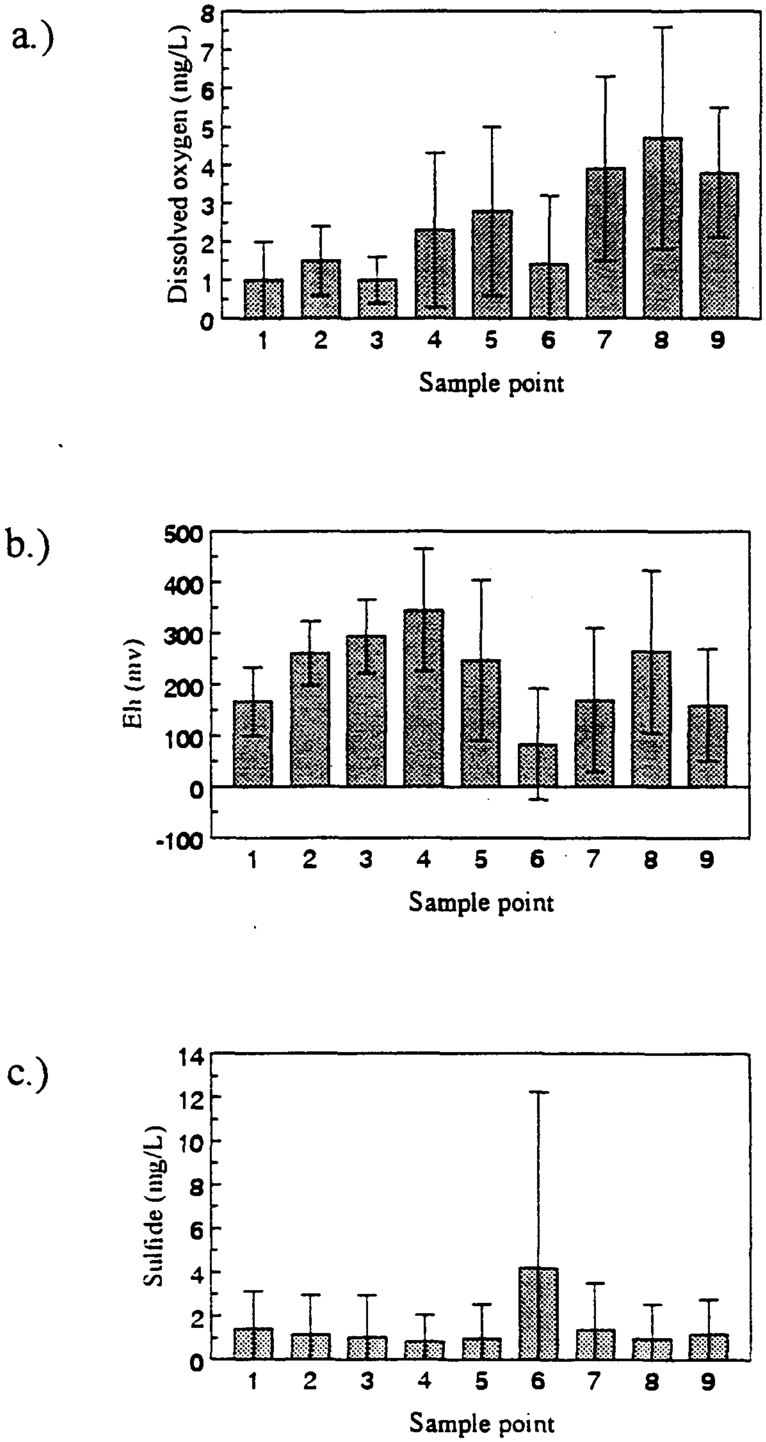

Figure 1.25. Mean post construction performance of a.) dissolved oxygen, b.) Eh, and c.) sulfide at the Jones Branch wetland for the period July 1995 through October 1996.

*Performance Assessment*

Analytical results from post renovation water quality were very encouraging. Bi-weekly performance data revealed dramatic changes in water quality after renovation and indicated good consistency in treatment efficiency. The anoxic limestone drains appeared to have had an influence on mine water chemistry. Although ALD influent and effluent surface water data did not indicate a rise in pH, determinations made at the pipe openings using a submersible pH probe revealed an increase from 3.46 ± 0.27, at the inlet, to 4.61 ± 0.72 exiting the drain. Apparently, pH did increase through the drain, however, this increase promoted hydrolysis as drainage entered the first precipitation basin and pH was subsequently lowered. Observations of pH levels below 6.2 exiting the drain may indicate that the ALD was not fully functioning (Faulkner and Skousen, 1994). Low contact time between AMD and limestone within the ALD's may explain the inefficiencies observed at Jones Branch. Using a porosity of 35% (Skousen, 1995) for limestone and average influent flow rates, retention time for each drain was determined to be 2.4 hours. Faulkner and Skousen (1994) recommended a retention time of 15 to 20 hours for optimal alkalinity generation, thus, the Jones Branch ALD's were not operating at maximum efficiency levels.

Elevations in calcium concentration through the ALD's were evident in twenty of the twenty six sampling events. An average $Ca^{2+}$ increase of 18 mg $L^{-1}$ through the drains was observed during the post renovation period. By converting calcium to $CaCO_3$ it was determined that 2.4 kg of limestone are dissolved in the ALD's each day. Given that 7500 kg of limestone were originally placed in the drains and that the limestone is ≈ 80% pure $CaCO_3$, complete dissolution should occur in 6.44 years if current conditions prevail. Water quality data did not suggest retention of Fe or Mn in the ALD's, however, precipitation of $Al(OH)_3$ and, on occasion, gypsum may have occurred. Potential clogging of the ALD's was anticipated due to findings in previous research (Brodie et al., 1993; Faulkner and Skousen, 1994; Hedin and Watzlaf, 1994; Hedin et al., 1994), however, the 30 cm gate valves allow periodic flushing of the drain to remove unarmored precipitates. In addition, the use of PVC pipe in construction allows for removal of spent or coated limestone with an industrial vacuum system and relatively simple replacement. Therefore, what was lost in alkalinity generation by this design may have been replaced by long term gains involving precipitate removal and limestone recharging.

The modified SAPS design also appeared to be functioning as designed during the post renovation period. Results reveal that limestone dissolution and sulfate reduction in the substrate are producing an adequate amount of alkalinity to raise pH levels for sufficient precipitation of metal carbonates in reduced zones and metal hydroxides in oxidized zones. Results also suggest that sulfate-reducing bacteria may have contributed to treatment by precipitating heavy metals as insoluble sulfides and produced a net alkaline drainage capable of neutralizing acidity from metal hydrolysis. Samples of limestone extracted from the substrate showed no evidence of armoring. This indicates diffusion of organic matter into the limestone zone surrounding the perforated pipe and ultimate reduction of any oxidized drainage that may enter the subsurface drains. Solution samples from the surface and within the substrate revealed that anoxic conditions persisted in the subsurface zone (Figure 1.26). Inhibition of armoring was confirmed by transposing interstitial points from Figure 1.26 to iron and sulfur stability diagrams created by Loomis and Hood (1984), which suggest that iron existed in the $Fe^{2+}$ form at Eh and pH conditions observed in the treatment wetland.

The dissolution of limestone within the wetland system contributed to the generation of alkalinity and neutralization of ≈ 42 metric tons of acidity per year. An estimation of the systems longevity is difficult to determine based upon exhaustion of the organic compost because many factors contribute to its saturation (Wieder, 1993). However, a budget of the acidity consumed by limestone dissolution can be created to estimate the systems life expectancy. Approximately 320 metric tons of limestone are found within the wetland system at Jones Branch. At 80% purity, the limestone can neutralize 42 metric tons of acidity per year for 6.07 years. Thus, based on these optimal conditions for dissolution, limestone would need to be replaced in the wetland substrate and in the ALD's after six years of operation.

The renovation of the Jones Branch wetland cost ≈ $60,000 and, based on limestone dissolution rates, is expected to maintain efficiency rates for six years. With an average influent flow rate at 37.1 lpm, nearly 15 metric tons of of iron and 42 metric tons of acidity were treated per year by the wetland system. If current conditions remain constant, the system will precipitate nearly 90 metric tons of iron and treat 252 metric tons of acidity in six years. From this it was determined that the per ton cost of acid

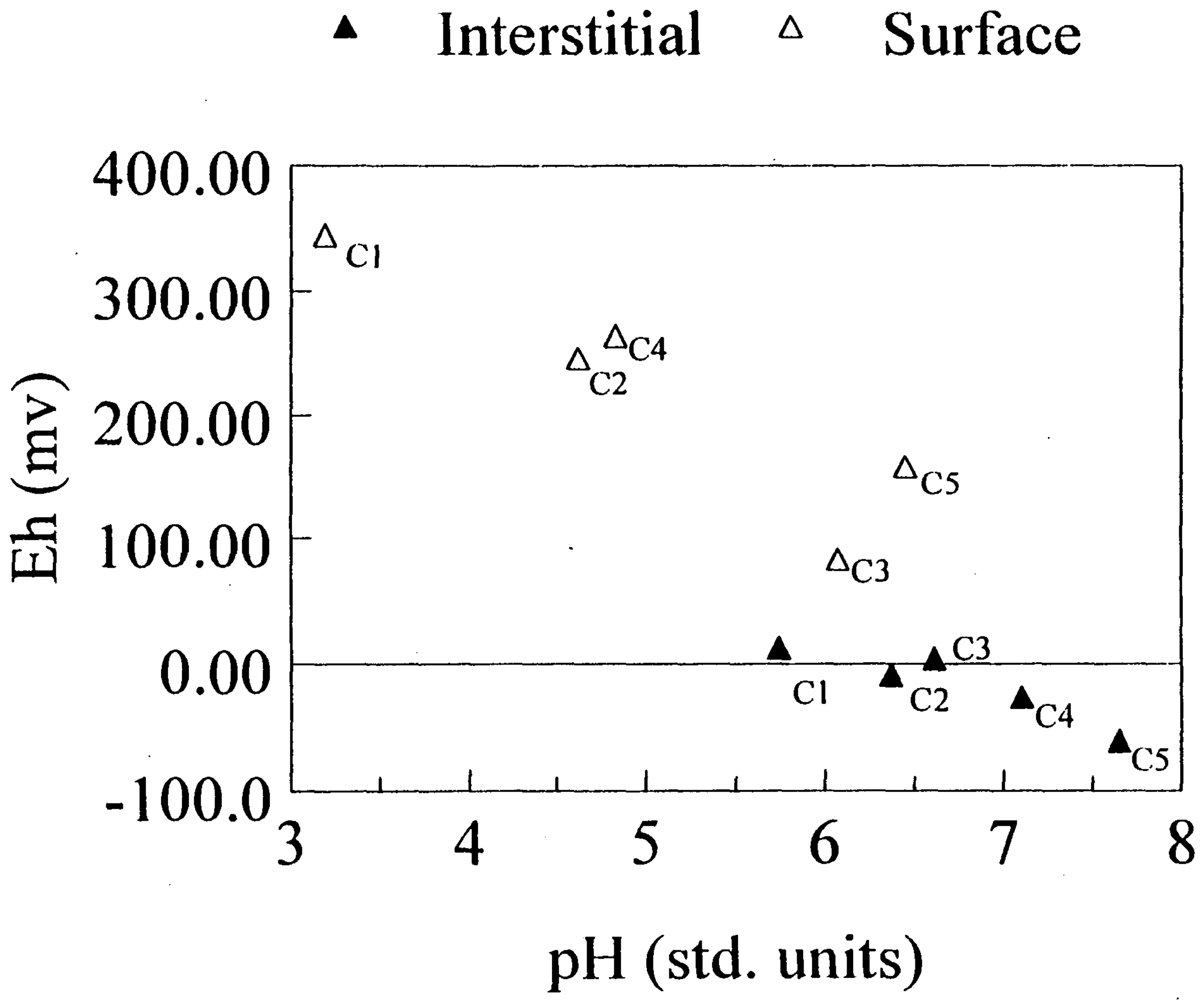

Figure 1.26. Interstitial and surface water Eh and pH values for all wetland cells at the Jones Branch wetland.

neutralization is $227 over the six-year period. This cost is comparable to AMD treatment using calcite alone, and from 7% ($Ca(OH)_2$) to 92% (NaOH) lower than estimates for conventional treatment with caustic materials as described by Skousen et al. (1990).

***Jones Branch Water Quality***

Water quality in Jones Branch was monitored above and below the wetland throughout the study period for all parameters listed in Table 1.3. During the early months of post renovation, AMD flowed from the lagoon directly into Jones Branch to lessen the impact of transplant shock. Some drainage was also diverted during periods of high flow to reduce metal loads. Compared to average flow rates observed during the original wetland study (Chalfant, 1993), approximately 50 lpm less drainage was allowed to enter the renovated wetland system. Moreover, drainage from other sources periodically entered Jones Branch between the upstream and downstream sampling points. Therefore, conclusions which associate a change in the water quality of Jones Branch to that of the constructed wetland are purely speculative.

Water quality downstream from the wetland showed improvement over the first ten months of the post renovation period. Downstream pH levels met or were higher than upstream levels for the first 17 sampling events, however, downstream pH values fell below those observed upstream in ensuing samples (Figure 1.27 a). Upstream and downstream total Fe and Mn concentration remained relatively equal during the first 17 sampling events, as with pH, then increased in the downstream samples thereafter (Figures 1.27 b,c). Sulfate, solids, EC and Al displayed similar patterns to those described for Fe

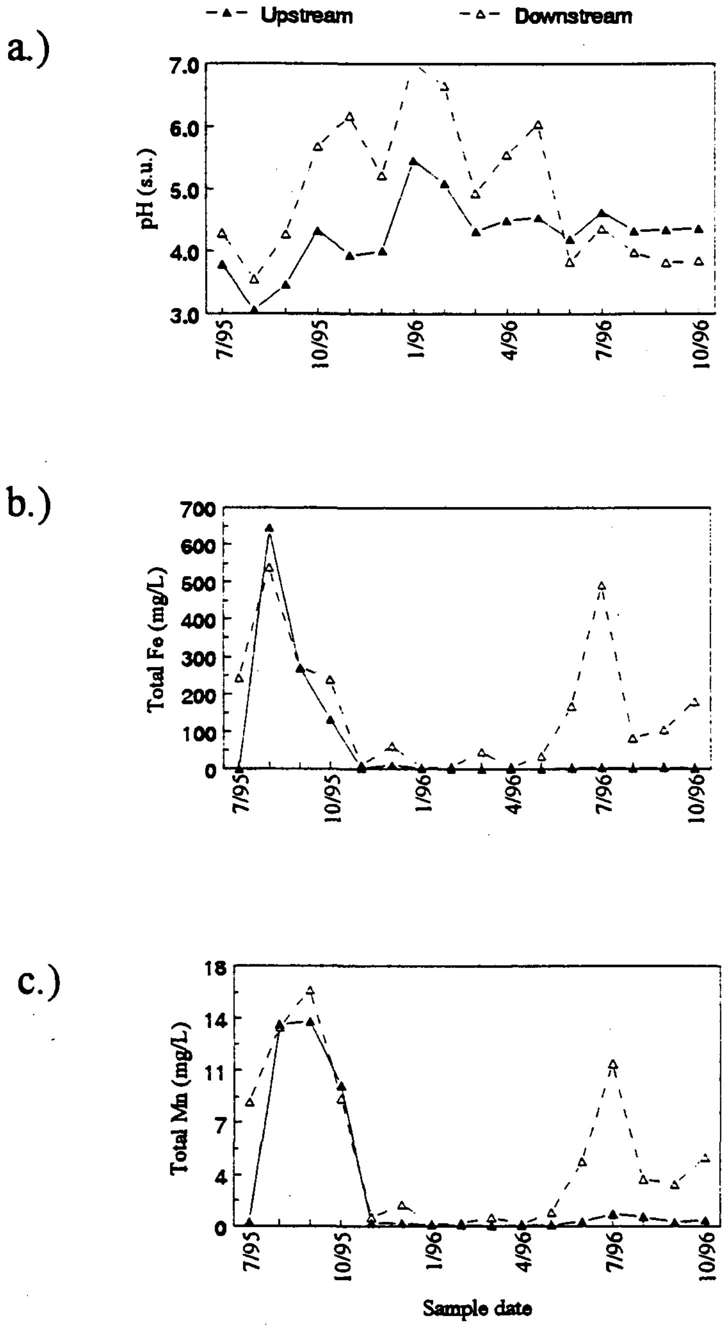

Figure 1.27. Upstream and downstream water quality for a.) pH, b.) total iron and c.) total manganese in Jones Branch.

and Mn samples. The reason for this shift in treatment is unclear because effluent samples from the wetland between the May 1996 and November 1996 period represent some of the best water quality data for the entire study period. Apparently, drainage that was diverted from the lagoon into Jones Branch or originating at a source between upstream and downstream sampling points had a profound influence on downstream water quality. The trends observed may also be indicative of a dilution effect. Jones Branch is an intermittent stream and often displays minuscule upstream flow rates during the summer months. Thus, downstream data accumulated during these low flow events actually represents mixed drainage that emanates from the mine seeps and effluent of the constructed wetland. Additional sampling is needed to fully understand the dynamics of water chemistry and to make evaluations on the impact that the wetland system has had on Jones Branch.

## CONCLUSIONS

In an attempt to improve treatment efficiencies at the Jones Branch AMD treatment wetland, a two phase renovation project was developed that incorporated ALD and SAPS technology. Analytical results from post-renovation water quality monitoring were very encouraging. Mean iron concentrations decreased from 787 to 37 mg $L^{-1}$, pH increased from 3.38 to 6.46 and acidity was reduced from 2244 to 119 mg $CaCO_3$ $L^{-1}$. Renovation has resulted in the retention of 98% Al, 95% Fe, 94% acidity, 56% $SO_4^{2-}$, and 48% Mn within the wetland. Mass loading data indicates that 18.7 metric tons of iron were retained and 53.1 metric tons of acidity were neutralized by the system during the post renovation period. Monthly performance data revealed dramatic changes in water quality after renovation and indicated good consistency in treatment efficiency

Prior to renovation, the surface flow system was curtailed by a two hour residence time and an aerobic acid forming environment. After renovation, results indicated that alkalinity generation from limestone dissolution and sulfate reduction occurred within the wetland substrate. However, quantification of the extent of alkalinity production by each process was uncertain. Evidence from the study suggested that the magnitude of gypsum precipitation in wetlands with carbonate substrates may be underestimated. Even though bacterially mediated sulfate reduction was evident in this system, major reductions in $SO_4^{2-}$ levels and alkalinity increases are probably more closely aligned with the dissolution of limestone. Oxygen demand by the organic substrate, however, was necessary in the subsurface environment to maintain reducing conditions so that armoring of the limestone did not occur. The combination of technologies utilized in the renovation and the sequence in which they occur within the wetland proved to be an adequate design for treatment of high metal load AMD. As a result, the system was capable of exceeding the design criteria of any technology alone. In addition, utilization of the subsurface flow system, as designed, increased residence time to nearly 94 hours and may contribute to lowering recommended sizing requirements for AMD treatment wetlands. This could have implications on AMD sites that are restricted by topography or available surface area and deemed inappropriate for treatment using constructed wetlands. Thus, modifications from the renovation have enhanced heavy metal removal processes, and contributed to increasing the life expectancy of the treatment system.

Although treatment efficiency improved and current designs appear to be functioning as intended, maintenance of the site must be performed to ensure continued success. Accumulation of precipitates within the ALD's and subsurface drains could lead to the demise of the system. Remediation of this problem at its onset is a simple process that could save thousands of dollars in future renovation expenses. Regular inspections at the site and evaluations of water samples within the wetland are a necessary measure to isolate potential problems and correct them before substantial damage occurs. With continued monitoring and maintenance, information shall be accumulated to evaluate the long-term usefulness of this treatment approach. In addition, results from this study and future research at the Jones Branch wetland may validate the applicability of incorporating wetlands in a restoration plan for the entire Rock Creek watershed.

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