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# RECIRCULATING - REDUCING AND ALKALINITY PRODUCING SYSTEM (RERAPS) FOR THE TREATMENT OF ACIDIC COAL PILE RUNOFF 

## by

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## A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Civil and Environmental Engineering
in the Graduate School of
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TUSCALOOSA. ALABAMA

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Submitted by William Edward Garrett, Jr. in partial fulfillment of the requirements for the degree of Doctor of Philosophy specializing in Environmental Engineering. Accepted on behalf of Faculty of the Graduate School by the dissertation committee:


## GLOSSARY AND ACRONYMS

## ADEM: Alabama Department of Environmental Management

ALD: Anoxic limestone drain
AMD: Acid mine drainage
ATP: Adenosine triphosphate, only occurs in living cells, basic energy transfer compound.

BLM: Biotic ligand model
CAD: Engineering design software package
CCC: Criterion continuous concentration established by the United States EPA as chronically toxic to aquatic life.

CFR: The Code of Federal Regulations is a codification of the general and permanent rules published in the Federal Register by the Executive departments and agencies of the Federal Government.

CPR: Coal pile runoff
$\mathbf{C r}$ (III): Reduced form of chromium
Cr(IV): Oxidized form of chromium
DO: Dissolved oxygen
DOM: Dissolved organic matter
EDTA: Ethylenediamineteraacetic acid and its sodium salts used to chelate soluble metal complexes
$\mathbf{E}_{n}$ : The theoretical voltage potential that corresponds to the generalized half-reaction or reduction reactions, Eh (volts) increases as the oxidized chemical species increase in water

EPRI: Electric Power Research Institute
Fe(II): Reduced forms of iron
Fe(III): Oxidized forms of iron
ICAP: Inductively coupled argon plasma spectroscopy instrument for measuring cation concentrations

MDL: Minimum detectable level of the laboratory instrumentation for the parameter measured

M-DOM: Metal ion and dissolved organic matter complex
MINTEQ: Geochemical equilibrium model developed by the EPA
$\mathbf{M n}$ (II): Reduced forms of manganese
NPDES: Authorized by the Clean Water Act, the National Pollutant Discharge Elimination System (NPDES) permit program controls water pollution by regulating point sources that discharge pollutants into waters of the United States.

ORP: Oxidation reduction potential
pE: Negative common logarithm for the molar concentration of electron transfer potential
pH: Negative common logarithm for the molar concentration of the hydronium ( $\mathrm{H}^{+}$) ion

RAPS: Reducing and alkalinity producing system
RAPS-based: Wetland treatment system which incorporates a RAPS component

ReRAPS: Recirculating reducing and alkalinity producing system
SAPS: Successive alkalinity producing system
SPSS: Statistical software package
TDS: Total dissolved solids
TSS: Total suspended solids
TU: Toxicity Unit
EPA: United States Environmental Protection Agency
VFS: Vertical flow system
WER: Water effluent ratio
WHAM: Windermere humic aqueous model

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#### Abstract

The electric utility industry has been subjected to increased environmental discharge restrictions and operational restraints regarding the treatment of stormwater runoff from coal storage operations. Pyrite oxidation processes within the coal combine with rain water to produce an acidic runoff, which can contain metal pollutants and is toxic to aquatic life. This research evaluated the treatment of coal pile runoff using an alternative constructed wetland design. This alternative design, which provided improved wetland performance, was based on the partial re-circulation of treated water into a detention basin located immediately upstream from a Reducing and Alkalinity Producing System. This modification created a semi-passive RAPS-based system which will be referred to as a Recirculating RAPS.

It was hypothesized that recirculation would moderate the pH in the detention pond resulting in the removal of metals such as Fe . AI, and Mn through co-precipitation chemical processes upstream from the RAPS component. This would therefore minimize the potential for Al hydroxide plugging in the RAPS substrate. It was further hypothesized that the entire ReRAPS wetland would remove sufficient amounts of contaminants from the CPR so that short term chronic toxicity tests would indicate that the whole water effluent was non-toxic to aquatic life.

After a three year stabilization period. the CPR had the following average influent concentrations: $12.8 \mathrm{mg} / \mathrm{L}$ of iron. $24.9 \mathrm{mg} / \mathrm{L}$ of aluminum. $2.9 \mathrm{mg} / \mathrm{L}$ of manganese, and $178.0 \mathrm{mg} / \mathrm{L}$ of acidity. The detention pond removed $82 \%$ of the total iron. $59 \%$ of the


aluminum, and $35 \%$ of the acidity loading prior to the RAPS component. Manganese was not removed in the detention pond and in the RAPS component, but was removed in the settling basin and drains. Follow-up toxicity testing found that the ReRAPS removed the toxicity of the CPR to levels which were only slightly toxic based on the seven day chronic toxicity test for larval Fathead minnow growth and Cladoceran reproduction. The residual toxicity may be due to the low levels of dissolved nickel and zinc. Ironically, the commonly used surrogate for trace metal removal, manganese, was found to have a possible protective effect against chronic toxicity.

## CHAPTER 1 INTRODUCTION

An alternative type of Reducing and Alkalinity Producing System (RAPS)-based wetland treatment system was conceptualized and constructed to treat acidic coal pile runoff (CPR). CPR typically contains dissolved aluminum (Al), iron ( Fe ), manganese $(\mathrm{Mn})$, and toxic trace metals such as copper $(\mathrm{Cu})$, nickel $(\mathrm{Ni})$, and zinc $(\mathrm{Zn})$. This wetland design modification created a semi-passive RAPS-based system which will be referred to as a Recirculating RAPS (ReRAPS). This semi-passive wetland incorporates the recirculation of treated (alkaline) water back to an equalization basin or detention pond so that the pH of water entering the RAPS component might be moderated along with the mass loading of acidic and metallic contaminants.

### 1.1 Hypothesis

It was hypothesized that the moderation of pH in the detention pond would remove metals such as Fe. AI, and Mn through co-precipitation chemical processes upstream from the RAPS component. This would therefore minimize the potential for Al hydroxide plugging in the RAPS substrate. It was further hypothesized that the entire ReRAPS wetland would remove sufficient amounts of contaminants from the CPR so that short term chronic toxicity tests would indicate that the whole-water effluent was non-toxic to aquatic life.

### 1.2 Background

An eleven-acre coal pile at Alabama Power Company`s Plant Gorgas is located adjacent to the Warrior River. Pyrite oxidation processes combine with stormwater to
create acidic runoff in carbonate-deficient (low $\mathrm{CO}_{3}{ }^{\mathbf{2 -}}$ minerals) coal piles. Acidic coal pile runoff (CPR) from coal storage areas is similar to acid mine drainage (AMD) and both can be toxic to aquatic organisms. The absence of a retaining structure around the coal pile has allowed the runoff and coal fines to flow directly into the river during storm events. The construction of a retaining dike to improve coal pile maintenance created a discharge point subject to the National Pollutant Discharge Elimination System (NPDES) limitations. Preliminary sampling of the CPR determined that the runoff was highly contaminated. CPR acidity was as high as $750 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$. A RAPS-based wetland option was pursued due to the lower long-term operation cost relative to other treatment options. Other treatment options considered, included a conventional chemical treatment system and a multi-pump system, which would route the acidic runoff to an ash pond. However, RAPS-based wetlands were reported to be susceptible to Al hydroxide plugging and there was no information on the toxicity removal benefits associated with these types of constructed wetlands. Therefore, a 2-1/2 acre treatment wetland was designed to include a new type of treatment, which reduced the potential for AI plugging. Bench scale tests were performed to evaluate various materials and aided in the design of the wetland. The wetland was constructed from 1996 to 1997 to treat the contaminated runoff originating from the Plant Gorgas coal pile. The treatment wetland became operational in January 1998.

Hydrological and chemical monitoring of the treatment wetland was performed to evaluate the new treatment design and the removal of toxic contaminants within this new type of wetland treatment system. The monitoring was performed during four consecutive years (1998-2001) during the wet seasons, which typically occurred from

January through May. Toxicity testing was performed at the conclusion of the four-year monitoring period to determine if the ReRAPS eliminated the toxic agents associated with the CPR. Recommendations concerning the design of this new type of wetland were also developed.

### 1.3 Research Objectives

### 1.3.1 Recirculating-Reducing and Alkalinity Producing System (ReRAPS)

In the last two decades several approaches have been developed to treat AMD. Many of these designs have been used to successfully treat AMD including the Reducing and Alkalinity Producing System (RAPS). The RAPS is an especially attractive approach due to low operation and maintenance costs. Also known as Vertical Flow Systems (VFS), this wetland "component" was first developed by Kepler and McCleary (1994) and was integrated into a wetland "system" known as a Successive Alkalinity Producing Systems (SAPS). The RAPS-based constructed wetland technology is the only passive low maintenance, non-conventional treatment method that has been developed to treat acidic aerobic waters containing relatively high concentrations of Al and Fe . However. reduced performance due to the accumulation of Al hydroxide precipitates has been reported for some systems (Watzlaf et al., 2000). When the removal of Mn is necessary. these systems incorporate rock drains to enhance bio-oxidative removal. While RAPSbased wetlands have been developed and continue to treat AMD. research is continuing in efforts to improve or optimize the design for the treatment of CPR. Unlike AMD, CPR flow to wetlands is more intermittent, resulting in "shock" loading of contaminants on the critical RAPS component. Of specific interest is a semi-passive design modification that would moderate the intensity of the CPR loading prior to the RAPS component.

This modification involved the partial re-circulation of treated water into a detention basin located immediately upstream from the RAPS component resulting in what is referred to as a semi-passive Recirculating Reducing and Alkalinity Producing System (ReRAPS). Garrett et al. (2001) first proposed the ReRAPS treatment option and this paper is provided in Appendix A. Pumping allows for the recirculation of alkalinity to a detention pond which adds alkalinity to the acidic runoff prior to the RAPS. Acidityremoving reactions in the detention pond usually occur in a predictable order that is consistent with the solubility products of the solids. Comparisons of the "environment of removal" for the primary contaminants in a passive RAPS-based wetland and in a ReRAPS wetland are given in Figure 1. In this semi-passive system, the environment of deposition for both Al and Fe could precede the RAPS and minimize the potential for plugging in the RAPS due to metal precipitates. This may be especially beneficial for the treatment of Mn , which is difficult to oxidize in the presence of Fe (II) (Sikora et al.. 2000). The recirculation of alkalinity and organic matter reduces limestone consumption and increases the long-term production of bacterially-derived alkalinity (i.e., $\mathrm{SO}_{4}{ }^{2-}$ reduction). Therefore. further investigations into the potential of contaminant removal and alkalinity generating processes within a recirculating wetland were warranted.

### 1.3.2 ReRAPS Pollutant Removal

In the United States, the Mining Guidelines (40 CFR-Chapter 1-Part 434) suggest the typical effluent limitations associated with wetlands designed to treat acidic drainage. Most RAPS-based wetlands have been designed to meet the regulatory guidelines based on the removal of less than $3 \mathrm{mg} / \mathrm{L}$ of Fe and less than $2 \mathrm{mg} / \mathrm{L}$ of Mn . The pH is typically limited to values between 6 and 9. Due to cost and logistical restraints. many
wetlands have been constructed with a goal of only reducing the impact due to abandoned mine activity.


Figure 1. Primary environment of pollutant deposition or consumption in a passive RAPSbased wetland and in a semipassive ReRAPS wetland.

Iron is listed as a toxic pollutant to freshwater aquatic organisms in the Environmental Protection Agency's (EPA) National Recommended Water Quality Criteria (EPA, 1999). Manganese is not listed as a toxic pollutant (EPA, 1999). However, Mn has been recognized as a relatively difficult pollutant to remove from the aqueous phase because Mn oxidation is slow below a pH of 8.5 (Brant \& Ziemkiewicz. 1997). Therefore, it is often considered a regulatory surrogate for the presence of metals that may be more toxic than Mn (Brant \& Ziemkiewicz. 1997; Royer et al., 1998;

Watzlaf, 1997). As a regulatory surrogate, the monitoring, controlling, and reporting of NPDES discharges would be based on the concentration of Mn in lieu of more toxic metals. As a result of the limited treatment ability of previously constructed wetlands and the common use of Mn as a monitoring surrogate, there has been very little information documenting the treatment of all of the EPA priority pollutants in the RAPSbased wetlands.

Very few systems, if any, have been developed with the treatment goal of eliminating toxicity in the whole water effluent of the wetland. Toxicity in coal related drainages can be exerted on freshwater aquatic organisms by minor (e.g., $\mathrm{Cu}^{2+}, \mathrm{Ni}^{2+}, \mathrm{Zn}^{2+}$ ) and major ions (e.g., salinity, $\mathrm{K}^{+}, \mathrm{SO}_{4}{ }^{2}$ ). Therefore, this research investigated if Mn can be used to predict the removal of toxic trace metals to levels that are chronically non-toxic (i.e., EPA CCC) in a RAPS-based wetland. The level of dissolved salts that can accumulate and exert major ion toxicity (e.g.. $\mathrm{K}^{+}, \mathrm{SO}_{4}{ }^{2-}$ ) was also investigated along with any organic compounds that may leach from the industrial coal storage pile.

Published design criteria for the RAPS-based wetlands are primarily based on the mass loading of AI, Fe and Mn . There is concern over the use of Mn as a regulatory parameter and there has been little confirmation over the value of using Mn as a monitoring surrogate for the toxic trace elements (e.g., $\mathrm{Cu}, \mathrm{Ni}, \mathrm{Zn}$ ) in wetland systems designed to treat acidic drainages (Royer et al., 1998). Therefore, the use of Mn as a monitoring parameter may actually cause some wetlands to be over-designed when considering the ultimate goal of toxicity removal.

Concerning the goal of "complete" toxicity removal. there has been little information documenting the removal or accumulation of major ions such as sulfate ( $\mathrm{SO}_{4}{ }^{2-}$ ), sodium
$\left(\mathrm{Na}^{+}\right)$, and calcium $\left(\mathrm{Ca}^{2+}\right)$ in constructed wetlands. The ReRAPS design option recirculates treated wetland water back to the detention pond and, depending on the hydrologic conditions, can cycle-up total dissolved solids in the wetland effluent. Therefore, the amount of recycling that can occur in the ReRAPS may be limited by the toxicity associated with the accumulation of major ions.

Therefore, to address these questions and to gain a better understanding of acidic runoff treatment, the following specific research elements were conducted:

- The general performance of the ReRAPS wetland during the first four years of operation was characterized.
- The level of contaminant removal in the Plant Gorgas ReRAPS relative to the U.S.EPA National Recommended Water Quality Criteria for Non Priority and Priority Pollutants (EPA, 1999) was explored.
- Contaminant concentrations in the ReRAPS were evaluated based on the removal of toxicity to aquatic organisms. Toxicity testing was performed to confirm the removal of toxic metal agents using the ReRAPS treatment.
- The results of the toxicity testing were evaluated using the EPA CCC for priority pollutants, the major ion toxicity models developed by the Gas Research Institute (Mount et al., 1997), and regression analyses techniques.
- The merits of using Mn as a surrogate for trace metal removal in RAPS-based wetlands were evaluated.
- The significant removal of Al and Fe in the detention pond prior to the RAPS component was confirmed.


## - The factors effecting alkalinity production and limestone consumption in the RAPS component were evaluated.

- The issues concerning the design of a ReRAPS wetland were identified.

The use of the RAPS-based wetlands in the electric utility industry may be a costeffective option for the treatment of stormwater runoff, CPR, or other acidic waste streams produced by a steam electric generating facility. The use of a semi-passive (pumping) wetland in an industrial setting is not a limitation because of the accessibility of electricity. Increased regulatory restrictions and the potential application of this low maintenance technology require a greater understanding of the applicability for constructed wetlands to the electric utility industry.

### 1.4 Organization of Study

A literature review follows the introduction of this research (Chapter 2). The literature review includes a general overview of the chemical processes involved in the production of acidic CPR. Then, an overview of the agents found in CPR that act together or separately to exert toxicity on aquatic organisms precedes a description of the predominant chemical processes that can remove the toxic agents from the aqueous phase. The various types of passive wetland components that have been used to take advantage of these removal processes are then described. Also, the Plant Gorgas ReRAPS wetland is described along with the environmental regulatory discharge limitations that the system is required to meet. A description of the conceptual design. the bench scale study results which aided in the design. and the construction techniques. are all presented in the methods section (Chapter 3). The field techniques. laboratory
analyses and statistical analyses used to evaluate the performance of the wetland are also described in the methods section. Four years of wetland research data are presented in the results section (Chapter 4). General monitoring under various operating conditions was conducted from 1998 through 2000. During 2001, the ReRAPS was intensively monitored during 41 days of CPR treatment. The relative magnitude of the sampling during 2001 was sufficient to perform statistically significant contaminant removal estimates. The treatment period included 4 storm events, which produced measurable amounts of CPR during January through March 2001. The intensive monitoring data allowed for an analysis of factors that affected detention pond and RAPS treatment performance. The toxicity testing performed during April through May 2001 are also presented in the results section. More detailed results are presented in Appendix A-G along with the laboratory quality control protocol. This research concludes by applying the results of this study and experiences gained during the operation of the wetland to application of the ReRAPS design when treating various types of acidic runoff (Chapter 5).

## CHAPTER 2 LITERATURE REVIEW

### 2.1 Acidic Coal Pile Runoff Chemistry

Coal fired power plants in the Eastern United States typically burn bituminous coal from the Appalachian Region. Bituminous coal piles produce a runoff similar to acid mine drainage (AMD). The acidic runoff from such piles typically contains high levels of dissolved sulfate ( $\mathrm{SO}_{4}{ }^{2}$ ) . AMD values reported by Wildeman et al. (1993) show that the sulfur content is inversely proportional to the pH of the drainage water. Coal pile runoff (CPR), like AMD, is acidic due to the oxidation of sulfide minerals such as iron disulfide $\left(\mathrm{FeS}_{2}\right.$, pyrite) in the presence of water. The stratigraphically deeper coals of the Appalachian Basin in the Eastern United States generally have lower sulfur than the shallower deposits (EPA, 2001a). The following equations presents a simplified pyrite oxidation process, which has been frequently described (Brock et al., 1994; Brodie et al.. 1993; EPA. 2001a; Rose \& Cravotta. 1998; Snoeyink \& Jenkins, 1980; Stumm \& Morgan. 1981; Wildeman et al., 1993).

$$
\begin{gather*}
2 \mathrm{FeS}_{2(\mathrm{~s})}+\underset{\text { Pyrite Oxidation }}{7 \mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Fe}^{2+}+4 \mathrm{SO}_{4}{ }^{2-}+4 \mathrm{H}^{+}} \begin{array}{c}
\text { (Equation 1) } \\
4 \mathrm{Fe}^{2+}+\mathrm{O}_{2}+4 \mathrm{H}^{+} \xrightarrow[\text { Ferrous Iron Oxidation }]{\text { nucrena }} 4 \mathrm{Fe}^{3+}+2 \mathrm{H}_{2} \mathrm{O} \\
\text { (Equation 2) } \\
\mathrm{Fe}^{3+}+3 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Fe}(\mathrm{OH})_{3(\mathrm{~s})}+3 \mathrm{H}^{+} \\
\text {Ferric Iron Hydrolysis }
\end{array} \text { (Equation 3) }  \tag{Equation1}\\
\text { (E) }
\end{gather*}
$$

$$
\begin{gather*}
\mathrm{FeS}_{2(\mathrm{~s})}+14 \mathrm{Fe}^{3+}+8 \mathrm{H}_{2} \mathrm{O} \rightarrow 15 \mathrm{Fe}^{2+}+2 \mathrm{SO}_{4}{ }^{2-}+16 \mathrm{H}^{+}  \tag{Equation4}\\
\text {Ferric Iron Oxidation of Pyrite }
\end{gather*}
$$

In this process, soluble iron sulfate salts are first slowly formed under acidic conditions (Equation 1). Bacteria such as Thiobacillius ferrooxidans serve as a catalyst during this initial oxidation process (Equation 2). The yellow and white iron sulfate salts are easily dissolved and hydrolyzed in the runoff. The runoff can therefore contain high levels of dissolved ferrous iron $\left(\mathrm{Fe}^{2+}\right)$ and sulfate ( $\mathrm{SO}_{4}{ }^{2}$ ). Ultimately, the ferrous iron is oxidized further to form the ferrous $\left(\mathrm{Fe}^{2+}\right)$ and ferric $\left(\mathrm{Fe}^{3+}\right)$ oxyhydroxides, which form the characteristic yellow and red color in waters known as "yellow boy" (Equation 3). Ferric iron also becomes an oxidant of pyrite, further enhancing the process (Equation 4). The resulting runoff typically contains a significant amount of dissolved $\mathrm{Fe}^{2+}$ because the oxidation of $\mathrm{Fe}^{2+}$ to $\mathrm{Fe}^{3+}$ is relatively slow compared to the overall oxidation of pyrite (Brock et al., 1994).

The production of acidity from pyritic sulfur in coal can be neutralized by the production of alkalinity from calcarious minerals in the same coal. The dissolution of calcite $\left(\mathrm{CaCO}_{3}\right)$ in an open system. where proton acidity $\left(\mathrm{H}^{+}\right)$is consumed and carbon dioxide gas $\left(\mathrm{CO}_{2}\right)$ is produced, is illustrated by the following reaction:

$$
\begin{equation*}
\mathrm{CaCO}_{3(\mathrm{~s})}+\mathrm{H}^{+} \rightarrow \mathrm{Ca}^{2+}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \tag{Equation5}
\end{equation*}
$$

Carbonate Dissolution

The resulting acidity of CPR is therefore controlled by the balance of the two processes in the leachate of the stored coal. An overall "neutralized" reaction can be
written to describe pyrite oxidation (acid production) and carbonate dissolution (acid neutralization) in an open system such as a coal pile:

$$
\begin{gather*}
\mathrm{FeS}_{2(\mathrm{~s})}+2 \mathrm{CaCO}_{3(\mathrm{~s})}+3.75 \mathrm{O}_{2}+1.5 \mathrm{H}_{2} \mathrm{O} \rightarrow \\
\mathrm{Fe}(\mathrm{OH})_{3(\mathrm{~s})}+2 \mathrm{SO}_{4}{ }^{2-}+2 \mathrm{Ca}^{2+}+2 \mathrm{CO}_{2}  \tag{Equation6}\\
\text { Pyrite Oxidation and Carbonate Dissolution }
\end{gather*}
$$

The acidity produced in the runoff is primarily determined by the amount of pyrite and carbonate in the coal. However, other factors that can influence the rate of acidity generation are the size of the coal particles, pyrite surface area. moisture content. pH . oxygen availability, and temperature (Rose \& Cravotta. 1998). In carbonate-deficient coals, where pyritic oxidation processes predominate, the chemistry will be similar to those reported for AMD where most pHs range from 3 to 4.5 (Rose \& Cravotta. 1998). The acidity associated with runoff accounts for the total amount of base required to neutralize the acid produced by the hydrolysis of the metal ions in solution. Other than $\mathrm{Fe}^{2+}$ (Equation 2) and $\mathrm{Fe}^{3+}$ (Equation 3), the hydrolysis of Al and Mn also predominant in acidic runoff:

$$
\begin{gather*}
\mathrm{Al}^{3+}+3 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Al}(\mathrm{OH})_{3(\mathrm{~s})}+3 \mathrm{H}^{+}  \tag{Equation7}\\
\text {Hydrolysis of } \mathrm{Al} \\
\mathrm{Mn}^{2+}+0.5 \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{MnO}_{2(\mathrm{~s})}+2 \mathrm{H}^{+} \\
\text {Hydrolysis of } \mathrm{Mn}
\end{gather*} \text { (Equation 7) }
$$

Based on Equations 2.3.7. and 8, the acidity in $\mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ of acidic runoff can be approximated using the following equation (Rose \& Cravotta. 1998):

Calculated Acidity $=50\left[\frac{3 C_{\mathrm{e}^{1}}+2 C_{f \mathrm{r}^{2}}}{55.85}+\frac{3 C_{A l^{1}}}{26.98}+\frac{2 C_{\mathrm{M} n^{2}}}{54.94}+10^{(3-p H)}\right] \quad$ (Equation 9) Where C is the concentration in $\mathrm{mg} / \mathrm{L}$ of the subscripted species and the divisor is the molecular weight of the subscripted species.

The acidity or net alkalinity (total alkalinity - hot peroxide acidity), not the pH , is the best indicator of the severity of acidic runoff. The calculated acidities are comparable to the measured acidities using the hot peroxide technique (Rose \& Cravotta. 1998). The hot peroxide technique is used because hydrogen peroxide and heating ensure that Fe and Mn are oxidized prior to titration with a base (American Public Health Association (APHA), 1989). Other metals that exist in the ionic form in acidic runoff do not contribute significantly to the overall acidity, but can contribute significantly to the aquatic toxicity.

### 2.2 Aquatic Toxicity of Acidic Drainage

Many agents in acidic runoff can act together or separately to exert toxicity on aquatic life. Numerous case studies have documented the overall detrimental effects of AMD on aquatic ecosystems (EPA, 2001a). Numerous laboratory studies have assessed the effects of individual trace metals on test species. However, very few studies have attempted to assess the toxicity of mixed acidic waters on test species. Nearly all of these studies have focused on the toxicity of metals in the water. Also. salinity toxicity is of special concern in this study because a recirculating wetland can potentially "cycle-up" or concentrate dissolved salts in the wetland water.

The specific mechanisms of toxicity for each agent associated with acidic runoff are difficult to describe and are beyond the scope of this report: nevertheless. there exist
several useful concepts or models that help to describe in bulk empirical terms how the toxicity can be quantified. Two empirical models have recently been developed to explain the effects of dissolved ions on aquatic organisms. The Biotic Ligand Model (BLM) describes the effects of soluble toxic metals (e.g., $\mathrm{Cu}, \mathrm{Ni}$, and Zn ) on aquatic life (Di Toro et al., 2001; Santore et al., 2001). The Gas Research Institute (GRI) model, or major ion model, has been developed to describe the effects of major ions (e.g., $\mathrm{SO}_{4}{ }^{2}$. $\mathrm{Ca}^{2+}$ and $\mathrm{K}^{+}$) on aquatic life (Mount et al., 1997). A model has not been developed which can account for mixed solutions of minor and major ions.

### 2.2.1 Metal Toxicity (Minor Ions or Heavy Metals)

The metallic agents that exist in trace amounts can be described as minor ions. They are also known as "heavy metals," which include the transition and post transition elements: chromium ( Cr ), cobalt (Co), nickel ( Ni ), copper $(\mathrm{Cu})$, zinc $(\mathrm{Zn})$, silver ( Ag ), cadmium $(\mathrm{Cd})$, mercury $(\mathrm{Hg})$, thallium $(\mathrm{Tl})$, and lead $(\mathrm{Pb})$, along with the metalloids: arsenic (As), selenium (Se), and antimony (Sb) (SenGupta. 2002). In the aqueous phase. these metals may exist as cations, anions, nonionized species. and complex macromolecules.

Minor ion toxicity is exerted by direct interference with the ceilular metabolic processes of the aquatic organism (Di Toro et al., 2001; Santore et al.. 2001). Generally, these metals and metalioids have toxic properties because they are relatively strong Lewis acids or electron acceptors (Langmuir. 1997). These types of cations are considered "soft" because they have an affinity to form complexes with $\mathrm{O}-\mathrm{N}$-, and S-containing ligands (Pearson. 1973). The soft cations therefore bind strongly with the sulfhydryl groups in proteins of cells (SenGupta. 2002). Because the sulfhydryl groups form active
sites on proteins for crucial metabolic processes, their blockages, through heavy metal binding, result in toxic effects to the organism (Forstner, 1979).

The threshold concentration for toxicity of metals to aquatic organisms is largely a function of concentration and differs for each heavy metal. With the exceptions of Cd, Hg and Pb , some metals are also required micronutrients and are used at very low concentrations. It is recognized that the dissolved portion of these metals is responsible for most of the toxicity to aquatic organisms, and that the toxicity to an aquatic organism in the pH range of 6 to 9 is dependent on many physical and chemical properties, including hardness (Newman \& Jagoe, 1994).

Increased hardness reduces the toxicity of the minor ions. Hardness is commonly defined as the sum of multivalent cations dissolved in water (American Public Health Association (APHA), 1989) and is typically reported as an equivalent quantity of calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$. The $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$ ions are usually the predominant cations. These "hard" cations can compete for the same proteins involved in cellular metabolism. preventing potential blockages through heavy metal binding. Therefore, an increase in calcium and magnesium hardness will reduce the toxic effects of cationic heavy metals to aquatic organism. However, the presence of toxic divalent cations (e.g., $\mathrm{Fe}^{2+} . \mathrm{Cu}^{2+}, \mathrm{Ni}^{2+}$. $\mathrm{Zn}^{2+}$ ) contributes to the hardness when the EDTA titrimetric method is used for determining hardness (APHA. 1989). Therefore, in order to account for only the contribution of the Ca and Mg hardness the following equation is used (APHA. 1989).

$$
\begin{aligned}
& \text { Hardness. mg equivalent/ } \mathrm{CaCO}_{3}= \\
& (\mathrm{Ca} . \mathrm{mg} / \mathrm{L} * 2.497)+(\mathrm{Mg} . \mathrm{mg} / \mathrm{L} * 4.116)
\end{aligned}
$$

(Equation 10)

The average hardness typically exceeds $300 \mathrm{mg} / \mathrm{L}$ (as $\mathrm{CaCO}_{3}$, based on Equation 10) throughout the Plant Gorgas wetland system. According to the EPA (1999), these waters. as with most AMD, are considered very hard.

The presence of organic acids and minerals may also reduce metal toxicity because they form relatively stable, nontoxic chemical ligands with the toxic minor ions (Brezonik et al., 1991 ; EPA, 1984a, 1984b, 1984c; Geisy \& Alberts, 1982; Honeyman. 1988; Leppard, 1993).

A Biotic Ligand Model (BLM) for acute toxicity of metals to aquatic organisms has recently been developed by Di Toro et al. (2001) and Santore et al. (2001). The interaction of the factors which effect the toxicity of these minor metals and metalloids is best understood through describing the conceptual BLM. The BLM improves upon the assumptions of the previously developed free ion activity model, which relates toxicity to the concentration of the calcium and magnesium (hardness). As presented in Figure 2. the BLM defines the bioavailability of the metal by considering the aqueous speciation of the metal (e.g., $\mathrm{M}^{2+}, \mathrm{MOH}^{+}, \mathrm{MHCO}^{+}, \mathrm{MCl}^{+}$) and cation-metal competition (e.g., $\mathrm{Ca}^{2+}$. $\mathrm{H}^{+}, \mathrm{Na}^{+}$) at the biotic ligand. The model uses the Windermere humic aqueous model (WHAM) of metal-dissolved organic matter (M-DOM) complexation.

The BLM is based on the premise that mortality occurs when the metal-biotic ligand complex reaches a critical concentration. For fish, the biotic ligands are suspected to be the sodium or calcium channel proteins in the gill surface that regulates the ionic composition of the blood. The model assumes that biotic ligands exist for other aquatic organisms and have the potential of converting total metal concentrations to the appropriate bio-available fraction. The model also has the potential of evaluating the
behavior for mixtures of metals. Presently, however, the model has only been applied to single metals for predicting acute toxicity (i.e., Cu or $\mathbf{A g}$ ) (Di Toro et al., 2001; Santore et al., 2001).


Figure 2. Schematic diagram of the Biotic Ligand Model (BLM) after Di Toro et al. (2001).

### 2.2.2 Major Ion Toxicity

Agents that contribute significantly to the salinity or conductivity of the water can also be toxic to freshwater aquatic life. These agents are described as major ions (e.g., $\mathrm{SO}_{4}{ }^{\mathbf{2 -}}, \mathrm{K}, \mathrm{Mg}^{2 \cdot}$ ). The sulfate ion is a predominant ion resulting from the pyritic oxidation processes associated with CPR and AMD. Goodfellow et al. (2000) have reviewed the effects of major ions on aquatic organisms. A listing of toxicity of these major ions to aquatic organisms can be found in a publication of the American Petroleum Institute (1998). Overwhelming the osmotic functions of the freshwater organism exerts
major ion toxicity. The toxicity associated with ion imbalances in the aquatic environment occurs when ion concentrations and molar ratios exceed the physiological tolerance range of the selected test organisms (Goodfellow et al., 2000). An assessment of the total dissolved solids (TDS) and conductance represents an integrated measure of all ions in freshwater. Correlations between increasing TDS or conductivity and toxicity may vary with ionic composition. Therefore, TDS or conductivity may not be the best predictor of major ion toxicity. However, for general monitoring purposes, if freshwater effluents have a conductivity above $2,000 \mu \mathrm{~S} / \mathrm{cm}$, the dissolved solids can be high enough to cause a toxic response (Goodfellow et al., 2000). The EPA has no water quality recommendations concerning the toxicity of TDS to freshwater aquatic organisms (EPA. 1999).

The effects of the major ions on the most commonly used freshwater test species have been studied by the American Petroleum Institute (1998) and the Gas Research Institute (Gas Research Institute. 1992; Mount et al.. 1997).

Mount et al. (1997) have published the series of logistic regression models (also known as the Gas Research Institute or GRI models) developed from their research. which predict the acute toxicity to two cladocerans (Ceriodaphnia dubia and Daphnia magna), and the fathead minnow (Pimephales promelas). After testing over 2,900 ion solutions it was determined that the toxicity was ion specific. For example, their results indicated that fathead minnows are more sensitive to $\mathrm{SO}_{4}{ }^{2-}$ than $C$. dubia. However, for most solutions the relative species sensitivity was $C$. dubia $>D$. magna $\sim P$ promelas. The relative toxicity was $\mathrm{K}^{+}>\mathrm{HCO}_{3}{ }^{-} \sim \mathrm{Mg}^{2+}>\mathrm{Cl}^{-}>\mathrm{SO}_{4}{ }^{2 \cdot}$. Sodium and calcium were found to not act as significant predicting variables for toxicity. The presence of multiple
cations with molar concentrations greater than $10 \%$ was found to have a protective effect on the two cladoceran species tested (C. dubia and Daphnia magna). Therefore, the logistic regression models that predict the probability of C. dubia and D. magna survival include variables that account for the presence of multiple ions. No such protective relationship was found to exist for the fathead minnow. The linear logistic regression models that predict the probability of survival based on the major ion concentrations and the number of predominant cations are in the following form:

$$
\begin{gather*}
\log i t(P)=\ln [P / 1-P)]=\beta_{0}+\beta_{1} X_{1}+\beta_{2} X_{2}+\quad+\beta_{n} X_{n}  \tag{Equation11}\\
P=100 /\left(1+e^{-\log n(P)}\right)
\end{gather*}
$$

(Equation 12)
Where:
$P=$ proportion of control reproduction, survival or growth
$\beta=$ regression coefficient
$X=$ water quality concentration or parameter value (i.e.. TUs)
$n=$ total number of significant terms in the model

The Alabama Department of Environmental Management (ADEM) typically uses the C. dubia and the fathead minnow for toxicity testing of freshwater effluent discharges to the surface waters of the State. The regression coefficients for predicting the $48 \mathrm{~h} C$. dubia and 96 h fathead minnow survival are presented in Table 1 (Mount et al., 1997). The units for the ion concentrations are $\mathrm{mg} / \mathrm{L}$. and because the equation is based on firstorder concentrations the variables can be converted to a molar basis by simply dividing each coefficient in Table 1 by the molecular weight of each ion. The variables that are not significant ( $\mathrm{NS}=\mathrm{p}>0.05$ ) are excluded from the model.

The model has performed well in predicting major ion toxicity in field collected samples. A strong correlation ( $\boldsymbol{R}^{2}=0.95$ ) was found between predicted and observed survival of C. dubia for oil field-produced water (Mount et al., 1997). Strong relationships were also found between predicted and observed survival of $C$. dubia exposed to produced waters associated with coalbed methane operations in Alabama (Mount et al., 1992) and with irrigation drain waters (Dickerson et al., 1996).

Table 1
Regression Coefficients for the 48 hC . dubia and 96 h Fathead Minnow Survival GRI Model (Mount et al., 1997)

| Coefficient | C. dubia (48-h) | Fathead minnow (96-h) |
| :--- | :---: | :---: |
| Constant | 8.83 | 4.70 |
| $\mathrm{~K}^{+}$ | -0.0299 | -0.00987 |
| $\mathrm{Mg}^{2+}$ | -0.00668 | -0.00327 |
| $\mathrm{Cl}^{-}$ | -0.00813 | -.00120 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -0.00439 | -0.000750 |
| $\mathrm{HCO}_{3}{ }^{-}$ | -0.00775 | -0.00443 |
| Major cations (NumCat) $^{\text {NumCat }^{*} \mathrm{~K}^{+}}$ | -0.446 | NS |
| NumCat $^{*} \mathrm{Cl}^{-}$ | 0.00870 | NS |
| NumCat* SO |  |  |

The model has been used to determine whether the presence of toxicants other than major ions may be indicated in produced waters from various fossil fuel production sites (Tietge et al., 1997). Differences between the observed and predicted toxicity were used to make inferences as to the causative factors (i.e., major ion or metal toxicity). Tietge et al. (1997) further evaluated the inferences by conducting a modified Phase I Toxicity Identification Evaluation (TIE) study (EPA, 1991). During this TIE study. laboratory water reconstituted to the same major ion concentrations as produced water was evaluated for toxicity. The results of the TIE study indicated that the $C$. dubia model could accurately predict the acute toxicity in field collected samples. However, the fathead minnow model may overpredict toxicity in field collected samples (Tietge et al.. 1997).

Therefore, because the ReRAPS water has a relatively high conductivity ( $>1000$ $\mu \mathrm{S} / \mathrm{cm}$ ), the major ion toxicity models (Mount et al., 1997) may be helpful when evaluating the toxicity of CPR and the waters in the ReRAPS. The model is capable of distinguishing the toxic effects of individual major ions and accounts for the protective effects of multiple major ions to $C$. dubia and fathead minnow. The model is also applicable when predicting the toxic effects of waters with mixtures of both major (e.g.. $\mathrm{SO}_{4}{ }^{2-} . \mathrm{Ca}^{2+}$, and $\mathrm{Mg}^{2+}$ ) and minor ions (e.g., $\mathrm{Zn}^{2+}, \mathrm{Ni}^{2+}$. and $\mathrm{Cu}^{2+}$ ). Deviations between the predicted effects may be attributed to the presence of other toxicants. such as minor metal ions or organic pollutants. The model may also be used to project changes in major ion toxicity resulting from any changes in the ReRAPS processes such as increased recirculation of treated waters through N12. An increased recirculation rate may cycle-
up or concentrate dissolved solids in the ReRAPS and increase the potential for toxicity in the treated waters of the system.

### 2.2.3 EPA Recommendations

The minor ions or heavy metals are included in the United States Environmental Protection Agency's (EPA) list of pollutants for freshwater aquatic organisms (EPA. 1999). A review of the literature has shown that all 13 metal pollutants recommended by the EPA (1999) as aquatic toxicants can be associated with coal storage or coal mine drainage activities. All of these metals exist in the cationic form in acidic water except for As and Se which exist as oxianions. There are no specific criteria recommended for the major ions.

The Continuous Criterion Concentrations (CCC) are the most limiting regulatory criteria for aquatic life and are the EPA's criterion for the concentrations that can be continuously tolerated by an aquatic organism. Table 2 presents the total metal CCCs for the EPA priority and nonpriority pollutants for freshwater organisms. The EPA developed CCCs for some of the metals using the Free Ion Activity Model (FIAM) and has not updated the criterion using the BLM approach (EPA. 1999). The FIAM relies only on $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$ hardness to moderate the effects of the trace metal ion. The hardness $\left(\mathrm{Ca}^{2+}\right.$ and $\left.\mathrm{Mg}^{2+}\right)$ for waters throughout the wetland nodes were similar and averaged $546 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ (range $169-789 \mathrm{mg} / \mathrm{L}$ ). The maximum hardness values for use in calculating the CCC for hardness dependent metals is limited to $400 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ (EPA. 2002). Because the ReRAPS hardness values typically exceeded this value. the CCCs for priority pollutants in the CPR and in the ReRAPS waters were calculated using the $400 \mathrm{mg} / \mathrm{L}$ maximum hardness value.

### 2.2.4 Evaluating the Potential for Toxicity

The value of evaluating wetland toxicity removal without performing chronic or acute tests is questionable when evaluating the toxicity of waters with mixtures of potentially toxic major and minor ionic species. The increased availability of toxicity test data generated by effluent and surface water monitoring in the United States suggests that many freshwater effluents may contain priority pollutants at higher levels than the EPA criteria and yet be non-toxic to test species (Delos, 1992; Diamond et al., 1997; Diamond et al., 1994). Evidence of interaction between the major and minor ions make it difficult to distinguish the causative factors of toxicity in mixed effluents (Dwyer et al. 1992: Ingersoll et al.. 1992). In such situations. salt tolerant test species are often compared to freshwater species to determine if a major ion effect may exist.

Short of actually performing the toxicity test. the removal of toxicity in the wetland can be evaluated using a modified Hazard Quotient Procedure (HQP) adopted from the Organization for Economic Co-operation and Development (OECD) (2001). When using this European approach for assessing environmental risks, the ratio of the Predicted Environmental Concentration (PEC) over the Predicted No Effect Concentration (PNEC) is calculated. Ratio values of greater than $l$ are indicative of possible toxic effects. When applying this method for assessing the removal of toxicity in the wetland. the total (unfiltered) concentration of a metal can be considered a conservative estimator of the actual PEC. The use of total metal (unfiltered) measurements would equal or overpredict the actual concentration of the causative species. considering that most ligand bound species would be included. The PNEC is best-determined using long-term multigeneration exposure testing of aquatic organisms. Although scientifically limited. the

EPA CCC could be used as a qualitative PNEC for each of the priority metals. For example, the EPA CCC values are not necessarily species specific.

Table 2
The EPA Recommended Water Quality Criterion Continuous Concentrations (CCC) for
Priority and Non-priority Metal and Metalloid Pollutants of Fresh Water Aquatic Life

| EPA Status | Hardness <br> Dependence Range <br> $(\mathrm{mg} / \mathrm{L}$ as CaCO3) | Pollutant | EPA CCC (ug/L) |
| :--- | :---: | :---: | :---: |
| Priority | NA | Arsenic (As) | 150 |
|  | 400 | Cadmium (Cd) | 7.30 |
|  | 400 | Chromium III (Cr(III)) | 268 |
|  | NA | Chromium VI (Cr(VI)) | 11 |
|  | 400 | Copper (Cu) | 30.5 |
|  | 400 | Lead (Pb) | 18.6 |
|  | NA | Mercury (Hg) | 0.77 |
|  | 400 | Nickel (Ni) | 168 |
|  | NA | Selenium (Se) | 5 |
|  | 400 | Silver (Ag) | 44 |
|  | 400 | Zinc (Zn) | 388 |
| Non-Priority | NA | Aluminum (Al) | 87 |
|  | NA | Iron (Fe) | 1000 |

Note. CCC ranges are calculated for hardness dependent pollutants using the maximum allowable hardness value of $400 \mathrm{mg} / \mathrm{L}$. which can be used in the CCC calculations. Hardness in the Plant Gorgas ReRAPS wetland averages $526 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$. CCC for Ag is based on the Criteria Maximum Concentration (CMC) because CCC for Ag have not been developed by the EPA (EPA. 1999).

Recognizing the limitations and assuming additive chronic effects (toxicity or concentration addition) among the trace metals a classification of the wetland water can be calculated as follows:

$$
\begin{equation*}
\sum_{\eta} \frac{C_{1}}{C C C_{1}}=\text { TUs or Toxicity Units } \tag{Equation13}
\end{equation*}
$$

Where: water classified as chronically toxic if TUs $>1.0$
$C_{1}=$ concentration of component $i$
$C C C_{1}=$ EPA continuous criterion concentration (as calculated in Table 2 for total metals
$\eta$ = number of components

Equation 13 is a semi-qualitative estimate of cumulative toxicity based on normalizing the concentrations of total contaminants to the CCC for the metallic priority pollutants. Assuming toxicity additivity, the waters within the wetland may be classified as toxic when the Toxicity Unit (TU) values exceed 1. Equation 13 would have more scientific value if the EPA CCC value were replaced by species specific No Observable Effect Concentration (NOEC) values and if the concentrations of dissolved (filtered) metals were used. Regardless of the approach, the extrapolation of the lab chemistry results to actual biological effects in the field should be recognized as a conservative estimate of where the treated water in the wetland may exhibit NOEC characteristics (Chapman et al., 1998).

High concentrations of Mn are toxic to aquatic life when compared with trace metals (Stubblefield et al., 1996). However, the application of the regulatory standards for Mn are based partly on the fact that it can act as a surrogate for other (more toxic) metals such as $\mathrm{Cr} . \mathrm{Cu}, \mathrm{Pb}, \mathrm{Hg}, \mathrm{Ni}$, and Zn (Watzlaf. 1988. 1997). As previously described. Mn is relatively difficult to remove from the aqueous phase relative to the other trace metals (Brant \& Ziemkiewicz. 1997). Royer et al. (1998) have evaluated the use of Mn as a predictor of heavy metal removal in passive wetlands receiving acidic coal mine drainage. Using regression techniques, they found that Fe and Co (cobalt) were the only
metals that were positively related to $\mathbf{M n}$. Mn is often used as a regulated parameter in the electric utility and mining industries. Its value as a regulated parameter in wetland applications still requires further study.

Kleinman and Watzlaf (1988) have reviewed the history of the development of mine water standards relative to the use of Mn. Initially, Mn was included by the EPA in the mining industry standards as a representative priority pollutant due to the suspected adverse toxic and economic effects. Later, the assumed toxic effects of Mn were deemphasized and its use as a surrogate or indicator of heavy metal pollutants was emphasized. Current Mn standards originated with the observation by the EPA that during the treatment of AMD using a caustic. eight metals (As, $\mathrm{Cr}, \mathrm{Cu}, \mathrm{Pb}, \mathrm{Hg}, \mathrm{Ni}, \mathrm{Se}$. and Zn ) were precipitated from solution as soluble Mn was reduced to a level of $2 \mathrm{mg} / \mathrm{L}$ (Watzlaf, 1997).

### 2.2.5 Toxicity Testing

Direct toxicity testing of the CPR and ReRAPS waters to discern the causative agents (i.e., metal or common ion effects) should consider the value of chronic versus acute toxicity testing. Goodfellow et al. (2000) recommend that it is more important to measure the salinity tolerance for chronic versus acute toxicity testing because the growth and reproductive endpoints are more sensitive to the energy-taxing requirements of osmoregulation than the acute endpoint of survival. Therefore, it should be noted that the empirical models developed by the Gas Research Institute were not developed to predict chronic toxicity (i.e.. C. dubia reproduction. fathead minnow growth and survival $=7 \mathrm{~d}$ ) and that a chronic toxicity model for the major ions has not been developed. David Mount (personal communication) of the EPA suggests that a doubling of the ion
concentration may estimate the chronic effects (i.e., $\approx$ LC25, $25 \%$ lethal concentration) of the surface waters in the ReRAPS.

Therefore, when assessing the effects of trace metals and common ions on toxicity in the CPR and ReRAPS the following approach that has been adopted from Goodfellow et al. (2000) can be applied.

- As a general screening tool, freshwater effluents can have an adverse impact on freshwater test species, if conductivity measurements are above $2.000 \mu \mathrm{~S} / \mathrm{cm}$.
- Correlations between toxicities and total dissolved solids (TDS) may also be indicative of major ion effects.
- Evaluations of the predicted major ion effects can be performed using the predictive logistic regression major ion toxicity models developed by the Gas Research Institute (Gas Research Institute, 1992; Mount et al., 1997).
- Significant differences in species sensitivities may be indicative of a common ion effect if the predominant ions are known to exhibit unique sensitivity patterns.

Another approach may include the manipulation of the effluent using the EPA Phase I Toxicity Identification Evaluation (TIE) procedures (Mount. 1989: Norberg-King, 1991). These sample manipulations can aid in discerning the type of toxic agent. Other effluent manipulations can include chemical fractionation schemes, which incorporate toxicity testing before and after resin treatments, and the testing of synthetic or mock effluents which mimic the suspected toxic agent. Using some or all of the above recommendations. a weight-of-evidence approach can be used to identify the mode of toxicity in the CPR and ReRAPS waters.

Agents that contribute significantly to the salinity or conductivity of the water can be toxic to freshwater aquatic life. These agents are described as major ions (e.g., $\mathrm{SO}_{4}{ }^{2-}, \mathrm{K}^{+}$, $\mathrm{Mg}^{+2}$ ). Major ion toxicity is exerted by overwhelming the osmotic functions of the freshwater organism. High concentrations of ionic salts or major ions such as sulfates $\left(\mathrm{SO}_{4}{ }^{2}\right.$ ) can effect the osmotic functions of aquatic organisms. The toxicity associated with ion imbalances in the aquatic environment occurs when ion concentrations and molar ratios exceed the physiological tolerance range of the selected test organisms (Goodfellow et al., 2000). An assessment of the total dissolved solids (TDS) represents an integrated measure of all ions in freshwater. Correlation between increasing TDS or conductivity and toxicity may vary with ionic composition. Therefore. TDS or conductivity may not be the best predictor of major ion toxicity. However, for general monitoring purposes, if freshwater effluents have conductivity above $2.000 \mathrm{uS} / \mathrm{cm}$, the dissolved solids can be high enough to cause a toxic response (Goodfellow et al., 2000).

The effects of the major ions on the most commonly used freshwater test species (Ceriodaphnia dubia, Daphnia magna, and Pimephales promelas) have been studied (American Petroleum Institute. 1998; Gas Research Institute, 1992; Goodfellow et al.. 2000; Mount et al.. 1997). The relative species sensitivity was $C$. dubia $>$ D. magna $\sim P$ promelas. The sensitivity to certain salts may be similar (i.e.. $\mathrm{CaSO}_{4}$ ) among species or can vary greatly (i.e., NaCl ). A salinity/toxicity model has been developed for these test species (Gas Research Institute. 1992; Gulley et al., 1992). Goodfellow et al. (2000) have reviewed these studies and found that the relative toxicity was $\mathrm{K}^{+}>\mathrm{HCO}_{3}{ }^{-}-\mathrm{Mg}^{2+}$ $>\mathrm{Cl}^{-}>\mathrm{SO}_{4}{ }^{2-}$. Sodium and calcium were found to not act as significant predicting variables for toxicity. The significant presence of two or more types of cations were
found to reduce the toxicity of $\mathrm{Cl}^{-}$and $\mathrm{SO}_{4}{ }^{2-}$. A preliminary application of the $C$. dubia model to field collected samples shows a high degree of accuracy (Dickerson et al., 1996; Goodfellow et al., 2000).

### 2.3 Wetland Contaminant Removal Processes

Agents associated with acidic runoff that exert toxicity to aquatic organisms exist in either the dissolved (i.e., minor or major ions) or suspended state (i.e., amorphous Al). The toxicity is eliminated when the toxic agents are immobilized or removed. Trace metals are mobilized or immobilized in the RAPS-based wetland via processes such as precipitation/dissolution, formation of complex compounds, sorption/desorption and/or reduction/oxidation. Various separation strategies are encouraged in the design of the wetland. Figure 3 presents the strategies that are used for metal separation in most RAPS-based wetlands. Strategies such as precipitation and bio-oxidation are primarily used to achieve pollutant separation from the aqueous phase. The precipitation and biooxidation processes are optimized at increased pH . The pH is increased through limestone dissolution and bio-reduction processes. Other processes such as sulfide precipitation. and absorption/co-precipitation exist but their relative "contaminant removal" contributions in RAPS-based systems are unknown.

Brief descriptions of the chemical processes that effect the performance of RAPSbased wetlands are presented in the following paragraphs. The detailed descriptions of the following processes have been previously published by Langmuir (1997). Snoeyink and Jenkins (1980). and Stumm and Morgan (1981).


Figure 3. A schematic illustrating various constructed wetland processes for metal separation from the aqueous phase. Adopted from SenGupta (2002).

### 2.3.1 Limestone Dissolution and Acidity Consumption

The initial treatment goal of the RAPS-based wetland is to consume acidity and therefore increase the pH . Limestone (calcium carbonate, $\mathrm{CaCO}_{3}$ ) dissolution is the primary means of generating alkalinity to consume acidity. The production of alkalinity is also achieved through bioreduction processes which will be discussed later.

The following reactions which Brodie et al. (1993) have applied to anoxic limestone drains (ALDs) are applicable within the limestone portion of the wetland and assume that the deeper waters behave as a closed system (i.e., no atmospheric gas exchanges).

$$
\begin{align*}
\mathrm{CaCO}_{3(\mathrm{~s})}+2 \mathrm{H}^{-} & \rightarrow \mathrm{Ca}^{2 \cdot}+\mathrm{H}_{2} \mathrm{CO}_{3}  \tag{Equation14}\\
\mathrm{CaCO}_{3(\mathrm{~s})}+\mathrm{H}_{2} \mathrm{CO}_{3} & \rightarrow \mathrm{Ca}^{2 \cdot}+2 \mathrm{HCO}_{3}^{-} \tag{Equation15}
\end{align*}
$$

$$
\begin{equation*}
\mathrm{CaCO}_{3(\mathrm{~s})}+\mathrm{H}^{+} \rightarrow \mathrm{Ca}^{2+}+\mathrm{HCO}_{3}^{-} \tag{Equation16}
\end{equation*}
$$

Limestone reacts with proton acidity at low pH ( $\mathrm{pH}<6.4$ ) to form free calcium and dissolved carbon dioxide or carbonic acid (Equation 14). Carbonic acid further reacts with calcium carbonate to produce bicarbonate alkalinity (Equation 15). As Equations 14 and 15 proceed to increase the pH above 6.4, Equation 16 becomes predominant where the bicarbonate becomes the major $\mathrm{CO}_{2}$ species. If limestone dissolution occurred in an "open system" then Equation 5, which was previously used to describe the dissolution of coal pile carbonates, would predominate. Note that every $1 \mathrm{mg} / \mathrm{L}$ increase in $\mathrm{Ca}^{2+}(40.1$ $\mathrm{g} / \mathrm{mol}$ ) will stoichiometrically yield $2.497 \mathrm{mg} / \mathrm{L}$ of generated alkalinity as $\mathrm{CaCO}_{3}(100.1$ g/mol).

### 2.3.2 Aluminum and Iron Precipitation (Acid/Base Equilibrium)

Another treatment scheme is increasing the pH to levels that achieve the minimum solubility of the metal pollutant. This treatment scheme is promoted through limestone dissolution and the recirculation of treated alkaline water.

Fe. AI, and Mn are the predominant metals found in AMD and CPR. Fe and AI oxyhydroxides precipitates will form in the wetland water as the pH is increased above 3.5 and 4.5 , respectively. However. Mn will be more difficult to remove or precipitate because it does not autooxidize until the pH exceeds 8.5.

The $\mathrm{Fe}(\mathrm{III})$ and $\mathrm{Al}(\mathrm{III})$ species equations in Table 3 are expressed as a $\mathrm{pC}-\mathrm{pH}$ diagram in Figure 4. Dissolved iron or aluminum concentrations (moles/liter) previously measured in the Plant Gorgas coal pile runoff are indicated by a reference line (Figure 4). The diagram only estimates the boundary condition for the solution. However, based on this diagram. iron hydroxides will begin to form at $\mathrm{pH}>2.5$ and Al-hydroxide will begin
to form at $\mathbf{p H}>6.0$. These theoretical equilibrium concentrations presented in Figure 4 can be estimated for more complex mixtures of soluble cations and anions at various $\mathbf{p H s}$ by using the EPA MINTEQ model (Allison et al., 1991; Langmuir, 1997). Although the theoretical minimum solubilities for metal hydroxides are low, these levels are seldom achieved in conventional treatment systems due to poor solid/liquid separation. slow reaction rates, pH fluctuations and the presence of other cations and complexing agents in the wastewater (Banerjee, 2002). These factors that negatively affect the performance of a conventional treatment system would be even more difficult to control in unsteady-state wetland treatment systems.

Table 3
Equilibrium of Various Dissolved Fe(III) and Al(III) Species and Respective Precipitants

| $\begin{aligned} & \hline \text { Species } \\ & \hline F e(\text { III }) \end{aligned}$ |  | Reactions | Constants |
| :---: | :---: | :---: | :---: |
|  | 1 | $\mathrm{Fe}^{3+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{FeOH}^{2+}+\mathrm{H}^{+}$ | $\operatorname{LogK}_{1} \mathrm{Fe}^{3+}=\mathbf{- 2 . 1 6}$ |
|  | 2 | $\mathrm{Fe}^{3+}+2 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Fe}(\mathrm{OH})_{2}{ }^{+}+2 \mathrm{H}^{+}$ | $\operatorname{LogK}=-6.74$ |
|  | 3 | $\mathrm{Fe}(\mathrm{OH})_{3(\mathrm{~s})} \leftrightarrow \mathrm{Fe}^{3+}+3 \mathrm{OH}$ | $\operatorname{LogK}_{50}=-38$ |
|  | 4 | $\mathrm{Fe}^{3+}+4 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Fe}(\mathrm{OH})_{4}+4 \mathrm{H}^{+}$ | $\log K=-23$ |
|  | 5 | $2 \mathrm{Fe}^{3+}+2 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Fe}_{2}(\mathrm{OH})_{2}{ }^{4+}+2 \mathrm{H}^{+}$ | $\log K=-2.85$ |
| Al(III) | 1 | $\mathrm{Al}^{3+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Al}(\mathrm{OH})^{2+}+\mathrm{H}^{+}$ | Log $K_{1}=-5$ |
|  | 2 | $7 \mathrm{Al}^{3+}+17 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Al}_{7}(\mathrm{OH})_{17}{ }^{4+}+17 \mathrm{H}^{+}$ | $\log K=-48.8$ |
|  | 3 | $13 \mathrm{Al}^{3+}+34 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Al}_{13}(\mathrm{OH})_{34}{ }^{5+}+34 \mathrm{H}^{+}$ | Log $K=-97.4$ |
|  | 4 | $\mathrm{Al}(\mathrm{OH})_{3(\mathrm{~s})} \leftrightarrow \mathrm{Al}^{3+}+3 \mathrm{OH}^{-}$ | Log $\mathrm{K}_{\text {so }}=-33$ |
|  | 5 | $\mathrm{Al}(\mathrm{OH})_{3(5)}+\mathrm{OH}^{-} \leftrightarrow \mathrm{Al}(\mathrm{OH})_{4}{ }^{-}$ | $\log \mathrm{K}_{\text {st }}=1.3$ |
|  | 6 | $2 \mathrm{Al}^{3+}+2 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{Al}_{2}(\mathrm{OH})_{2}^{4+}+2 \mathrm{H}^{+}$ | $\log K=-6.3$ |

Nole. $\left(\mathrm{Fe}(\mathrm{OH})_{3}\right.$ - Ferric Hydroxide and $\mathrm{Al}(\mathrm{OH})_{3}$ - Aluminum Hydroxide) from Snocyink and Jenkins (1980).


Figure $f$. Equilibrium concentrations of five hydroxo iron (III) and six aluminum (III) complexes in a solution in contact with freshly precipitated $\mathrm{Fe}(\mathrm{OH})_{\left.3_{(s)}\right)}$ and $\mathrm{Al}(\mathrm{OH})_{3_{(s)}}$ at $25^{\circ} \mathrm{C}$ in pure water. Horizontal reference line represents the maximum ( Ct , total dissolved) concentration of dissolved Fe and Al measured in the coal pile runoff. This figure is based on information presented in Table 3.

### 2.3.3 Bioreduction and Sulfide Precipitation Processes

Biological oxygen depletion and chemical reduction of the wetland water are treatment schemes that promote sulfide precipitation of metals and alkalinity generation through sulfate reduction. This treatment scheme is promoted by routing water through an organic compost which has been augmented with limestone sand. The compost provides a carbon source for microbial metabolic activity and the limestone sand promotes favorable microhabitat $\mathbf{p H}$ levels.

The removal of metals from acid runoff using wetlands originally focused on bioreduction processes in peat bogs or compost wetland components. Bioreduction processes are promoted in anoxic water where both dissolved oxygen ( $<1 \mathrm{mg} / \mathrm{L}$ ) and oxidation reduction potentials (ORP $<-100 \mathrm{mv}$ ) are low. Heavy metal cycling, transport and removal within the wetland are effected by redox reactions. Sulfate is reduced to sulfide by sulfate reducing bacteria within the anoxic substrates. Heavy metal precipitation is facilitated due to the low solubility products of metal sulfides.

Bacteria mediate the bioreduction processes and our understanding of metal-reducing bacteria is still limited. For example. the fact that bacteria can use metals as terminal electron acceptors has only been known for less than 25 years (Chapelle, 1993). The biological locations where the reducing reactions take place are both intracellular and extracellular. Highly crystalline minerals are produced directly by the bacteria and amorphous minerals are produced through indirect bacterial mediation (Lowenstam. 1981).

The bacteria in a reducing wetland component, as with all living organisms, must have three things to survive: (1) an electron donor (energy source), (2) a carbon source
(often the same as the electron donor), and (3) an electron acceptor. Nutritional (e.g.. trace metals, vitamins) and physical (e.g., pH , temperature) requirements must be met for optional metabolism to occur. It should be noted that the electron donors and carbon sources for the biooxidative processes are typically not limiting because autotrophic or photosynthetic processes primarily drive the system, which relies on solar energy and the availability of photosynthetic nutrients such as phosphorus ( P ) and nitrogen (N). Whereas, the bioreductive processes may be more limited by the type and lack of carbon source. Therefore, the metal removal processes that rely on bioreduction will be limited by the availability of carbon. The simple short chain organic acids (e.g., formic. lactic. acetic, propionic, and butyric acids) and alcohols (e.g.. ethanol) are typical electron donors and carbon sources for metal reducing bacteria.

Oxidation-reduction processes that occur in the RAPS are no different than processes that have been described for natural wetlands (Kadlec \& Knight. 1996; Vymazal. 1995). Microorganisms catalyze oxidation-reduction (also called redox) reactions as they metabolize organic carbon in the RAPS. Catabolic reactions result in the release of useable chemical energy for the microbes and the microbes use this energy to synthesize ATP. During this process the organic matter in the compost is used as an electron donor and free oxygen is used as the final electron acceptor. Free oxygen within the RAPS decreases rapidly with depth due to aerobic bacteria respiration. A consortium of microbes is required as cellulose in the compost is converted to starches. and starches are then converted to sugars. Catabolism of glucose provides a simplified aerobic respiration reaction (Kadlec \& Knight. 1996):

$$
\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+6 \mathrm{O}_{2} \rightarrow 6 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}
$$

(Equation 17)
Aerobic catabolism of glucose

As water passes down through the compost, oxygen is rapidly consumed in the upper organic layer. Below this zone, obligate aerobes no longer function. As the oxygen is depleted, fermenting microorganisms will partially oxidize organic substrates in an anaerobic environment using internally balanced redox reactions (Brock et al., 1994). The following are two examples of glucose fermentation (Kadlec \& Knight, 1996):

$$
\begin{equation*}
\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+6 \mathrm{O}_{2} \rightarrow 2 \mathrm{CH}_{3} \mathrm{CHOHCOOH} \tag{Equation18}
\end{equation*}
$$

Fermentation of glucose to lactic acid by lactic acid bacterium

$$
\begin{equation*}
\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+6 \mathrm{O}_{2} \rightarrow 2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}+2 \mathrm{CO}_{2} \tag{Equation19}
\end{equation*}
$$

Fermentation of glucose to ethanol by yeast

Compared to aerobic respiration, fermentation yields relatively little energy for the microbe due to the incomplete oxidation of the organic molecule and due to the small differences in the reduction potential between the electron donor (e.g.. glucose) and the terminal electron acceptor (e.g., lactic acid, ethanol). In this fermentation example, another organic compound serves as the electron acceptor. However. inorganic reactants are used by certain bacteria as electron acceptors as well. The utilization of inorganic electron acceptors such as nitrate $\left(\mathrm{NO}_{3}{ }^{-}\right)$, sulfate $\left(\mathrm{SO}_{4}{ }^{2-}\right), \mathrm{Fe}(\mathrm{III})$, manganic manganese ( $\mathrm{Mn}^{4+}$ ) and carbon dioxide $\left(\mathrm{CO}_{2}\right)$ allows for non-fermentative microorganisms to exist in anaerobic environments.

Microorganisms, primarily bacteria, reduce these compounds in a sequential order based on the molecules relative oxidizing power (ability to accept electrons). The
sequential reduction of compounds, in most cases is governed by the laws of thermodynamics. This order is based on the ability of the substance to accept electrons or be reduced. The reduction (redox) potential or ability to donate electrons (Eh) is measured electrically using hydrogen $\left(\mathrm{H}_{2}\right)$ as a standard. The redox potential of a solution is a measure of the proportion of oxidized to reduced substances (Boyd. 1979). Substances with a higher potential for accepting electrons relative to hydrogen have a positive Eh. If oxidizing conditions exist, electrons will flow from the hydrogen electrode to the solution and the electron flow in volts is assigned a positive value. If reducing conditions exist, electrons will flow from the solution to the hydrogen electrode and the electron flow in volts is assigned a negative value. Substances with a relatively low potential for accepting electrons have a negative Eh. Substances with a higher potential for accepting electrons are used first. The Eh for wetland soils will range from +700 mv in oxidized (oxygenated) surface waters to -300 mv in anaerobic muds. As water passes down through the compost. unique species of microbes will utilize specific chemicals to accept electrons and be reduced. The presence of certain bacterial species, the type of organic substrate, pH , and the presence of other electron accepting compounds will affect the reduction of specific compounds (e.g., $\mathrm{NO}_{3}{ }^{\circ}, \mathrm{SO}_{4}{ }^{2-} . \mathrm{Fe}(\mathrm{III})$. $\mathrm{Mn}_{4}{ }^{+}$. and $\mathrm{CO}_{2}$ ). As the water in the RAPS becomes increasingly reduced. chemicals other than oxygen act as electron acceptors. A theoretical order of predominant redox reactions and Eh levels that might occur with increased depth in the compost is presented in Table 4. The retention of water in the compost effects the extent of reduction. The oxidation-reduction front in the RAPS will vary according to the loading of the oxidants and reductants.

Table 4
Typical Bioreduction Reactions which will Predominate in the Wetland Compost at Various Eh Values

## Redox Potentials

| (Eh, mv) | Reduction Half-Reaction | Name of Reaction |
| :---: | :--- | :--- |
| $>+300$ | $\mathrm{O}_{2(2 \mathrm{a})}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}^{-}$ | Aerobic respiration |
|  | $2 \mathrm{NO}_{3}{ }^{-}+12 \mathrm{H}^{+}+10 \mathrm{e}^{-} \rightarrow \mathrm{N}_{2(\mathrm{~g})}+6 \mathrm{H}_{2} \mathrm{O}$ | Denitrification |
| $+220-200$ | $\mathrm{MnO}_{2(\mathrm{~s})}+4 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Mn}^{2+}+2 \mathrm{H}_{2} \mathrm{O}$ | Manganic Mn reduction |
| $>+120$ | $\mathrm{Fe}(\mathrm{OH})_{3(\mathrm{~s})}+3 \mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}+3 \mathrm{H}_{2} \mathrm{O}$ | Ferric hydroxide reduction |
| $>+220$ | $\mathrm{NO}_{3}+10 \mathrm{H}^{+}+8 \mathrm{e}^{-} \rightarrow \mathrm{NH}_{4}^{+}+3 \mathrm{H}_{2} \mathrm{O}$ | Nitrate reduction |
| $>+220$ | $\mathrm{NO}_{3}{ }^{-}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{NO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}$ | Nitrate reduction |
| $>+100$ | $\mathrm{Fe}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}$ | Ferric Iron reduction |
| -75 to -150 | $\mathrm{SO}_{4}{ }^{2-}+9 \mathrm{H}^{+}+8 \mathrm{e}^{-} \rightarrow \mathrm{HS}^{-}+4 \mathrm{H}_{2} \mathrm{O}$ | Sulfate reduction |
| -250 to -350 | $\mathrm{CO}_{2(\mathrm{~g})}+8 \mathrm{H}^{+}+8 \mathrm{e}^{-} \rightarrow \mathrm{CH}_{4(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}$ | Methanogenesis |

Note. Eh values will decrease with depth and is a function of retention during flow through conditions. Table values and reactions are modified from Brock (1994), Kadlec and Knight (1996). Snoeyink and Jenkins (1980), and Vymazal (1995).

Due to the pyrite oxidation processes, $\mathrm{SO}_{4}{ }^{2-}$ will generally exist in the wetland water as the predominant ion. Therefore, the reduction of $\mathrm{SO}_{4}{ }^{2-}$ is an important wetland chemical process because proton acidity is consumed and metal sulfides are formed as bacterially-derived alkalinity is generated. Note that as all of the compounds in Table 4 are reduced. proton acidity is consumed. The production of sulfides can precipitate various reduced metals such as iron. vanadium. cobalt. and nickel as metal sulfides (Goldschmidt. 1958).

Alkalinity is produced due to sulfate reduction based on the following assumed stoichiometric relationship:

$$
\begin{equation*}
2 \mathrm{CH}_{2} \mathrm{O}+\mathrm{SO}_{4}{ }^{2-} \xrightarrow{\text { saccena }} \mathrm{H}_{2} \mathrm{~S}+2 \mathrm{HCO}_{3}- \tag{Equation20}
\end{equation*}
$$

Bacterially-derived Alkalinity Generation through Sulfate Reduction

Where:
$1 \mathrm{mg} / \mathrm{L}$ decrease in sulfate yields $1.04 \mathrm{mg} / \mathrm{L}$ alkalinity as $\mathrm{CaCO}_{3}$

According to Equation 15,2 moles of bicarbonate $\left(\mathrm{HCO}_{3}\right)$ are generated when one mole of calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$ is dissolved. Therefore. for every $1 \mathrm{mg} / \mathrm{L}$ decrease in $\mathrm{SO}_{4}{ }^{2-}(96 \mathrm{~g} / \mathrm{mol})$ will yield $1.04 \mathrm{mg} / \mathrm{L}$ alkalinity as $\mathrm{CaCO}_{3}(100 \mathrm{~g} / \mathrm{mol})$.

Fe and Mn are redox sensitive species and will migrate through compost in the reduced states without precipitating and coating the substrate (armoring). Redox processes have little direct effect on the precipitation and dissolution of aluminum. As the pH of the acidic runoff waters increases inside the compost. dissolved aluminum will form as amorphous Al -hydroxides $\left(\mathrm{Al}(\mathrm{OH})_{\mathrm{n}}\right)$. Although aluminum does not coat the substrate. the amorphous material could eventually effect the porosity of the compost depending on the loading of AI.

### 2.3.4 Oxidation and Precipitation of Reduced (Anoxic) Iron

Reaeration of anoxic water containing chemically reduced iron $\left(\mathrm{Fe}^{2+}\right)$ is a treatment scheme that promotes the precipitation of iron as ferric hydroxide ( FeOOH ) according to the following reaction:

$$
\begin{gather*}
4 \mathrm{Fe}^{2+}+\mathrm{O}_{2}+4 \mathrm{H}^{+} \rightarrow 4 \mathrm{Fe}^{3+}+2 \mathrm{H}_{2} \mathrm{O}  \tag{Equation21}\\
\text { Ferrous Oxidation }
\end{gather*}
$$

$$
\begin{gather*}
4 \mathrm{Fe}^{3+}+12 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3}+12 \mathrm{H}^{+}  \tag{Equation22}\\
\text {Ferric Hydrolysis } \\
4 \mathrm{Fe}^{2+}+\mathrm{O}_{2}+10 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3}+8 \mathrm{H}^{+}  \tag{Equation23}\\
\text {Overall Oxidation of } \mathrm{Fe}^{2+}
\end{gather*}
$$

The previous reactions are similar to reactions contributing to the formation of acidic runoff from the coal pile (Equations 2 and 3). Athough bacteria can catalyze the reaction, ferrous iron will primarily autooxidize in circumneutral water containing free oxygen. Based on the overall reaction (Equation 23), two moles of acidity are produced for every mole of ferrous iron oxidized. A depression of pH to levels below 5.5 will limit ferric hydrolysis and removal of iron (Wildeman et al., 1993). However, any bicarbonates produced during limestone dissolution will buffer the decrease in pH (Wildeman et al.. 1993).

For example. the rate of oxygenation of $\mathrm{Fe}(\mathrm{II})$ in water with $\mathrm{pH}>5$ was found to be first order with respect to both $[\mathrm{Fe}(\mathrm{II})]$ and $\left[\mathrm{O}_{2}\right]$ and second order with respect to $\left[\mathrm{H}^{+}\right]$ (Stumm \& Morgan, 1981).

$$
\begin{equation*}
r_{\text {rell }}=\mathrm{k}_{\mathrm{H}}[\mathrm{Fe}(\mathrm{II})]\left[\mathrm{H}^{+}\right]^{-2}\left[\mathrm{O}_{2(\mathrm{~m})}\right] \tag{Equation24}
\end{equation*}
$$

Where:

$$
r_{\text {tell }}=\text { rate loss, moles } / \mathrm{L}-\mathrm{min}
$$

$k_{\prime \prime}=3 \times 10^{-12}$ moles $/$ L-min @ $20^{\circ} \mathrm{C} . \mathrm{pH}<5$, reaction rate constant
[molar concentration] $=$ moles $/ \mathrm{L}$ or M

The oxidation rate constant ( $k_{11}$ ) for Equation 24 was developed with dissolved Fe (II) concentrations of less than $5 \times 10^{-4} \mathrm{M}$. or $28 \mathrm{mg} / \mathrm{L}$ (Stumm \& Morgan. 1981).

Confounding parameters such as $\mathrm{Cu}^{2+}$ and $\mathrm{Co}^{2+}$ cations, increased temperature, and light. all increase the reaction rate (Singer \& Stumm, 1970; Stumm \& Lee, 1961; Sung \& Morgan, 1980). Increased ionic strength and the presence of unoxidized organic compounds cause rate reductions (Stumm \& Morgan, 1981 and Sung \& Morgan, 1980). The oxidation rates presented by Singer and Stumm (1970) indicate that Equation 24 may be applied at pH values as low as 4.7 and may be incorporated into a portion of a model explaining the removal of Fe (II) from water in a wetland component.

### 2.3.5 Bio-oxidation of Manganese

As previously discussed, of the three predominant metals typically found in coal drainage, Mn is the more difficult to remove using RAPS-based wetlands. This is because uncatalyzed $\mathrm{Mn}(\mathrm{II})$ oxidation does not occur readily until the pH is greater than 10 (Brezonik. 1994). However, high pH moderation for Mn precipitation is not possible in the RAPS-based wetland. As previously described pH values of greater than 8.5 are required to achieve a rapid autooxidation of Mn. RAPS-based wetland water will rarely exceed $\mathrm{pH}>8.5$ due to carbonate buffering. Fortunately, the microbially mediated oxidation of manganese in RAPS-based wetlands plays a key role in the retention of this metal. The biomediation of Mn is promoted by routing water through substrate, which promotes the growth of an attached aerobic biofilm community at neutral pH. Many microbes have been identified from surface waters and from the attached biofilm community (epilithic community) which bio-mediate the oxidation of dissolved metals (Robbins. 1998).

The removal process might best be described as a biologically mediated process due to the possibility for multiple oxidation processes to occur within the microenvironment.

Manganese (II) oxidation can occur quicker at lower pH (6 to 9) with autocatalysis from Mn sorption onto Mn oxide precipitates (McBride, 1994), catalysis via microorganisms (Bender et al., 1994; Ghiorse, 1984), or sorption onto other solids (Davies \& Morgan. 1989).

The removal of manganese is primarily a biooxidative process. Rock drains are used to promote the biomediation of soluble manganese $\left(\mathrm{Mn}^{2+}\right)$ into manganese dioxide $\left(\mathrm{MnO}_{2}\right)$. The rocks within the drain simply provide attachment substrate for the active microbes and will develop a black slime from the formation of manganese dioxide (Pyrolusite). A variety of algae and bacteria are capable of facilitating the following reaction (Ehrlich, 1990; Robbins et al., 1999).

$$
\begin{equation*}
2 \mathrm{Mn}^{2+}+\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\text { micribe }} 2 \mathrm{MnO}_{2(\mathrm{~s})}+4 \mathrm{H}^{+} \tag{Equation25}
\end{equation*}
$$

Biooxidation of maganous $\mathbf{M n}$ to manganic $\mathbf{M n}$

Manganese removal has been associated with black microbial coatings (Brant \& Ziemkiewicz 1997; Gordon, 1989; Gordon \& Burr, 1988; Thornton. 1995) and green algae microbial mat consortium (Phillips et al., 1994). Biooxidation processes are likely promoted by photosynthetic algae through oxygen $\left(\mathrm{O}_{2}\right)$ release and carbon dioxide $\left(\mathrm{CO}_{2}\right)$ uptake which promote an aerobic alkaline microenvironment (Bender et al.. 1994). Numerous integrated strategies are used by the attached microbial (epilithic) community to oxidize Mn (Robbins et al., 1999). Many organisms such as bacteria. cyanobacteria. diatoms, green algae and fungi have been identified as participating in the biomediation of Mn (Robbins et al.. 1999).

The biooxidation of manganese is controlled by the sequential order of redox reactions presented in Table 4. Based on Table 4. microbes will prefer to oxidize ferrous
iron ( Fe (II)) over reduced manganese $\left(\mathrm{Mn}^{2+}\right.$ ) due to the higher energy yield obtained from the reduced iron. Therefore, all ferrous iron (Fe(II)) must be removed from the water to obtain optimal manganese ( $\mathrm{Mn}^{2+}$ ) removal (Burdige et al., 1992; Hedin et al.. 1994a; Sikora et al., 2000). Microbially induced iron oxidation does occur in wetlands; however, the contribution is relatively minor compared to the Fe precipitation processes.

The oxidation of manganese (Equation 26) does not follow the same rate law as Fe (II) oxidation (Equation 24). The rate of $\mathrm{Mn}(\mathrm{II})$ oxidation with $\mathrm{pH}>9$ was found to likely follow an autocatalytic model dependent on oxygen and pH (Stumm \& Morgan, 1981):

$$
\begin{equation*}
r_{\mathrm{Mn}(I I)}=k_{o}[M n(I I)]+k[M n(I I)]\left[\mathrm{MnO}_{2}\right] \tag{Equation26}
\end{equation*}
$$

Where:

$$
k=k_{H}\left[O_{2(a q)}\right]\left[H^{+}\right]^{-2}
$$

However. Equation 26 may not be appropriately applied when explaining manganese removal within a wetland when $\mathrm{pH}<9$. As previously discussed (Equation 25) the oxidation of Mn (II) in natural systems is primarily catalyzed through microbial processes and is dependent on the absence of Fe (II).

### 2.3.6 Kinetics for Removal Processes

Acid-base equilibrium equations provide insight when equilibrium conditions exist and may be useful during design when instantaneous equilibrium is assumed. Snoeyink and Jenkins(1980) state that acid-base calculations are fairly accurate and robust for various treatment systems. However. equilibrium calculations are often too simplistic to adequately describe the rates of natural redox and precipitation processes. Although equilibrium establishes the potential bounds for redox and precipitation reactions, the rate
often controls the extent of the reaction. Natural treatment processes often provide insufficient time to establish equilibrium. Other factors which reduce the accuracy of natural redox and precipitation equilibrium calculations include the following (Snoeyink \& Jenkins, 1980):

- Slow equilibrium establishment,
- Shifting solid phases,
- Changing degree of crystallinity or seeding.
- Supersaturation effects,
- Competing reactions,
- Inaccurate equilibrium constants,
- Competing effects microbes, and
- Alternate redox routes.

Due to these factors, the prediction of contaminant removal in constructed wetlands have typically relied on empirically developed mass removal estimates. Removal rates based on area or volume of specific wetland components will vary based on climate and contaminant loading patterns.

Although it is recognized that these processes effect the rate of contaminant removal. it is prudent to understand that the rate limiting removal processes for $\mathrm{Fe}^{2+}$ and $\mathrm{Mn}^{2+}$ oxidation, may act as limiting factors which control the effective size of the wetland.

### 2.3.7 Co-precipitation/Adsorption

The co-precipitation/adsorption of trace metals is a secondary treatment process. which can be associated with the precipitation of metals due to pH moderation. the
precipitation of metal sulfides, the precipitation of reduced iron through aeration, or the bio-oxidation of Mn .

Co-precipitation/adsorption is a process whereby dissolved metals may be incorporated (co-precipitated) as an impurity within the matrix of precipitates composed primarily of other substances (e.g., iron oxyhydroxide). The metal ion may be physically entrapped within the pore spaces, or may be absorbed on the precipitate surface. Iron coprecipitation/adsorption is a commonly used process for metal removal in conventional treatment systems (Banerjee, 2002). However, the relative contribution of the process for Fe removal in the RAPS-based system is unknown. Coprecipitation and absorption may occur as a result of either precipitation or biooxidation processes.

The pH and the initial metal-oxyhydroxide concentration are the most significant variables affecting the adsorption of various metal species (Banerjee. 2002: EPRI. 1990). Higher oxyhydroxide concentrations increase coprecipitation/absorption processes. Cation metal removal is favored by higher pH and oxyanions removal is favored by lower pH . The range of pH where the removals abruptly change is called the "absorption edge."

As previously stated, Fe and Al oxyhydroxides will form in the wetland water as the pH is increased above 3.5 and 4.5, respectively. Iron and aluminum oxyhydroxides have been shown to coprecipitate $\mathrm{Cd}, \mathrm{Cu}, \mathrm{Pb}$, and Zn (Crawford et al., 1993; Ford et al., 1997: Karthikeyan et al.. 1997; Kinniburgh et al., 1976; Martinez \& McBride. 1998; McBride. 1978: Spadini et al., 1994). Freshly formed amorphous iron oxides have a high binding capacity (Banerjee. 2002) and are capable of removing cations such as $\mathrm{Cu}, \mathrm{Pb}, \mathrm{Zn}$. and Cr (Appleton et al., 1988: Benjamin et al.. 1982: Davis \& Leckie. 1978: Graddle \& Laitenen.
1974). However, a number of complex interacting factors control the binding capacity for the metal ions, or inversely, the solubility of the metals. Among the factors which control the solubility of these metal ions are metal loading, chemical form (i.e., metal solid-phase speciation), pH , metal-solid reaction time (i.e., aging), and complexing agents (i.e., ligands) present in solution (Martinez \& McBride, 2001). The solubility of $\mathrm{Cd}, \mathrm{Cu}$. Pb , and Zn in laboratory solutions during and after simultaneous coprecipitation with Fe (hydr)oxide at pHs of 6 and 7 was investigated by Martinez and McBride (2001). The dissolved iron levels ( $277 \mathrm{mg} / \mathrm{L}$ ) that were precipitated during this study are likely higher than those typically found in acidic runoff. However, the solubility and availability (based on citrate extractions) of $\mathrm{Cd}, \mathrm{Cu}, \mathrm{Pb}$. and Zn was found to be affected by the type of metal, pH of the solution. and hysteresis (prior coprecipitation). Depending on the pH . the process is capable of removing oxyanions of metals such as arsenate, chromate, and selenite (Banerjee, 2002).

A review of the literature by Banerjee (2002) has found that concentrations of heavy metals can be consistently reduced to about $0.5 \mathrm{mg} / \mathrm{L}$ in conventional treatment systems by Fe-hydroxide precipitation process with proper pH control. clarification and filtration. The overall removal of minor ion due to iron copreciptation in constructed wetlands designed to treat acidic drainage has not been reported.

### 2.3.8 Major Ion Solubility

Within the ReRAPS wetland, major ions can be mobilized or immobilized via mineralization processes. Therefore, the upper limits for concentrations of major ions are controlled primarily by the solubility product of the respective mineralogy.

The concentration of dissolved salts or major ions that could exert osmotic stresses on freshwater aquatic organisms are affected by the solubility products of their respective solid phases and by any competing common ion effect (Langmuir, 1997). For example. Langmuir (1997) shows where the aqueous concentration of $\mathrm{Ca}^{2+}$. resulting from calcite (limestone) dissolution, will increase in the presence of a completing ligand. such as $\mathrm{SO}_{4}{ }^{2-}$ from gypsum ( $\mathrm{CaSO}_{4} \cdot{ }^{-7 \mathrm{H}_{2}} \mathbf{0}$ ). Therefore, precipitation processes may remove supersaturated ions. However, there are no treatment processes that are able to reduce the major ion content of the wetland water below the saturation concentration of the salt.

### 2.4 Passive Treatment of Acidic Runoff

Any acidic runoff treatment scenario must be predicated on the ultimate neutralization of acidity. The consumption of acidity moderates pH and creates an "environment of deposition" for the metals (AI. Fe , and Mn ) which predominate in acid runoff associated with coal mining and coal storage activities. Constructed wetlands have been developed to passively generate alkalinity through dissimilatory $\mathrm{SO}_{4}{ }^{2-}$ reduction, carbonate dissolution, or a combination of these processes.

### 2.4.1 Compost Wetlands

Compost wetlands generate alkalinity and form metal precipitates through $\mathrm{SO}_{4}{ }^{2-}$ reduction processes. Compost wetlands promote the development of microbe-catalyzed reducing conditions. The organic substrate serves as a carbon source and electron donor for microbes. Microbes that can use oxygen for aerobic respiration cause the oxidationreduction potential (ORP) to decrease. Still other microbes use other ions (e.g., Fe(III). $\mathrm{SO}_{4}{ }^{2-}$ ) as electron acceptors. Given sufficient contact time and organic material. reducing conditions can develop in the RAPS. However. the land area needed for bacterially
moderated $\mathrm{SO}_{4}{ }^{2-}$ reduction often exceeds the available land area. Therefore, the use of compost wetlands is limited (Watzlaf \& Hyman, 1995).

### 2.4.2 Anoxic Limestone Drains (ALDs)

ALDs are buried beds of limestone that intercept acidic water and add alkalinity through limestone or calcite dissolution (Turner \& McCoy, 1990). The ALD is limited to the treatment of acidic waters requiring less the $300 \mathrm{mg} / \mathrm{L}$ of net alkalinity and which have less than $1 \mathrm{mg} / \mathrm{L}$ of AI, ferric iron $\mathrm{Fe}(\mathrm{III}$ ), and dissolved oxygen (DO) (Hedin \& Nairn. 1992; Hedin \& Watzlaf, 1994; Watzlaf \& Hyman. 1995). The alkalinity generation limitation in an ALD is based on the solubility of calcite and the partial pressure of $\mathrm{CO}_{2}$ (Hedin \& Watzlaf. 1994). ALDs are tolerant of both Fe (II) and Mn (Watzlaf et al., 2000). However, Al and $\mathrm{Fe}(\mathrm{III})$ will often precipitate and plug the ALD (Hedin \& Watzlaf, 1994). Also the presence of Fe(II) and dissolved oxygen will cause Fe-armoring of the limestone and reduce limestone dissolution (Nairn et al., 1992).

### 2.4.3 Reducing and Alkalinity Producing Systems (RAPS)

The Reducing and Alkalinity Producing System (RAPS) component combines the treatment processes of the compost wetland and the ALD. Within the past 12 years. the RAPS has been successfully used to treat acid mine drainages (AMD) which are saturated with DO and contain greater than $1 \mathrm{mg} / \mathrm{L}$ of either Al or Fe (III) (Watzlaf et al.. 2000). This downflow component consists of three layers: standing water, compost. and limestone. Water is forced down through the compost and limestone. The reduced alkaline water is routed from the bottom of the limestone using a perforated pipe network. Combining both alkalinity generating processes ensures that limestone
dissolution will occur in a reduced environment and thus prevents armoring. Design considerations and construction techniques are provided by Skovron and Clouser (1998).

### 2.4.4 Rock Drains

The gravel bed or rock drain is another component that has been developed because Mn is a difficult metal to remove in surface water components due to the relatively slow kinetics associated with Mn(II) oxidation (Stumm \& Morgan, 1981). The removal rates for Mn (II) are 20 times lower than Fe (II) for settling basins with rates ranging from 0.5 to $1 \mathrm{~g} / \mathrm{m}^{2} / \mathrm{d}$ (Hedin \& Watzlaf, 1994).

Rock drains add surface area which promote biotic and abiotic catalytic processes to aid the removal of Mn (EPRI, 1998). Rock drains promote Mn removal through sorption onto Mn oxide precipitates (McBride, 1994), catalysis via microorganisms (Bender et al. 1994; Ghiorse, 1984), and sorption onto other solids (Davies \& Morgan. 1989). Several studies have shown that limestone is an effective and inexpensive substrate for passively removing Mn (Brant \& Ziemkiewicz. 1997; Sikora et al.. 1996; Sikora et al., 2000; Watzlaf, 1997).

Rock drains were evaluated by Sikora et al. (2000) using saturated flow-through mesocosms to determine the optimal engineering design criteria for Mn oxide precipitation. Their study, which used simulated AMD. determined that when compared to the other non-carbonate substrate, limestone favored Mn oxide precipitation due to greater pH . Temperature did not effect Mn removal. However. Fe(II) oxidation in the presence of dissolved oxygen (DO), high oxidation reduction potential (ORP), and high pH precluded $\mathrm{Mn}(\mathrm{II})$ removal. They found that the ideal pH and redox conditions for Mn removal were pHs from 6.8 to 7.2 and redox greater than 500 mV . With $3 \mathrm{mg} / \mathrm{L}$ organic
carbon, an influent DO of at least $0.35 \mathrm{mg} / \mathrm{L}$ is recommended for every $1 \mathrm{mg} / \mathrm{L} \mathrm{Mn}$ removed. The Mn (II) loading rates of 5 to $10 \mathrm{~g} / \mathrm{m}^{2} / \mathrm{d}$ are recommended for 2 cm diameter aggregate at the previously described optimal DO, pH , and redox levels. The size of the aggregate used can dramatically effect the required size of the rock drain because biofilm surface increases with decreasing aggregate size. Therefore, rock drains can potentially reduce the required treatment area by 10 fold when compared to the removal rates recommended for settling basins. Based on biofilm area calculations presented by Kadlec and Knight (1996), a porosity of $44 \%$ and a 2 cm diameter size, the recommended Mn (II) loading rate can be adjusted for biofilm area to 0.05 to $0.1 \mathrm{~g} / \mathrm{m}^{2} / \mathrm{d}$. The rate of manganese removal has been found to be strongly related to the initial concentration (Brant \& Ziemkiewicz, 1997; Sikora et al., 2000). This is expected, based on the theoretical discussion presented in Section 2.3.5 and Equation 26.

### 2.5 RAPS-Based Wetland Systems and Limitations

In practice, RAPSs. ALDs. settling ponds, aerobic wetlands. and rock drains are used as unit operations or components in an overall passive RAPS-based wetland treatment system. The traditional use of these components still present passive treatment limitations.

### 2.5.1 Delayed Mn Removal

A passive wetland system which relies on a successive series of RAPS. followed by a setting basin or other type of surface flow component, is described as a Successive Alkalinity Producing System (SAPS). This type of wetland system was first developed by Kepler and McCleary (1994). As previously described, the presence of Fe (II) precluded the removal of Mn . The amount of $\mathrm{Fe}(\mathrm{II})$ which can be oxidized and removed
is primarily limited by the dissolved oxygen (DO) content and the pH (Watzlaf et al.. 2001). The oxidation of reduced metals and precipitation of metal hydroxides within the settling basin and rock drain will consume hydroxide and depress pH . Therefore, the oxidation of Fe (II) is a self-limiting process if Fe (II) concentrations are high enough. As an example, approximately $2.8 \mathrm{mg} / \mathrm{L}$ of Fe (II) will reduce pH levels in unbuffered water to a point where the kinetics for autooxidation ( pH 4 ) are very slow. The passing of Fe(II) from the RAPS to the settling basin delays the removal of Mn until the Fe (II) is oxidized. If excessive concentrations of Fe (II) still exist in the settling basin. additional RAPS/settling basin systems are used to generate more alkalinity (Kepler \& McCleary, 1994: Skovran \& Clouser, 1998; Watzlaf \& Hyman, 1995). In this environment, the removal of $\mathrm{Mn}(\mathrm{II})$ is again delayed.

### 2.5.2 RAPS Plugging

RAPS plugging has been reported to be a concern (Skousen et al.. 1998). Metal oxides, metal sulfides, and other suspended solids can potentially plug the RAPS substrate. A surface flow wetland or settling basin preceding the RAPS is used to prevent the potential plugging due to existing suspended solids such as metal oxides, silts, clays, and coal fines. Field studies have shown that Mn entering the RAPS will behave conservatively: however, there is evidence that RAPS are retaining Fe and Al (Watzlaf et al., 2000).

Fe is likely retained in the upper portion of the compost where the microbial reduction is minimal and the pH is approaching neutrality (due to the presence of alkaline material within the compost). However, the reducing environment within RAPS may fluctuate as microbial activity also fluctuates with the seasonal water temperature
changes. Fluctuations in the reducing conditions may promote a retention and release cycle for Fe in the RAPS. Researchers have yet to perform long term mass balances in full-scale systems to determine if Fe retention is seasonal or continual.

In a passive RAPS-based wetland, the environment of deposition for dissolved Al is limited to the voids within the RAPS substrate. When the RAPS was first proposed. it was believed that the pooling of water over a large surface area perpendicular to the downward flow pattern would theoretically reduce the risk of plugging (Kepler \& McCleary, 1994; Watzlaf \& Hyman, 1995). Periodic high-flow flushings are being performed manually as preventative maintenance on the RAPS (Kepler \& McCleary, 1997; Watzlaf et al., 2000). This maintenance is accomplished by opening a control valve on the underdrain piping of the RAPS and allowing for a relatively rapid drop of the pooled RAPS water. Greater than $\mathbf{8 0 \%}$ recovery of AI has been achieved during a single flush (Kepler \& McCleary, 1997). A passive flushing system has been developed to automatically perform the same process on a routine basis using a dosing siphon (Vinci \& Schmidt, 2001). The long-term benefits of flushing systems will require more operating time to be fairly evaluated. Other than the consumption of limestone, the longterm performance of the RAPS-based wetland may therefore be limited by Al plugging.

### 2.5.3 Bacterially-Derived Alkalinity Production Limitations

Although the amount of alkalinity generated from a RAPS is theoretically nonlimiting due to the unlimited potential contribution of $\mathrm{SO}_{4}{ }^{2-}$ reduction. field results have shown that bacterially-derived alkalinity production is seasonally variable and that alkalinity generation is still primarily dependent on limestone dissolution (Watzlaf et al.. 2000). The high alkalinity generation values that have been reported are associated with
systems that are less than three years old. These systems will likely experience reductions in bacterially-derived alkalinity production over time because of the loss of readily decomposable organics (Watzlaf et al., 2000). A wetland preceding the RAPS may be useful for contributing suspended organic matter to the RAPS. However, extremely low pH water may not support the production of wetland flora capable of generating a sustaining supply of suspended organic matter.

### 2.5.4 Site Constraint Limitations

Site constraints and highly variable flows can limit the applicability of passive systems. For example, when there are site constraints such as topographic limitations. acidic runoff may require detention and pumping so that treatment can be achieved. The peak flows associated with acidic stormwater may dictate unacceptably large RAPS land area. A detention pond preceding the RAPS would typically be used for moderating and retaining the maximum probable runoff event. A detention pond outlet structure can be sized so that a fifteen-hour retention criterion is maintained in the RAPS limestone. This fifteen hour limestone retention criteria used by Kepler and McCleary (1994) for sizing the RAPS component within their SAPS is the same recommendation for ALDs (Hedin \& Nairn. 1992; Hedin \& Watzlaf, 1994). Again, a pump may be used to moderate flows to the wetland and could minimize the required treatment area.

### 2.6 Benefits of Pumping and Recirculation

The use of a pump to move water through the wetland may overcome many of the previously described limitations associated with the passive RAPS-based wetland. The use of a pump could recirculate treated water and reuse alkalinity generated within the
wetland. The reuse of alkalinity may also promote a metal removal process that has not been possible when passively treating highly acidic runoff.

The recirculation of alkalinity back to a detention pond presents the opportunity to add alkalinity and suspended organic matter to the runoff prior to the RAPS. Acidity removing reactions in the detention pond will then occur in a predictable order that is consistent with the solubility products of the solids. The first reaction to occur is the neutralization of proton acidity. This reaction will raise the pH , which will decrease the solubility of the metal hydroxides (Hedin \& Watzlaf, 1994). As the pH is raised, Fe precipitates as ferric hydroxide between pH 3 and 4. Between pH of 4 and 5 , Al precipitates as Al-hydroxide. The precipitation of Fe and Al may promote the process of coprecipitation and absorption of metals prior to the RAPS. This may be especially beneficial for the pretreatment of Mn which is difficult to oxidize in the presence of Fe(II) (Sikora et al., 2000). The coprecipitation/absorption of other trace metals may also be possible (SenGupta. 2002).

In this semi-passive system, the environment of deposition for both Al and Fe could precede the RAPS, therefore minimizing the potential for RAPS plugging due to metal precipitates. The recirculation of alkalinity and organic matter would reduce limestone consumption and increase the long term production of bacterially-derived alkalinity for severely acidic runoff. It is a logical progression to investigate the potential development of contaminant removal and alkalinity generating processes within a recirculating wetland. These potential benefits of recirculation are the main aspects of the research conducted during the present study.

A potential problem associated with the ReRAPS option is that the recirculation of treated water in the wetland system will concentrate the dissolved solids in the water. Gypsum or hydrated calcium sulfate $\left(\mathrm{CaSO}_{4} \bullet \mathrm{nH}_{2} \mathrm{O}\right)$ will be the predominant mineral to form. The long-term implications of the formation of minerals in the system. especially in the RAPS substrate are unknown. Studies performed by George Watzlaf (personal communications) have found no evidence of gypsum precipitate formation in RAPSs.

### 2.7 Summary of Literature Review

The purpose of this chapter was to summarize the physical, biological, and chemical processes associated with the treatment of acidic waters using constructed wetlands. How this research contributes and adds to the understanding and improvement of these wetland treatment processes was also given.

Pyritic oxidation processes responsible for the production of acidic coal pile runoff (CPR) are presented. The agents of toxicity associated with CPR and a brief review of the factors that affect the aquatic toxicity of these agents are also discussed. Various methods for assessing the removal of toxic agents from the wetland water are presented. Brief reviews of the chemical processes that are involved in the removal of these toxic agents along with the various wetland components that have been used to promote these processes, are also presented.

CPR is similar to acid mine drainage (AMD) where the predominant dissolved metals are Fe. AI. and Mn. The hydrolysis of these metals contributes to the acidity of the runoff. The amount of acidity associated with each of the metals can be determined using the stoichiometric relationship recommended by Rose and Cravotta (1998).

Acidic CPR produces a mixture of agents which are toxic to aquatic life. Trace metals (minor ions) are the probable agents of toxicity in the CPR. The recirculation of treated water in the wetland could increase the salinity of the wetland water and create major ion toxicity. Factors which influence trace metal toxicity to aquatic life are best explained using the Biotic Ligand Model (BLM) (Di Toro et al., 2001; Santore et al., 2001). The Gas Research Institute (GRI) model has been developed to predict the toxic effects of major ions on aquatic test species (Gas Research Institute, 1992; Mount et al., 1997). Models have not been developed to explain the toxic effects of mixtures of trace metals and major ions on aquatic test species. There have been no studies that have evaluated the removal of toxicity in RAPS-based wetlands. The use of manganese ( $\mathbf{M n}$ ) as a regulatory trace metal surrogate has been questioned and affects the design of treatment wetlands. Therefore, the removal of toxicity in the CPR by the wetland was evaluated using a "weight-of-evidence" approach which includes the following:

- The cumulative toxicity (Toxicity Unit. TU) of the water was semi-qualitatively evaluated by normalizing the trace metal concentrations to the EPA Criterion Continuous Concentration (CCC) (EPA. 1999).
- Direct toxicity testing of the CPR and wetland water evaluated species sensitivity. and associations between toxicity and wetland chemistry, including $\mathbf{M n}$.
- The GRI model was used to evaluate the potential of major ion toxicity (Mount et al.. 1997).

The trace metals along with Fe . Al. and Mn are removed in RAPS-based wetlands primarily using precipitation and bio-oxidation processes. Both processes are optimized at higher pH . Therefore, the initial treatment goal of wetlands is to consume acidity
which increases pH . As the pH increases, Fe will form precipitate above pH 3.5 and Al will form precipitate above 4.5. Manganese is more difficult to remove because precipitates do not readily form until $\mathbf{p H}>8.5$. Therefore, $\mathbf{M n}$ removal processes in RAPS-based systems rely primarily on microbially mediated oxidation processes which are promoted using rock drains.

Alkalinity is generated in the wetland via bio-reduction processes and limestone dissolution in the RAPS component. RAPS plugging due to metal precipitates can reduce the operational life of the wetland. All RAPS-based wetlands are operated passively without the benefits of pumping. The use of a pump and an alternative RAPS-based wetland design option, which recirculates treated alkaline water to a detention pond. can improve wetland performance. One aspect of this research was to design and construct a Recirculating RAPS-based (ReRAPS) wetland. The main aspect of this research was to investigate the removal of contaminants and alkalinity-generating processes in the ReRAPS wetland.

## CHAPTER 3 METHODS

Testing of the ReRAPS design, which included an evaluation of metal removal prior to the RAPS component and the removal of toxicity, required the design. construction, and operation of the full-scale alternative wetland. The following is an overview of the methodology used to evaluate the ReRAPS wetland.

The conceptual wetland design and bench scale testing of potential substrate for the RAPS component was followed by an extensive construction effort (Sections 3.1-3.7). The water quality monitoring of the ReRAPS began immediately after the system was constructed and started operation (Sections 3.8). Long-term water quality monitoring was performed to identify an operational time period during which alkalinity production would be relatively stable. Identifying a stable alkalinity production period was important because the performance of the detention pond is directly dependent on the amount of alkalinity produced at the outlet of the RAPS component. Intensive water quality monitoring was performed during this stable operational period with enough frequency that statistically significant removal of key contaminants could be identified within most of the major wetland components. The intensive monitoring was performed during a winter and early spring time period when four measurable CPR events caused acidic contaminant loading to the ReRAPS detention pond.

Many different water quality (Section 3.9). morphologic (Section 3.10), and hydrologic (Section 3.11) parameters were measured and statistically (Section 3.12) analyzed during the monitoring period. Significant statistical decreases in the
concentrations of contaminants and increases in alkalinity allowed for the calculation of contaminant removal and alkalinity generation rates.

The intensive monitoring effort was followed by a series of direct toxicity testing of the CPR and ReRAPS waters to confirm the removal of contaminants and to identify the agents of toxicity (Sections 3.13). Data from both the intensive monitoring and toxicity testing were used to develop a weight-of-evidence approach for identifying the primary agents of toxicity in the treatment system.

### 3.1 The Plant Gorgas ReRAPS (Recirculating RAPS) Wetland

A schematic of the Plant Gorgas ReRAPS wetland is depicted in Figure 5. In this wetland, water is routed through thirteen nodes (N1-N13). Contaminated coal pile runoff passes through Nl into the detention pond during each runoff event. A portion of the alkaline water produced by the system is recirculated back to the detention pond via NI2. which is located immediately upstream from the RAPS component (N2-N5). As with all RAPS-based wetlands, a settling basin (N5-N7) follows the RAPS component. A series of vegetative wetlands and rock drains (N7-N10) are used to further encourage the complete removal of Mn and other trace metals downstream from the settling basin. Treated water is retained in the wetland storage basin (N10-N12/13). Excess water that is not recirculated through N12 is discharged to a large receiving stream through N13. The inlets for both N12 and N13 are in close proximity and therefore contain similar water chemistries.

The pumps that route water from the detention pond to the RAPS were activated at preset stage elevations. The pumps operated at 75 gpm at higher stage elevations. but were normally operated at the 45 gpm rate between the upper and lower stage settings.

Below the lower setting, the pumps were off. Water was maintained in the detention pond to help moderate the pH immediately after each runoff event.


Figure 5. A schematic of the Plant Gorgas Wetland configuration.

### 3.2 Regulatory Treatment Requirements

The Plant Gorgas wetland treatment system is considered a stormwater treatment process and has been actively treating acidic runoff since January 1998. The system was designed to meet the average monthly regulatory discharge limits of less than 3 and $2 \mathrm{mg} / \mathrm{L}$ for Fe and Mr , respectively. The average monthly total suspended solids (TSS) was not to exceed $35 \mathrm{mg} / \mathrm{L}$ and the pH was to be maintained between 6 and 9 at the discharge. For four years the ReRAPS has consistently met the discharge limitations. Recently, a new NPDES permit has been assigned to the ReRAPS. The new permit now requires "best management practices" and does not require further water quality monitoring at the discharge.

### 3.3 Wetland Design and Construction

The coal pile runoff (CPR) chemistry and the area available for construction of the treatment system dictated the conceptual design of the wetland. A characterization of the runoff chemistry that was performed during 1996 is presented in Table 5. These values clearly indicate that the water was extremely acidic and contains very high levels of soluble metals. Also, it should be noted that the level of contaminants presented in Table 5 influenced the conceptual design of the treatment wetland and that it was later discovered that these high concentrations would not be representative of the CPR after the system became operational. The high concentrations were due to the long-term accumulation of sulfate salts within an inadvertently created evaporative pool at the base of the coal pile. These salts were resolubilized and treated within the wetland soon after operation began.

Table 5
Chemical Characterization of the Plant Gorgas Coal Pile Runoff
Performed during 1996

| Chemical Parameter | Minimum | Maximum |
| :--- | :--- | :--- |
| pH (SU) | 3.0 | 3.4 |
| Acidity (mg/L as $\left.\mathrm{CaCO}_{3}\right)$ | 250 | 750 |
| Total Iron (mg/L) | 480 | 660 |
| Total Manganese (mg/L) | 22 | 32 |
| Total Aluminum (mg/L) | 140 | 185 |

The basic approach for the design of the wetland followed the schematic presented in Figure 6 which includes the recirculation concept and was modified from Davis (1995) and Kepler and McCleary (1994). Surface waters requiring treatment are classified as either net alkaline (alkalinity > acidity) or net acidic (acidity > alkalinity). Net alkaline water requires only oxygenation and retention. Net acidic water containing low DO and low Al , initially require alkalinity generation. An anoxic limestone drain (ALD) followed by a settling basin are the components typically used to treat this type of water. The Plant Gorgas CPR is net acidic, saturated with DO, and contains high levels of dissolved Al (Table 5). The treatment options for the CPR are restricted to an organic substrate wetland or a RAPS-based system (Figure 6). A RAPS-based system was chosen during the conceptual design of the treatment system due to the limited amount of available area.


Figure 6. A constructed wetland design decision tree for the treatment of mine drainage or coal pile runoff which has been modified from Kepler and McCleary (1994) and Davis (1995). In the diagram the RAPS component replaces SAPS.

A RAPS-based system that incorporates the recirculation of treated water back to an equalization basin or detention pond was conceptualized so that the pH of water entering the RAPS might be moderated along with the mass loading of contaminants entering the component (Figure 6). It was believed that the moderation of pH prior to the RAPS would remove metals in the detention pond and encourage optimal microbial activity (e.g., sulfate reducing and other bacteria) in the RAPS substrate. It was also believed that with sufficient retention time. that discharge water would meet the NPDES regulatory limits of 9 SUs $>\mathrm{pH}>6$ SUs. total iron $<3 \mathrm{mg} / \mathrm{L}$, total manganese $<2 \mathrm{mg} / \mathrm{L}$ and total suspended solids $\mathbf{~} 50 \mathrm{gm} / \mathrm{L}$.

Due to topographic limitations, pumping was required to route water from the detention pond to the RAPS component. However, it was believed that pumping would further moderate the shock loading effects of contaminants on the wetland system by controlling flow. More importantly, it was hypothesized that given enough retention time that pH moderation in the detention pond would remove metals ( Fe and Al ) upstream from the RAPS component. This would minimize the potential for Al hydroxide plugging in the RAPS substrate. A significant removal of metals prior to the RAPS would eliminate the need for another series of RAPS/settling basin components or SAPS (Kepler \& McCleary, 1994).

Approximately $21 / 2$ acres adjacent to the coal pile were available for the construction of the wetland. The actual design and construction of the recirculation-based wetland was accomplished in two phases. The Phase 1 wetland was designed to produce compliance grade water. The regulatory guidelines for the United States electric utility industry and for the United States mining industry are presented in Table 6. The
regulatory limits permitted by the Alabama Department of Environmental Management (ADEM) for the wetland discharge are also presented in Table 6. The inability to meet the pH and total iron limits after the Phase 1 wetland became operational would have required additional RAPS components to be constructed during Phase 2. However. the Phase 1 system did meet the total iron, total $\mathbf{M n}$, and pH regulatory requirements. The Phase 2 system was therefore constructed to further reduce T-Mn using a series of shallow cells with aquatic vegetation and limestone aggregate drains as recommended by Sikora et al. (1996). It was further hypothesized that the entire ReRAPS wetland would remove enough contaminants from the CPR so that whole water effluent would be nontoxic to aquatic life.

Design factors such as mean flow rates, space limitations, and topography, dictated the size and type of routing within the components. Approximately $21 / 2$ acres were available for the wetland after a portion of the existing 11 -acre coal pile was removed. One-half of the wetland area was positioned at the base of the coal pile and required that a portion of the runoff which flowed into the detention pond would occasionally be backed-up into the base of the coal pile. The detention pond was sized to retain a 6 -inch rain in an 11-acre catch basin. Pumping of the water from the detention pond was required so that the remaining area could be completely allocated to the remaining wetland components.

The construction of the ReRAPS used many of the recommendations published by Skovran and Clouser (1998) for portions of the wetland. Earth embankments were properly sized and incorporated proper fill material. cutoff trenches. freeboard. anti-seep collars. grout. and emergency spillways to ensure stable and impervious structures. The
resulting component materials, area, and volume were based on availability. The detention pond, RAPS, oxidation/precipitation basin, cattail filter, and alga storage basin were constructed during Phase 1. The algae storage basin area was further developed during Phase 2 to construct the aggregate limestone rock drains and other cells where aquatic vegetation was encouraged to proliferate. Photographs of the Plant Gorgas ReRAPS wetland are presented in Figures 7 and 8.

Table 6
The EPA electric utility and mining industry guidelines for coal related discharges

| Effluent Characteristic | Minimum | Maximum | Monthly Average |
| ---: | :---: | :---: | :---: |
| Steam Electric Guidelines |  |  |  |
| pH (SU) | 6.0 | 8.5 | NA |
| Total Susp. Solids (mg/L) | NA | 50 | NA |
| Total Iron (mg/L) | NA | NA | NA |
| Total Manganese (mg/L) | NA | NA | NA |
|  | Mining Guidelines |  |  |
| pH (SU) | 6.0 |  |  |
| Total Susp. Solids (mg/L) | NA | 9.0 | NA |
| Total Iron (mg/L) | NA | 70 | 35 |
| Total Manganese (mg/L) | NA | 6.0 | 3.0 |
|  | ADEM, Limitations |  | 2.0 |
| pH (SU) | 6.0 | 9.0 | NA |
| Total Susp. Solids (mg/L) | NA | 50 | NA |
| Total Iron (mg/L) | NA | 6.0 | NA |
| Total Manganese (mg/L) | NA | 4.0 | NA |

Note. The discharge limitations that are permitted by the Alabama Department of Environmental Management (ADEM) are also presented.


Figure 7. Photograph overlooking the Plant Gorgas ReRAPS wetland adjacent to the Warrior River in Walker County, Alabama. The surface water of the RAPS component is lower right.


Figure 8. Photograph overlooking the Plant Gorgas ReRAPS wetland adjacent to the Warrior River (on far right) in Walker County, Alabama. The detention pond is located at the base of the coal pile. Note that the pump house is located in the detention pond.

### 3.4 Detention Pond Design and Construction

The detention pond was designed to contain a 10 -year, 24 -hour rain event (Birmingham, AL, 6 inch). Approximately 0.3 acres of the available wetland area was down gradient from the base elevation of the coal pile. This area was used as the equalization or detention basin designed to contain the majority of a 6 -inch rain event. The 6 -inch rain event required a 1.35 million-gallon ( $4.1 \mathrm{ac}-\mathrm{ft}$ ) basin to retain the runoff from the combined coal pile and wetland areas (11 ac). However, rains approaching 6 inches were expected to back up into the adjacent wetland storage area and into the base of the coal pile. This storage requirement (6-inch rain) assumed a $25 \%$ infiltration loss, no storage in the coal voids and an instantaneous time of concentration.

Due to site topography, the RAPS component was placed at higher elevations than the detention basin. Therefore, pumps were required to route the water from the detention pond to the RAPS. A two week withdraw of the 6 inch event would require a 60 gpm pump rate. Low and high volume events were routed out of the detention pond into the RAPS using a one ( 30 gpm ) or two-pump ( 30 gpm and 45 gpm ) combination.

Due to the topographic limitations. the 11 -acre coal pile required containment so that the runoff could be routed to the detention pond via French drains and culverts. A concrete pad was constructed so that coal, which washed toward the culvert leading to the detention pond, could be maintained using small bulldozer equipment.

### 3.5 RAPS Design-Supporting Column Studies

Column studies were performed to select the types of organic and alkalinityproducing substrates used in the RAPS component. Figure 9 presents a photograph of the bench scale testing systems that were used.


Figure 9. Column study apparatus for determining appropriate substrate for the RAPS component.

RAPS, traditionally, are constructed using spent mushroom compost as an organic substrate. However, only those organic materials readily available in Alabama were considered as viable substitutes for the Plant Gorgas ReRAPS. These materials were evaluated based on their potential to produce favorable microenvironments for sulfate reducing bacteria (SRB) while maintaining good porosity. Four types of organic substrates were tested: aged pine shavings (soil conditioner), fresh chicken litter, composted (>6 months) horse manure, and a mixture of the three previous types. The mixture was comprised of a 7:6:2:1 ratio (air dry volume) of horse manure, chicken manure, pine shavings, and limestone sand, respectively. Approximately $6 \%$ of the dry volume of the organic mixture was limestone sand. X-ray diffraction determined that the limestone sand was comprised of $90 \% \mathrm{CaCO}_{3}$. The other 3 treatments were also augmented with 6\% limestone sand (air-dry volume)

The organic substrates were evaluated using glass down-flow columns ( 2 -inch diameter). Peristaltic metering pumps were used to continuously feed acidic CPR to the top of each down flow column for three months. Three inches of water was pooled on top of the organic layer and the system was operated at approximately 12 hours of retention within the organic material ( $75 \%$ pore volume, measured). The pore volume is the volume of water required to completely saturate the organic mixture. The flow rate for the bench scale systems was set for $0.64 \mathrm{ml} / \mathrm{min}$. Every week period, approximately 10.5 exchanges were achieved. Water samples were collected from a plastic column. which received the effluent from the down flow glass column. The plastic column was used as an up-flow collection reservoir for effluent sampling. The up-flow reservoirs were used to minimize reaeration and provide sufficient sample volume of chemically reduced column effluent. Approximately 350 mls were collected every week for analysis. The pH and ORP from the influent and effluent were measured at least weekly. The log numbers of SRBs collected from the surface of glass beads, which were continuously exposed to the effluent in the up-flow collection reservoir. and the log number of SRBs in the water, were determined using serial dilution test kits specific for SRBs (Scott \& Davies, 1992). The relative hydraulic conductivity of the various organic substrates were evaluated by monitoring the level of CPR water in the columns. An increase in the water level indicated low porosity. Excess effluent collected in a receiving flask was used to replace the sample volume removed from the collection reservoir, thereby minimizing any disturbance to the microbial consortium or retention changes in the organic columns.

Results from three months of continuous flow through testing using highly acidic CPR (acidity $>400 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ ), clearly indicated that material mixed with chicken litter produced an effluent that was highly reduced (chemically) with oxidation reduction potential (ORP) values of less than $\mathbf{- 3 0 0} \mathbf{m v}$. Results from the log dilution counts of SRBs in bulk water and on glass beads also clearly indicated that the microbes thrived in material associated with chicken litter. Effluent from the pure chicken litter and mixed material, which included chicken litter, was black due to the production of black ferrous sulfide. Effluent from the horse manure was red indicating that the iron was in the ferrous state.

Results from the down flow glass columns also indicated that substrate which included partially composted chicken manure produced an effluent that was most reduced chemically and promoted significantly higher SRB numbers. However, the use of pure chicken manure (i.e., compost) was unacceptable due to the low porosity of the material. which ultimately caused the plugging of the column. Therefore, a mixture of horse and chicken manure along with pine shavings and limestone sand was used to construct the RAPS component.

Carbonate fluorapatite (phosphate rock. $\mathrm{Ca}_{10}\left(\mathrm{PO}_{4}, \mathrm{CO}_{3}\right)_{6} \mathrm{~F}_{2-3}$ ) from Florida was evaluated as a potential limestone substitute due to the reported ability to generate alkalinity in acidic water containing high levels of Fe and Al without armoring or plugging (Choi. 1996). The treatment effectiveness of the two types of alkalinity producing rocks were tested using a series of large 4 -inch diameter PVC columns (Figure 9). The bench scale column systems were set to treat the runoff water using a 24-hour retention rate within the substrate ( $50 \%$ void or pore volume estimated). Each
column contained 6 inches of the mixed organic material chosen for the RAPS, layered on top of 3 feet of alkaline rock ( 1 -inch diameter). CPR was continuously metered into the top of the substrate column, which maintained 6 inches of water above the organic layer. The water then continued to flow down through 3 feet of alkalinity producing rock. The discharge from the substrate column was routed to an up-flow-collecting vessel with a surface discharge. Regular measurements of total metals, pH. total alkalinity, and ORP were performed on a weekly basis. The alkaline rock columns were evaluated for over 6 months.

The monitoring results found that both systems produced similar amounts of alkalinity and pH . Mn was not retained in any of the systems and there was some retention of $\mathrm{Fe}(<20 \%)$ in the limestone rock. However, most of the $\mathrm{Al}(>80 \%)$ was retained in both columns. The effect of continual aluminum build-up within the substrate was a concern due to the reports of Al plugging in anoxic limestone drains (ALDs). This concern supported the development of the recirculating design for the full-scale ReRAPS wetland. Due to minor performance differences between the columns, high-grade limestone $\left(>90 \%, \mathrm{CaCO}_{3}\right)$ from Calera. Alabama, was used in the constructed RAPS due to the lower material costs.

### 3.6 RAPS Component Design and Construction

Optimal retention within the limestone portion of the RAPS has been reported to be 12 to 24 hours (Kepler \& McCleary, 1994). The retention in the limestone portion of the RAPS was designed to not be less than 12 hours if $50 \%$ dissolution of the limestone had been consumed (assuming $50 \%$ void and 75 gpm flow). Therefore, the amount of 3-5 inch limestone used in the RAPS was a bulk volume that would retain the water for 24
hours at the maximum flow rate of $\mathbf{7 5} \mathrm{gpm}$. Water was pooled on top of the organic layer to a depth of approximately 3 feet. Approximately 6 to 12 inches of the mixed organic material, which was augmented with $15 \%$ limestone sand, was layered directly on top of 4 feet of limestone.

### 3.7 Design and Construction for Other ReRAPS Components

Two perforated 4 inch PVC pipes at the base of the limestone are used to route the discharge to the two standpipes inside of the oxidation/precipitation basin. The invert of the standpipes are used to control the water elevation in the RAPS cell. A shallow concrete splash pad is used to enhance aeration of the anoxic water discharging from the standpipes. A series of horizontal pipes were connected to the perforated drainage pipes at the base of the limestone and extended through an adjacent embankment to allow for the flushing of solids that may have accumulated in the RAPS.

The oxidation/precipitation basin was shaped like an elongated cell. The available area and volume limited this basin to a nominal retention of 3 days at the maximum flow rate. The Electric Power Research Institute (EPRI. 1998) recommends a 24 hour detention time to settle the amorphous limonite (iron oxyhydroxide sludge). Although the elongated design minimizes short-circuiting (Kadlec \& Knight. 1996). 5 concrete baffles with alternating drain opening levels were installed to ensure a plug flow treatment condition.

According to Brodie et al. (1993), a single oxidation precipitation basin can only remove $50 \mathrm{mg} / \mathrm{L}$ of iron due to the production of acidity. Acidity is reintroduced as the ferrous iron (FeII) is oxidized back to the ferrous state (FelII). Multiple series of RAPS with oxidation/precipitation basins would have been required if the levels of Fe (II) were
found to exceed $50 \mathrm{mg} / \mathrm{L}$ at the outlet of the RAPS after construction of the Phase 1 wetland.

The vegetative cell was filled with mud and cattail roots from an old coal slurry pond. Hand planting of cattails was performed to ensure the establishment of a dense stand of cattails. The water depth within the vegetative cells was approximately $1-3$ inches.

Monitoring during the first season of operation (winter 1998) confirmed that the initial components of the wetland (detention pond receiving recirculated treated water. RAPS, and settling basin) were capable of treating the runoff to levels meeting the NPDES limitations. Therefore, small basins and rock drains were constructed to promote Mn-biooxidation down gradient from the vegetative cell during the summer of 1998. Algae are allowed to proliferate in this final storage basin. Surface flow from this basin was then routed through drains that contain six inches of aggregate limestone. The treated water was collected in a final wetland storage basin where a portion of the water was recirculated back to the detention pond or discharged directly to the Warrior River. PVC standpipes and valves were designed and constructed so that the flows of the treated water at these two points could be adjusted.

### 3.8 Wetland Performance Monitoring

The Plant Gorgas ReRAPS wetland is a stormwater treatment system. Therefore. monitoring of the system was performed during the wet season in the southeastern United States (January-May). Normally, the fall season is the driest precipitation period in Alabama. However, the production of runoff from the coal pile will not occur until after late December. Typically, water was sampled at the primary nodes N1, N2. N4. N5. N7. N10. and N12/13. These nodes represent the inlets and outlets of the major wetland
components (Figure 5). Throughout the four-year monitoring period, a portion of the treated water was recirculated to the detention pond through node N12. Excess water was discharged to the river through node N13.

Two types of CPR treatment monitoring were performed. Long term and less frequent monitoring was performed during the first four years of operation and intensive monitoring was performed for 41 days during the fourth year of operation after the system reached a "treatment equilibrium." The longer term monitoring was intended to provide an evaluation of the wetland's performance on a "macro-scale" and the intensive monitoring was intended to evaluate the performance of the wetland on a "micro-scale."

Measurements performed in the field and in the laboratory during the long term monitoring included a complete range of water quality analyses (Section 3.8.1). Chemical analyses performed during the 41-day treatment period in 2001 was limited to total cations, total $\mathrm{SO}_{4}{ }^{2-}$, hot peroxide acidity, and alkalinity (Section 3.8.2). Detailed descriptions of the parameters measured during both of the monitoring programs are described in Section 3.8.3.

### 3.8.1 Long Term Monitoring

Long term water quality monitoring was performed from January 1998 through April 2001. This general monitoring was performed to determine if the wetland was able to meet the discharge requirements and determine the effects of the operational age of the system on concentrations of various water quality parameters. Changes in the CPR contaminant concentrations were also evaluated using this type of monitoring. During the long term monitoring (1998-2001), grab samples were collected at all of the wetland
nodes (N1 through N12/13) from 1 to 4 times per month while CPR was actively being treated.

### 3.8.2 Intensive 41-day 2001 Monitoring

During 2001, 41 consecutive days of monitoring was performed from January 29 through March 11 to evaluate the treatment of coal pile runoff resulting from four runoff producing rain events. Hydrologic and water quality monitoring was performed only at the primary nodes during the intensive monitoring period. This intensive monitoring was performed to develop data with sufficient sampling frequency to quantify contaminant removal and alkalinity production in the ReRAPS. A statistical analyses of the factors which influence the performance of the wetland was also performed using this data.

Bubble flow/level meters with microprocessors were used to continuously record water levels. Detention pond levels were continuously monitored just prior to the rain events and throughout each of the treatment periods. Typically, a $1.4 \mathrm{~cm}(0.6 \mathrm{in})$ rain or greater was required to produce CPR at N1. Figure 10 presents the daily average CPR flow. detention pond storage and rain depths and for the 41-day treatment period. Four rain events resulting in an average daily runoff of greater than $25 \mathrm{~m}^{3} / \mathrm{h}$ occurred within the 41 -day monitoring period. The pump operation timing cycle was measured by using a continuously recording conductivity monitor at N 2 . An 8 -inch pipe weir was continuously monitored at N12 to determine the recycle flow. The detention pond pump flow rates and recycle flow rates are presented in Figure 11. Manually measured flows were also performed at each of the primary nodes throughout the treatment period and were used as data control for the continuous flow monitoring equipment when applicable.


Figure 10. Calculated daily average coal pile runoff ( $\mathrm{N} 1, \mathrm{~m}^{3} / \mathrm{hr}$ ), measured detention pond storage ( $\mathrm{m}^{3}$ ), and measured cumulative rain depths times $10(\mathrm{~cm})$ during the 2001 41-day ReRAPS treatment of CPR.


Figure I/. Measured pump (N2) and recycle (N12) flows (m ${ }^{3} / \mathrm{hr}$ ) during the 200141 -day ReRAPS treatment of CPR.

Throughout the 41-day monitoring period, treated water was preferentially recirculated through N12. Excess treated water was routed through N13 to the river discharge. During a portion of the second storm event, N12 was temporarily shut off due to unrelated operational requirements for draining water away from the coal pile (Figure 11). Nevertheless, CPR treatment in the detention pond benefited from the presence of previously recirculated treated water in the detention pond during this time period.

Automatic water samplers were used to collect samples for total metal and anion analyses every three hours at N1, N2, N4 and N5 to improve loading estimates throughout the 41 -day monitoring period. The quality of the water passing through nodes N12 and N13 was similar. Field measurements for flow, pH, ORP, conductivity, and ferrous iron were performed 1 to 2 times per day throughout the 41-day CPR treatment at each of the primary nodes. Grab water samples for total alkalinity and acidity measurements were also collected during these site visits.

### 3.9 Sample Analyses

All sample collection, storage, chemical analyses, and field measurements were performed according to EPA (EPA. 1983, 1994a) methods, or Standard Methods (American Public Health Association (APHA), 1989). The chemical parameters that were measured during this study are presented in Table 7. Skovran and Clouser (1998) recommend that chemical monitoring for the treatment of acidic drainage, include pH , acidity, alkalinity, total Fe , ferrous $\mathrm{Fe}, \mathrm{Al} . \mathrm{Mn}, \mathrm{SO}_{4}{ }^{2-}$ and specific conductance. These parameters are included in a list of over 89 parameters listed in Table 7. Total cations were analyzed using the Atomic Emission Inductively Coupled Plasma Method (ICAP. EPA Method 200.7). Total anions were analyzed using ion chromatography (EPA

Method 300.0 and 340.2). Alkalinity (EPA Method 310.1) and acidity (Std. Methods 2310, hot peroxide) measurements were performed within 24 hours of sampling. All other laboratory measurements were performed within the holding time dictated by their respective methods. Field measurements included pH , water temperature, conductivity, dissolved oxygen (DO), oxidation-reduction potential (ORP) and ferrous iron (Hach Colorimetric Method).

Table 7
Chemical Parameters. Techniques and References used to Evaluate the Wetland

| Parameter | Technique | Reference |
| :--- | :--- | :--- |
| Water Temperature (C) |  <br> continuous recording <br> instruments |  |
| pH (SU) |  <br> continuous recording <br> instruments | EPA 150.1 |
| Acidity (mg/L as $\left.\mathrm{CaCO}_{3}\right)$ | Hot peroxide, potentiometric. <br> 4.5 \& 8.3 endpoints. base <br> titration | Std. Methods 2310 |
| Hardness (mg/L as $\left.\mathrm{CaCO}_{3}\right)$ | lon Coupled Argon Plasma <br> Emission (ICAP) | EPA 200.7 |
| Alkalinity (mg/L as CaCO 3 ) <br> Bicarbonate. carbonate. <br> hydroxide, \& total alkalinity | Acid titration EPA 310.1 <br> Solids (mg/L) <br> Total. suspended \& dissolved Gravimetric |  |
| Conductivity (umhos/cm) |  <br> continuous recording <br> instruments | EPA 120.1 |

(table continues)

| Parameter | Technique | Reference |
| :---: | :---: | :---: |
| Dissolved Oxygen (mg/L) | Hand held meters \& continuous recording instruments | Std. Methods 45000 |
| Oxidation Reduction Potential (mv) | Hand held meter |  |
| Turbidity (NTU) | Turbidometric | EPA 180.1 |
| Cations (mg/L) <br> $\mathrm{Al}, \mathrm{Sb}, \mathrm{As}, \mathrm{Ba}, \mathrm{Be}, \mathrm{Cd} . \mathrm{Ca}, \mathrm{Cr}$, $\mathrm{Co}, \mathrm{Cu}, \mathrm{Fe}, \mathrm{Pb}, \mathrm{Mg}, \mathrm{Mn}, \mathrm{Mo}, \mathrm{Ni}$, $\mathrm{K}, \mathrm{Se}, \mathrm{Si}, \mathrm{Ag}, \mathrm{Na}, \mathrm{Sr}, \mathrm{Tl}, \mathrm{Sn}, \mathrm{Ti}$, $\mathrm{Va}, \mathrm{Zn}$ | Atomic Emission ICAP, Dissolved ( 0.45 um filter) \& total metals <br> *Pore water, dissolved ( 0.10 um filter) | EPA 200.7 |
| Mercury (mg/L) | AA Cold Vapor, total Hg | EPA 245.1 |
| Anions (mg/L) <br> Cl, I, Br, sulfate, F | Ion Chromotography, Dissolved ( 0.45 um filter) \& total anions <br> *Pore water, dissolved (0.10 um filter) | EPA 300.0 |
| Sulfide (mg/L)* | Colorimetric. <br> Spectrophotometric | EPA 376.2 |
| Nitrogen ( $\mathrm{mg} / \mathrm{L}$ as N ) <br> Ammonia, Nitrate, Nitrite. Total Kjeldahl* | Colorimetric. segmented flow analyzer <br> *TKN. predigestion. Colorimetric, segmented flow analyzer | $\begin{aligned} & \text { EPA 350.1. } 353.2 . \\ & \text { 354.1. \& } 351.2 \end{aligned}$ |
| Phosphorus ( $\mathrm{mg} / \mathrm{L}$ as P ) <br> Ortho-phosphate \& total phosphorus | Colorimetric. <br> Spectrophotometric | EPA 365.2 |
| Organic Carbon (mg/L) <br> Total organic carbon (TOC) | Combustion Infrared Method. Dissolved ( 0.45 um filter) \& total organic carbon | EPA 415.1 |

Note: parameters indicated with an "*" were not routinely sampled.

### 3.10 Morphometric Measures

Hydrographic, land, and photagrammetric (aerial photography analyses) survey data sets were combined into a digital terrain model. The areas and volumes of the wetland were calculated using a digital CAD package. Included in Table 8 are the typical operating surface areas, volumes, and retention times for each of the main wetland components (Garrett et al., 2001). Retention within each of the ReRAPS components is based on tracer studies also presented by Garrett et al. (2001) in Appendix A. The tracer study confirms that the detention pond was not susceptible to seepage or to groundwater inflow. However, the detention pond was susceptible to short-circuiting.

## Table 8

ReRAPS Wetland Area. Volume, and Actual Retention ( $\tau_{u}$, d) for each of the Major Wetland Components at the Three Operating Pump Flows

|  | Detention <br> Pond <br> $(\mathrm{N} 1-2)$ | RAPS <br> Component <br> (N2-5) |  <br> Cattails <br> (N5-7) |  <br> Baisin <br> (N7-10) | Wetland <br> Storage <br> (N10-13) | Total |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| (N1-13) |  |  |  |  |  |  |
| Area (ha) | 0.13 | 0.09 | 0.09 | 0.09 | 0.28 | 0.68 |
| Volume <br> $\left(\mathrm{m}^{3}\right)$ | 841 | 885 | 632 | 414 | 876 | 3648 |
| $\tau_{a}, @ 114$ <br> $\mathrm{~L} / \min (\mathrm{d})$ | 3.4 | 5.4 | 5.5 | 1.5 | 2.6 | 18.5 |
| $\tau_{u}, @ 170$ <br> $\mathrm{~L} / \min (\mathrm{d})$ | 2.3 | 3.6 | 3.6 | 1.0 | 1.8 | 12.3 |
| $\tau_{a}, @ 284$ <br> $\mathrm{~L} / \min (\mathrm{d})$ | 1.4 | 2.2 | 2.2 | 0.6 | 1.1 | 7.5 |

### 3.11 Hydrologic Measures

Flow balance calculations were used to estimate the CPR volume according to the following equation:

$$
\begin{equation*}
\mathbf{S}_{1}-\mathbf{S}_{\mathrm{o}}+\mathbf{Q}_{\text {pump }}-\mathrm{Q}_{\text {recyck }}=\mathrm{Q}_{\mathrm{cp}} \tag{Equation27}
\end{equation*}
$$

Where:
$S_{t}=$ pond storage at $t$ hour, $\mathrm{m}^{\mathbf{3}}$, continuous stage readings
$S_{0}=$ initial pond storage, $\mathrm{m}^{3}$, continuous stage readings
$\mathrm{Q}_{\text {pump }}=$ pump house flow ( N 2 ), $\mathrm{m}^{3} / \mathrm{hr}$, continuous recording \& field measurements
$Q_{\text {recycle }}=$ recycle flow (N12), $\mathrm{m}^{3} / \mathrm{hr}$, continuous recording \& field measurements
$Q_{\text {cri }}=$ coal pile runoff flow ( N 1 ), $\mathrm{m}^{3} / \mathrm{hr}$, calculated
Evapotranspiration + seepage assumed equal to precipitation

The wetland was operated in a ReRAPS mode to treat the CPR using the following conditions:

- The intermittent pumping rate from the detention pond through N2 ranged from 170284 Lpm (45-75 gpm).
- Treated water was allowed to recirculate back through N12 to the detention pond at a rate of approximately $57-114 \mathrm{Lpm}$ (15-30 gpm).
- Runoff within the wetland catchments was routed back to the detention pond.
- Excess water was discharged to the river via a storage basin standpipe (N13) or was lost due to seepage or evapotranspiration.


### 3.12 Statistical Analyses and Performance Calculations

Statistical analyses were performed on the primary design parameters and on the toxic agents in the wetland. The primary design parameters included acidity, alkalinity, Ca. Al. Fe. and Mn (Section 3.12.1). Some of the design parameters were analyzed for general trends over the four-year operating period. Contaminant removals and alkalinity generations were performed using data obtained during the 41-day monitoring period in
2001. The factors affecting the removal of contaminants and the generation of alkalinity were also explored.

All of the constituents listed by the EPA (EPA, 1999) as being potentially chronically toxic to freshwater aquatic life were evaluated (see Table 2 and Section 3.12.2). The monitoring data from 2001 was also used to evaluate the removal of all potentially toxic minor and major ions. The value of using Mn as a surrogate for the toxic minor ions is explored. All of the statistical analyses were performed using SPSS (1999).

### 3.12.1 Analyses of Design Parameters

Data collected during the long term monitoring (1998-2001) were graphically analyzed for historical trends amongst the design parameters. A stormwater treatment system is susceptible to highly erratic flows and chemistry. To properly quantify the loading into the ReRAPS components, the daily average values for the node chemistry was weighted based on the flow of water through the nodes. Therefore, data from the 41day monitoring period in 2001 were used to develop an hourly matrix of actual and interpolated values for the entire monitoring period. An hourly flow and water chemistry database was developed for all of the primary nodes. Interpolated flow and water quality data were used for hourly periods where measurements were not obtained. The daily average flow and flow-weighted water chemistry concentrations for each of the nodes were calculated from this data matrix. The statistical analyses were performed using the daily flow-weighted averages.

Parametric analyses of differences between the wetland nodes require normality and homogeneous variances (Kleinbaum et al.. 1998). The Shapiro-Wilk tests for normality and the Levene test for homogeneity of variance were performed on the daily flow-
weighted values (SPSS, 1999). Standard transformation techniques (e.g., $\left.\ln (x+1), x^{1 / 2}\right)$ were attempted to satisfy the requirements for parametric testing. Analyses of the transformed data continued to show highly significant departures from normality and nonhomogeneity of variance among the wetland nodes for nearly all of the metal parameters detected by the laboratory analytical techniques. The erratic loading of contaminants entering the detention pond produced highly variable contaminant concentrations in the initial wetland components. The homogeneity of variance for the levels of contaminants between components is not satisfied due to the subsequent moderating effects of mixing and contaminant reductions. Therefore, the Wilcoxon Signed Rank non-parametric test was used to determine differences between the inlets and outlet concentrations for each of the major components. The Wilcoxon Signed Rank test is appropriate for determining if differences exist between the paired data because many of the daily flow-weighted averages among the nodes were related to each other over time (Gilbert, 1987). For example, the concentration of a contaminant at the outlet of a component during a specific time period is affected by the inlet concentration of the contaminant during the same general time period. This is due to the plug flow behavior of the ReRAPS system and the changing contaminant concentrations entering the wetland with each runoff event.

An analysis was also performed to determine if there were differences in the contaminant concentrations between each of the CPR treatment events which followed one of the four major runoff events. The non-parametric Kruskal-Wallis test was used to determine differences between data pooled by the CPR event (Gilbert. 1987).

The overall 41-day average flow-weighted values for acidity, alkalinity, $\mathrm{Ca}, \mathrm{Al}$. Fe, and Mn from the primary nodes were used along with the daily average flows, and area measurements to determine the contaminant removal efficiencies, removal rates, and alkalinity production rates.

Multivariate stepwise regression techniques were used to evaluate the various water quality and retention factors that may affect net alkalinity generation (limestone dissolution) and alkalinity production (total alkalinity concentration) in the RAPS component. The standard statistical techniques for the analyses are described by Kleinbaum et al. (1998).

### 3.12.2 Analyses of Toxic Agents

The analyses of the toxic agents were performed on the 2001 daily flow-weighted data. Results for parameters with less than the minimum detectable level (MDL) were assigned values of one-half the MDL (Gilbert, 1987). Again, the data for the toxic ions were highly variable due to the natural unsteady-state condition of the runoff and subsequent treatment within the wetland. In addition. due to the differences in variability and the lack of normality, the nonparametric Wilcoxon Sign Rank Test was used to evaluate significant differences between concentrations measured amongst the treatment nodes. A significant reduction in the flow-weighted average toxicant concentrations at the outlet node of a component is considered indicative of some level of removal within the component. The tests for node differences were also used to identify conservative major or minor ion behavior within the treatment system. The Wilcoxon Sign Rank test was also used to determine if average node concentration values were significantly greater than the laboratory MDL or the EPA CCC. The hardness dependent CCCs were
calculated based on the average hardness within the treatment nodes (N2-N10) according to Equation 10. Test for removal similarities using Pierson's correlation analyses (Kleinbaum et al., 1998) were performed to determine if meaningful predictive relations existed between the metallic design parameters (total $\mathrm{Al}, \mathrm{Fe}$, and Mn ) and the detectable EPA priority metal pollutants as presented in Table 2.

### 3.13 Toxicity Testing

Toxicity testing was performed to confirm the removal of toxic agents as the water passed through the wetland. The results of this chronic toxicity testing are evaluated based on the cumulative EPA toxicity units (priority metal pollutants. TUs), the major ion toxicity model developed by Mount et al. (1997), and analyses of other water quality parameters presented in Table 7 including the EPA organic priority pollutants.

Chronic toxicity tests were performed using two commonly used freshwater test organisms, the daphnid, Ceriodaphnia dubia, and the fathead minnow. Pimephales promelas. The tests were performed according to EPA procedures (EPA. 1994b). The tests were conducted on samples collected at various nodes within the wetland from March through April 2001 while the ReRAPS was actively treating CPR. Most of the samples were collected from nodes downstream from the RAPS component ( $>\mathrm{N} 5$ ) to confirm the treatment efficacy of the ReRAPS. All grab samples used to perform the testing were analyzed for total and dissolved cations and anions along with other water quality parameters presented in Table 7. A subset of these samples ( $n=5$; N4. N6. N9. N11, and N12; May 2001) were analyzed to determine if any organic priority pollutants were present in detectable levels in the samples. Table 9 presents a list of organic base
neutral and acid compounds that were measured in the samples used for toxicity testing.
Table 10 presents a list of volatile organic compounds that were also measured.

## Table 9

Organic Base/Neutral and Acid Compounds that were Measured in the Toxicity Testing Samples

Base/Neutral and Acid Compounds (EPA 625 Method, MDL 1-8 $\mu \mathrm{g} / \mathrm{L}$ )

| 1,2-Dichlorobenzene | 1.2-Diphenylhydrazine | 1,2,4-Trichlorobenzene |
| :--- | :--- | :--- |
| 1,3-Dichlorobenzene | 1.4-Dichlorobenzene | 2-Chloronaphthalene |
| 2-Chlorophenol | 2-Fluorobiphenyl | 2-Fluorophenol |
| 2-Methylnaphthalene | 2-Nitrophenol | 2.4-Dichlorophenol |
| 2,4-Dimethylphenol | 2,4-Dinitrophenol | 2.4-Dinitrotoluene |
| 2,4,6-Tribromophenol | 2,4,6-Trichlorophenol | 2,6-Dinitrotoluene |
| 3,3p-Dichlorobenzidine | 3,4-Benzofluoranthene | 4-Bromophenyl phenyl ether |
| 4-Chlorophenyl phenyl | 4-Nitrophenol | 4,6-Dinitro-o-cresol |
| ether |  |  |
| Acenaphthene | Acenaphthylene | Anthracene |
| Benzidine | Benzo(a)anthracene | Benzo(a)pyrene |
| Benzo(g,h,i)perylene | Benzo(k)fluoranthene | Bis(2-chloroethoxy)methane |
| Bis(2-chloroethyl)ether | Bis(2-chloroisopropyl)ether | Bis(2-ethylhexyl)phthalate |
| Butyl benzyl phthalate | Chrysene | Di-n-butylphthalate |
| Di-n-octylphthalate | Dibenzo(a,h)anthracene | Diethyl phthalate |
| Dimethyl phthalate | Fluoranthene | Fluorene |
| Hexachlorobenzene | Hexachlorobutadiene | Hexachlorocyclopenta diene |
| Hexachloroethane | Indeno(1,2.3-cd)pyrene | Isophorone |
| N-Nitrosodi-n-propylamine | N-Nitrosodimethylamine | N-Nitrosodiphenylamine |
| Naphthalene | Nitrobenzene-d5* | Nitrobenzene |
| P-Chloro-M-Cresol | Pentachlorophenol | Phenanthrene |
| Phenol-d5* | Phenol | Pyrene |
| Terphenyl-dl* 4 |  |  |

Note. * Compounds used for surrogate and internal standards

Table 10
Organic Volatile Compounds that were Measured in the Toxicity Testing Samples

| Volatile Compounds Measured (EPA 624 Method, MDL 0.5-5 $\mu \mathrm{g} / \mathrm{L}$ ) |  |  |
| :---: | :---: | :---: |
| 1,1,1,2-Tetrachloroethane | 1,1,1-Trichloroethane | 1,1,2,2-Tetrachloroethane |
| 1,1,2-Trichloroethane | 1,1-Dichloroethane | 1,1-Dichloroethene |
| 1,2,3-Trichloropropane | 1,2-Dibromo-3- <br> Chloropropane | 1,2-Dibromoethane (EDB) |
| 1,2-Dichlorobenzene | 1,2-Dichloroethane | 1,2-Dichloropropane |
| 1,4-Dichlorobenzene | 4-Bromofluorobenzene | Acetone |
| Acrylonitrile | Benzene | Bromochloromethane |
| Bromoform | Bromomethane | Carbon Disulfide |
| Carbon Tetrachloride | Chlorobenzene | Chlorodibromomethane |
| Chloroethane | Chloroform | Chloromethane |
| Cis-1.2-Dichloroethene | cis-1.3-Dichloropropene | Dibromofluomomethane* |
| Dibromomethane | Dichlorobromomethane | Dichloromethane |
| Ethylbenzene | m,p-Xylene | Methyl Butyl Ketone |
| Methyl Ethyl Ketone | Methyl Iodide | Methyl Isobutyl Ketone |
| o-Xylene | Styrene | Tetrachloroethene |
| Toluene | Toluene-d8* | Total Trihalomethanes |
| Trans-1,2-Dichloroethene | Trans-1,3-Dichloropropene | trans-1.4-Dichloro-2butene |
| Trichloroethene | Trichlorofluoromethane | Vinyl Acetate |
| Vinyl Chloride |  |  |

The toxicity tests were performed within 36 hours of sample collection. The testing was performed by Auburn Environmental Consulting and Testing (ACT), which is a toxicity testing laboratory located in Auburn. Alabama. Toxicity tests followed the guidance of the EPA (Lewis et al., 1994) for conducting chronic whole effluent toxicity tests. The C. dubia that were used in the tests (in house culture, ACT) were less than $\mathbf{8 h}$
old, while the fathead minnow (Florida Bioassay Supply) were less than 48 h old. Each C. dubia test was conducted in a $30-\mathrm{ml}$ plastic cup containing 15 ml of test solution. The fathead minnow tests were conducted in $\mathbf{6 0 0}-\mathrm{ml}$ glass beakers containing 250 ml of test solution. C. dubia testing was performed using one adult per replicate cup and 10 replicates per test (water sample). Fathead minnow testing was performed using fifteen larvae per replicate beaker and 4 replicates per test (water sample). Tests were conducted under a 16-h:8-h light : dark photoperiod; C. dubia and fathead minnow were tested at $25^{\circ} \mathrm{C}$. The $C$. dubia were fed $100 \mu \mathrm{l}$ of daphnid food (yeast/cerophyl/trout chow. YCT) and $100 \mu \mathrm{l}$ of algae suspension every 24 h . For fathead minnow testing, $150 \mu \mathrm{l}$ of concentrated brine shrimp nauplii was added every 12 h . Control water for all tests was moderately hard-reconstituted water (MHRW). Exposure periods were 7 days for both $C$. dubia and fathead minnow. with daily observations of mortality and reproduction. The criteria for death were no visible movement and no response to prodding. The dry weights of the surviving fathead minnow larvae were obtained at the end of the 7-day exposure period. Each set of toxicity tests included a reference toxicant test using NaCl . The LC50 values were computed to ensure that drifts in organism sensitivity did not occur between sets of test. Standard guidance for chronic effluent toxicity testing (Lewis et al. 1994) is to renew the test chambers with fresh effluent water. For these tests. all of the daily renewals were performed using only one grab sample per sample.

The results of the chronic toxicity testing and the water quality analyses were evaluated using various SPSS (i999) statistical routines (i.e., Dunnetts T3. correlation. hierarchial cluster. and linear regression analyses) and were ultimately incorporated into a simple logistic regression model. The logistic regression model was developed to predict
chronic effects in the ReRAPS water after evaluating factors such as TUs, the major ion concentrations. and other water quality parameters. The methodology used is similar to that used by Mount et al. (1997) when developing a statistical model for predicting major ion toxicity. The completed regression predicts a probability of survival based on the water quality parameters showing relationships to the chronic toxicity testing parameters (C. dubia reproduction, fathead minnow survival, and fathead minnow growth). The linear logistic regression model used is of the form

$$
\begin{gather*}
\log \operatorname{it}(P)=\ln [P / 1-P)]=\beta_{0}+\beta_{1} X_{1}+\beta_{2} X_{2}+\ldots \ldots \ldots+\beta_{\mathrm{n}} X_{\mathrm{n}}  \tag{Equation28}\\
P=100 /\left[1+e^{-\log \mu(P)}\right] \tag{Equation29}
\end{gather*}
$$

Where:
$P=$ proportion of control reproduction. survival or growth
$\beta=$ regression coefficient
$X=$ water quality concentration or parameter value (i.e., TUs)
$n=$ total number of significant terms in the model

During development of the model, various transformations (e.g.. $\ln$ ), factors (e.g.. major ion toxicity probability), and independent variable interactions (e.g. $\mathrm{TU} \times \mathrm{SO}_{4}$ interaction) were considered. The potential models were evaluated using the same criteria as presented by Mount et al. (1997): (1) each independent variable in the model must significantly improve the fit of the model to the data ( $\alpha=0.05$ ); (2) the model should maximize $R^{2}$ (maximize the amount of variance in the data that is explained by the model) and minimize the number of independent variables; and (3) the model should
provide reasonable predictions even when extrapolating outside the limits of the data used to generated the model.

Identification of the toxic agents in the CPR and ReRAPS waters will rely on the weight-of-evidence approach, which will include

- Comparison of inorganic and organic water chemistry to values that have been reported to cause toxicity to test organisms (e.g., conductivity. EPA CCC).
- Direct measurement of the short-term (7 day) chronic toxicity using the two test organisms.
- An evaluation of species insensitivity.
- Correlations between the calculated TUs, the major ion toxicity model results, water quality parameters, and the toxicity metrics. Logistic regression analyses of these variables were evaluated for predicting the toxic responses to the test species.

The use of effluent manipulations for identifying the toxic agents in the treatment system is beyond the scope of this research.

### 3.14 Summary of Methods

The purpose of this chapter was to describe the design of the wetland: the bench scale studies that supported the design efforts, the construction methodology, monitoring effort. analytical methodology. and data evaluations pertinent to this research.

Aluminum plugging concerns in the RAPS component led to the design and construction of the first recirculating RAPS-based wetland. This wetland is also the first constructed wetland designed to treat acidic effluent in the electric utility industry. The experimental monitoring design was developed to determine the treatment benefits associated with the unique recirculation design and to determine the contaminant removal
effectiveness of the wetland. The monitoring methodology incorporated a macroscopic or long term, multi-year evaluation of the wetland. A microscopic or intensive evaluation performed during the forth year of CPR treatment allowed for a statistical evaluation of the contaminant removal and alkalinity generation performance for each of the major wetland components. The field sampling and measurement techniques, laboratory chemical analyses, chronic toxicity testing, and quality assurance techniques follow widely accepted protocols. Foreknowledge of the water quality variability associated with CPR and the wetland water required the use of non-parametric statistical analyses to evaluate the significant removal of contaminants within each of the major wetland components. Regression techniques were used to evaluate factors effecting alkalinity production and toxicity reduction in the wetland. Finally, a weight-of-evidence approach" was used to determine the primary agents of toxicity in the CRP and wetland water.

No other constructed wetland that has been designed to treat CPR or AMD. has been so thoroughly evaluated for contaminant and toxicity removal.

## CHAPTER 4 RESULTS

The results of this study are based on the analyses of data collected during (1) long term periodic monitoring, (2) short term intensive or frequent monitoring, and during (3) a series of chronic toxicity tests.

The long term water quality monitoring data were evaluated graphically and are presented in Section 4.1. This information was used to determine if the CPR would remain acidic throughout the study period (Section 4.1.1) and determined the time period when the wetland performance was relatively stabile with respect to the production of alkalinity (Section 4.1.2). Alkalinity production from the RAPS component was determined to be relatively stable after three years of operation. Therefore, the intensive water quality and hydrologic monitoring activities were performed in 2001 during a 41day period. Both the long term and intensive monitoring activities were performed at the primary treatment nodes: N1, N2, N5, N7. N10, and N12/13 (Figure 12).

Graphical and statistical analyses of the intensive monitoring data are presented in Section 4.2. The intensive monitoring was performed with sufficient intensity so that significant differences in contaminant concentrations were detected between most of the primary treatment nodes (Section 4.2.I). The accurate assessment of loading into the wetland and the statistically significant differences between the primary treatment nodes allowed for the calculation of contaminant removal (Section 4.2.2) and alkalinity generation (Section 4.2.3) within the ReRAPS system. Regression analyses of the intensive monitoring data were used to evaluate factors which affect alkalinity generation
in the RAPS (Section 4.2.4) and mass balance calculations were performed to confirm contaminant removals in the detention pond (Section 4.2.5).


Figure 12. Primary sampling nodes during the long term and intensive monitoring studies.

Section 4.3 presents the results concerning the identification and removal of toxic agents in the wetland. In this section, the removal of trace metals during the intensive monitoring period (Section 4.3.1), toxicity testing results (Section 4.3.2), logistic regression analyses results (Section 4.3.3), and application of the GRI model (Section 4.3.4) were combined using a "weight-of-evidence" approach. The weight-of-evidence approach was used to determine the predominant toxic agents remaining in the wetland and the water quality factors that influence the toxic effects on the test species. Water collected for chronic toxicity testing was collected at all of the ReRAPS nodes with the exception of N3 and N5 (Figure 5). The merits of using the non-priority metal pollutants (i.e., AI, Fe, and $\mathbf{M n}$ ) as surrogates for potential trace metal toxicity was also evaluated using the cumulative TUs (Section 4.3.1).

### 4.1 Long Term Monitoring Results

The primary purpose for yearly periodic monitoring of the wetland from 1998 through 2001 was to determine if the CPR would remain contaminated and if the performance of the wetland had stabilized. The average monthly field measured values and chemical compositions of the water samples are summarized in Appendix B.

Figures 13-20 present box plots of the concentrations for parameters considered important for the design of RAPS-based wetlands during 1998, 1999, 2000, and 2001 at nodes N1, N2, N4, N5, N6, and N7. The SPSS (1999) box plot summarizes data based on the median, quartiles, outliers, and extreme values. The box represents the interquartile range, which contains $50 \%$ of values. A line across the box indicates the median. The whiskers are lines that extend from the box to the highest and lowest values. excluding outliers and extremes. Outliers $(0=$ outlier symbol $)$ are values between 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes ( ${ }^{*}=$ extreme symbol) are values more than 3 box lengths from the upper or lower edge of the box.

### 4.1.1 Yearly CPR Contamination

An evaluation of Figures 13-20 reveals that the CPR (N1) contaminant concentrations are highly variable and that the runoff remained acidic since the system began treatment in 1998. Contaminants typically accumulate in the stagnant water at the base of the 1 lac coal pile between intermittent rain events. Following the events. the contaminants are flushed through N1 into the detention pond. The mass and chemical composition of the CPR are affected by many factors including frequency of rain events. extent of pyrite oxidation in the stored coal. and moisture content of the coal.


Figure 13. Box plot of total iron in the detention pond (N1-N2), RAPS (N2-N5), settling basin and cattail filter (N5-N7) during the first four years of operation. Reference line represents the $3 \mathrm{mg} / \mathrm{L}$ regulatory limit for the wetland discharge (N10-N12/13).


Figure 14. Box plot of total manganese in the detention pond (N1-N2). RAPS (N2-N5). settling basin and cattail filter (N5-N7) during the first four years of operation. Reference line represents the $2 \mathrm{mg} / \mathrm{L}$ regulatory limit for the wetland discharge (N10-N12/13).


Figure 15. Box plot of pH in the detention pond (N1-N2). RAPS (N2-N5), settling basin and cattail filter (N5-N7) during the first four years of operation. Reference line represents the 6-9 regulatory limit for the wetland discharge ( $\mathrm{N} 10-\mathrm{N} 12 / 13$ ).


Figure 16. Box plot of suspended solids in the detention pond (N1-N2). RAPS (N2-N5). settling basin and cattail filter (N5-N7) during the first four years of operation. Reference line represents the $35 \mathrm{mg} / \mathrm{L}$ regulatory limit for the wetland discharge ( $\mathrm{N} 10-\mathrm{N} 12 / 13$ ).


Figure 17. Box plot of total aluminum in the detention pond (N1-N2), RAPS (N2-N5). settling basin and cattail filter (N5-N7) during the first four years of operation.


Figure 18. Box plot of acidity in the detention pond (N1-N2). RAPS (N2-N5), settling basin and cattail filter (N5-N7) during the first four years of operation.


Figure 19. Box plot of alkalinity in the detention pond (N1-N2), RAPS (N2-N5), settling basin and cattail filter (N5-N7) during the first four years of operation.


Figure 20. Box plot of total organic carbon in the detention pond (N1-N2). RAPS (N2N 5 ). settling basin and cattail filter (N5-N7) during the first four years of operation.

### 4.1.2 Yearly Wetland Performance

The magnitude and variability of the primary contaminants found in the CPR were quickly dampened as water passed through the successive components of the ReRAPS wetland. The overall average acidity in the CPR (N1=190 mg/L as CaCO3) was five fold greater than the acidity discharged from the detention pond pump ( $\mathrm{N} 2=34 \mathrm{mg} / \mathrm{L}$ ). The range of acidity concentrations at N2 were also greatly reduced when compared to N1 (Figure 18). The regulated parameters (total Fe, total $\mathrm{Mn}, \mathrm{pH}$, and suspended solids) at node N7 were treated to levels that would comply with the NPDES monthly average requirements (Figures 13-16). This indicates that regulatory compliance levels can be obtained without the later portion of the treatment wetland (N8-N12/13), which included the rock drains and additional open water retention prior to the river discharge.

The unusually high levels of total suspended solids in the system during 2001 was due to coal fines which were flushed into the detention pond ( $\mathrm{N} 1-\mathrm{N} 2$ ) after a major runoff events and remain suspended for days (Figure 16). Higher TSS levels at N2 when compared to Nl are likely due to the infrequent TSS sampling effort. The susceptibility of coal fines entering the wetland system through N 1 increased in 2000 when the type of coal stored at the power plant shifted from a coarse to a fine powder-like material. The finer material is a product of deeper mining extraction techniques.

The pH was reduced at nodes N 2 and N4 during 2000 and 2001 (6.8-7.8 yearly average range) when compared to the earlier years (5.2-5.3 yearly average range, also see Figure 15). Figure 19 indicates that the reduction in pH occurs concurrently with a reduction in alkalinity at the RAPS component discharge (N5). The reduction in alkalinity at N5 likely affects the performance of the entire ReRAPS wetland because of
the decrease in the amount of recirculated alkalinity. Figure 20 indicates that this reduction in alkalinity produced at N 5 is due to the decrease in the available organic carbon, which would serve as a food source for reducing bacteria within the substrate of the RAPS component. Based on this information, alkalinities of over $200 \mathrm{mg} / \mathrm{L}$ are achieved in the ReRAPS wetland while sufficient degradable organic matter exists (Figure 19). According to Figures 19-20, the 6-12 inch compost layer may contribute relatively high levels of bacterially-derived alkalinity for only 2 years. The net effluent alkalinity at N5 was reduced to $40 \mathrm{mg} / \mathrm{L}$ during the fourth year of operation. The $40 \mathrm{mg} / \mathrm{L}$ alkalinity production concentration likely represents a level of alkalinity that can be reliably recycled back to the detention pond in a ReRAPS which relies primarily on limestone dissolution.

Other RAPS have been reported to produce relatively high levels of alkalinity within the first few years of operation. Watzlaf et al. (2000) have reported that much of the alkalinity produced at the Howe Bridge RAPS during the first few summers of operation was due to $\mathrm{SO}_{4}{ }^{2-}$ reduction. Skovran and Clouser (1998) recommended a 6 month operational period before a RAPS component reaches "alkalinity generation" equilibrium. These results are consistent with what has been observed at the Plant Gorgas ReRAPS. Although alkalinity production decreased with operational age. the ReRAPS was capable of producing compliance grade effluent without further treatment by rock drains or additional open water retention. Based on the alkalinity monitoring. the performance of the ReRAPS had come into equilibrium or had stabilized after 2 years of operation.

### 4.2 Intensive Monitoring Results

The intensive 41-day monitoring that was performed during 2001 was used to evaluate contaminant removal and alkalinity generation between components based on flow-weighted concentrations ( $\mathrm{mg} / \mathrm{L}$ ) and loadings (grams per day). The same data set was also used to evaluate the potential toxicity (Section 4.3.1) of the wetland waters relative to the EPA CCC (EPA. 1999).

Confidences in the contaminant removal and alkalinity generation results are based on the analyses for significant differences ( $p<0.05$ ) in the daily flow-weighted concentrations between the nodes. The loading at each of the nodes is a calculated product of the flow-weighted concentrations (measured and interpolated) and the flows (measured).

The results of this study are predicated on the following assumptions:

- Increases in alkalinity and decreases in acidity are considered to be equal (Section 2.3.1).
- Measured increases in $\mathrm{Ca}^{+2}$ production are directly proportional to inorganic alkalinity production (Section 2.3.1).
- Differences in the total alkalinity and the inorganic alkalinity are attributed to bacterially-derived alkalinity (i.e.. $\mathrm{SO}_{4}{ }^{2-}$ reduction) (Section 2.3.1. Table 4).
$u$ The chemistry of the water recirculated through N12 is similar to the river discharge (N13).

The field measured values. chemical compositions of the water samples. and various rates are summarized in Appendix C to E . respectively. The daily flows and daily flowweighted average measurements for the primary contaminants are presented in

Appendix C. The daily contaminant loadings are presented in Appendix D. The contaminant removal rates are presented in Appendix E.

### 4.2.1 Primary Contaminant Concentration Reductions

The concentrations of primary contaminants were significantly reduced as water was routed through the wetland. Figures 21 through 26 present the flows and daily flowweighted average concentrations at each of the primary nodes during the 41-day treatment period. The vertical dashed lines represent the day of greatest average CPR flowing through N1. Four runoff events with flows of greater than 30 gpm occurred on the $1^{\text {st }}, 15^{\text {th }}, 19^{\text {th }}$, and $33^{\text {rd }}$ treatment days (Figure 21). Minimal runoff ( $<5 \mathrm{gpm}$ ) occurred during the $28^{\text {th. }} .29^{\text {th }}$, and $30^{\text {th }}$ treatment days because of an extended light rain event (Figure 10). Generally, the pH (Figure 22) of the CPR (N1) would increase and acidity (Figure 23) would decrease as the rain water diluted the contaminants which had accumulated due to pyritic oxidation processes between runoff events. The accumulation and dilution of acidity at the base of the coal pile was similar to the pattern of Al . Fe. and Mn concentrations which contributed to the acidity (Figures 24-26).

The mean contaminant levels along with the results of the Wilcoxon Signed Rank analyses of the paired data are presented in Table 11. Significant increases in pH ( $p<0.001$ ) and significant decreases in acidity ( $p<0.01$ ) were seen as water was routed through each component in the ReRAPS. Total AI was significantly reduced within each of the components. except for the settling basin where minimal AI levels were observed. Significant reductions of Fe and Mn were observed in all of the treatment components except in the RAPS. where conservative behavior was expected to occur due to chemically reduced conditions within this component.


Figure 21. Daily average flows in the ReRAPS wetland throughout the 41 -day treatment of 4 CPR events from January 29 through March 11. 2001. The storm events that occurred on treatment days I. 15, 19, and 33 are referenced using a dashed vertical line.


Figure 22. Daily pH in the ReRAPS wetland throughout the 41 -day treatment of 4 CPR events from January 29 through March 11. 2001. The storm events that occurred on treatment days 1.15.19, and 33 are referenced using a dashed vertical line.


Figure 23. Daily acidity in the ReRAPS wetland throughout the 41 -day treatment of 4 CPR events from January 29 through March 11, 2001. The storm events that occurred on treatment days $1.15,19$, and 33 are referenced using a dashed vertical line.


Figure 24. Daily average flow-weighted aluminum in the ReRAPS wetland throughout the 41 -day treatment of 4 CPR events from January 29 through March 11. 2001. The storm events that occurred on treatment days $1.15,19$, and 33 are referenced using a dashed vertical line.


Figure 25. Daily average flow-weighted iron in the ReRAPS wetland throughout the 41day treatment of 4 CPR events from January 29 through March 11. 2001. The storm events that occurred on treatment days $1,15,19$, and 33 are referenced using a dashed vertical line.


Figure 26. Daily average flow-weighted manganese in the ReRAPS wetland throughout the 41 -day treatment of 4 CPR events from January 29 through March II. 2001. The storm events that occurred on treatment days $1,15,19$, and 33 are referenced using a dashed vertical line.

Table 11
The Average Flow-Weighted Contaminant Concentrations at the Inlet and Outlet of each
ReRAPS Wetland Component along with the Wilcoxon Signed Ranked Tests for Differences in the Daily Averages

|  | ```Detention Pond (Inlet(N1) - Outlet(N2))``` | $\begin{gathered} \text { RAPS } \\ \text { (N2-NS) } \end{gathered}$ | $\begin{aligned} & \hline \text { Settling } \\ & \text { Basin } \\ & \text { (N5-N7) } \end{aligned}$ | $\begin{gathered} \text { Drains \& } \\ \text { Basins } \\ \text { (N7-N10) } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| pH (su) | 4.0-5.2*** | 5.2-6.8*** | 6.8-7.2 ${ }^{\circ \cdots}$ | 7.2-7.4** |
| Acidity (mg/L) | 178.0-38.4 ${ }^{\text {o. }}$ | 38.4-2.1 ${ }^{\text {c. }}$ | 2.1-1.4** | 1.4-0.5*** |
| Total Al (mg/L) | 24.85-4.48 ${ }^{\text {00 }}$ | 4.48-0.21 ${ }^{\text {®* }}$ | 0.21-0.27 ${ }^{\text {ns }}$ | 0.27-0.14 ${ }^{\text {a* }}$ |
| Total Fe (mg/L) | 12.81-0.77 ${ }^{\text {0. }}$ | $0.77-0.71{ }^{\text {ns }}$ | 0.71-0.34** | 0.34-0.11 ${ }^{\text {c* }}$ |
| Total Mn(mg/L) | 2.88-1.05 ${ }^{\text {** }}$ | $1.05-0.94{ }^{\text {ns }}$ | 0.94-0.28 ${ }^{\circ}$ | 0.28-0.01 ${ }^{* *}$ |

Note. Wilcoxon Signed Rank Paired Test for differences in node concentration: ns = Not significant, $p>0.05$, one tailed, ${ }^{*}=$ Significant concentration change. $p<0.05$, one tailed. ** $=$ Significant concentration change, $p<0.01$, one tailed, ${ }^{* * *}=$ Significant concentration change, $p<0.001$, one tailed

It should be noted that concentrations of acidity, AI, Fe, and Mn at the wetland storage basin outlet (N12/13) were slightly greater ( $p<0.01$ ) than the drains/basin outlet (N10). This final component is likely receiving a small amount of acidic seepage and did not realize any net removal of contaminants. The source of the seepage would come from abandoned coal mine or old coal storage activity in the project vicinity. Therefore. this component should only be considered as a storage basin for "mostly" treated water and is not included in any of the removal calculations for the ReRAPS.

Results presented in Table 11 show that significant contaminant concentration reductions were achieved in the detention pond when compared to the CPR (N1). The average levels of Fe and Mn at the detention pond outlet (N2) were significantly lower
( $\mathrm{p}<0.001$ ) than the permitted discharge requirements of 3 and $2 \mathrm{mg} / \mathrm{L}$, respectively. The average pH consistently exceeded ( $\mathbf{p}<0.001$ ) the lower regulatory limit of 6 at the RAPS discharge (N5).

### 4.2.2 Contaminant Removal Rates

A schematic of the ReRAPS is presented with the percent removals of the primary contaminants in Figure 27. Another schematic of the ReRAPS along with a tabular presentation of the concentrations, overall mass loading, percent removals, and removal rates for the contaminants are presented in Figure 28. About $35 \%$ of the CPR acidity, $59 \%$ of the total AI, and $82 \%$ of the total Fe were removed in the detention pond. These values are similar to the previous analyses performed by Garrett et al. (2001) which are presented in Appendix A. However, in contrast to these previous analyses, which were based on 14 days of consecutive daily sampling during 2000, no overall Mn removal was observed in the detention pond. The analyses of contaminant removal based on the 2001 data. which is presented in this research. is more appropriate due to the greater sampling frequency (8-24 samples/day) and, therefore, can account for the hourly loading variability associated with CPR. Therefore, the contaminant removal analyses of the 2001 data improves upon the analyses presented in Appendix A. Based on the 2001 data. diiution from recirculation was occurring. However, there is no evidence of significant mass removal of Mn in the detention pond. The mass balance relationships for contaminants in the detention pond will be presented later (Section 4.2.5).

| Detention | RAPS |  <br> Cattail Filter |  <br> Basins | Storage |
| :---: | :---: | :---: | :---: | :---: |




Figure 27. Cross sectional schematic of the ReRAPS along with cumulative removals (\%) for N1, N2, N5, N7, and N10



[^0]Figure 28. Cross sectional schematic of the ReRAPS along with tabular concentrations, loadings, percent removals, and removal rates for each of the main components (NI, N2. N5, N7, N10, N12/13) where applicable.

The removal rates for Fe and Mn in surface flow systems have been reported to range from 10 to $20 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$ and 0.5 to $1 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$, respectively (Hedin et al., 1994b). Sikora et al.
(2000) have recommended a design rate of 5 to $10 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$ for Mn -removal in rock drains constructed of limestone aggregate. The lower Fe removal rate within the detention pond $\left(0.81 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}\right)$ is likely due to the low Fe concentrations and low pH in the pond ( $\mathrm{pH} 4.0-$ 5.2) relative to other AMD loading rates on which these rates were based ( $\mathrm{pH} \sim 6-7$ ) (Hedin et al., 1994b). The Mn removal rates for the ReRAPS settling basin require a surface area that is 3 to 5 times greater than what was recommended by Hedin et al. (1994b). Mn removal rates in the ReRAPS rock drains were over 70 times lower than those reported by Sikora et al. (2000). The lower Mn removal rates in the settling pond ( $0.17 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$ ) and the drains/basin area ( $0.07 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$ ) are likely due to the low inlet Mn concentrations as well as lower pH (Section 2.3.5). The lower removal rates experienced within the Plant Gorgas ReRAPS may indicate that larger sizing factors may be required to achieve an effluent which approaches a non-toxic quality. Information on Alhydroxide removal rates in surface flow wetland systems does not exist. The sizing factors for Fe and Al removal in surface flow wetland components which receive mixtures of alkaline and acidic water require further study.

A Kruskal-Wallis Test was used to analyze for concentration differences between event periods (Gilbert, 1987; SPSS, 1999). This analysis revealed that highly significant ( $\mathbf{p}<0.001$ ) differences existed for each of the primary contaminants between the events for all of the hourly primary contaminant concentrations. The Al and Fe detention pond removals between the runoff events ranged from $0.6-1.4$ and $0.2-1.9 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$, respectively (Appendix E). The overall average Mn removal in the detention pond was low ( $0.019 \mathrm{~g} / \mathrm{d}-\mathrm{m} 2$ ). but also varied (Appendix E). It should be noted that the highest rate of AI. Fe. and Mn removal occurred during the second runoff event where removal rates
were $1.4,1.9$ and $0.1 \mathrm{~g} / \mathrm{d}-\mathrm{m} 2$, respectively (Appendix E). During this short treatment period, pH values were at their highest levels and averaged 5.9 (Appendix E). Therefore. maintaining higher pH values was shown to enhance the removal of metals in the detention pond.

### 4.2.3 RAPS Alkalinity Generation

The RAPS component produces alkalinity by both limestone dissolution and $\mathrm{SO}_{4}{ }^{2-}$ reduction. In the ReRAPS the total alkalinity generated within the RAPS and net alkalinity produced at the RAPS effluent are important design considerations. The total alkalinity that can be generated affects the longevity of the system and amount of acidity loading that can be treated. The net alkalinity that can be produced at the effluent ultimately affects the pH and the removal of Al and Fe in the detention pond.

Table 12 presents the data obtained from the RAPS influent and effluent during the four CPR treatment events. Shown in Table 12 are (1) flow averages and ranges: (2) limestone/compost void retention averages and ranges; (3) the net effluent alkalinity: (4) the measured total alkalinity generated by the RAPS; (5) the alkalinity produced by limestone dissolution (based on increase in calcium. where a $1 \mathrm{mg} / \mathrm{L}$ increase stoichiometrically yields $2.497 \mathrm{mg} / \mathrm{L}$ of alkalinity as $\mathrm{CaCO}_{3}$. Section 2.3.1); (6) the noncalcium. or organically derived alkalinity (based on differences between the measured total alkalinity and the alkalinity produced by limestone dissolution); (7) The alkalinity that "may" be produced by $\mathrm{SO}_{4}{ }^{2-}$ reduction (based on decreases in $\mathrm{SO}_{4}{ }^{2-}$, where a $1 \mathrm{mg} / \mathrm{L}$ decrease stoichiometrically yields $1.042 \mathrm{mg} / \mathrm{L}$ of alkalinity as CaCO 3 . Section 2.3.3): and (8) the specific rate of generation of alkalinity calculated as grams per day per square
meter of surface area measured at the top of the compost layer (based on the measured total alkalinity generated).

Table 12
The Quantification of Alkalinity Generation within the

## RAPS Component during each of the Four CPR Treatment

Periods, which Occurred within $\$ 1$ days during 2001

| Treatment Period | (1) Flow. $\mathrm{m}^{3} / \mathrm{hr}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | Average | Min | Max |
| 1 (14 d) | 8.8 | 1.2 | 17.9 |
| 2 (4 d) | 11.8 | 7.8 | 15.6 |
| 3 (14d) | 7.2 | 0.2 | 16.1 |
| 4 (9 d) | 8.5 | 2.6 | 9.6 |
| Overall | 8.5 | 0.2 | 17.9 |
| Treatment | (2) Retention- $\tau_{a} \mathrm{hr}$ |  |  |
| Period | Average | Min | Max |
| 1 (14d) | 45 | 22 | 329 |
| 2 (4 d) | 33 | 25 | 50 |
| 3 (14d) | 54 | 24 | 1960 |
| 4 (9 d) | 46 | 41 | 154 |
| Overall | 46 | 22 | 1960 |
| Treatment Period | (3) Net Effluent Alkalinity (mg/L) | (4) Total Alkalinity Generated (mg/L) | (5) Limestone Alkalinity Generated ( $\mathrm{mg} / \mathrm{L}$ ) |
| 1 (14 d) | 26.2 | 38.4 | 38.2 |
| 2 (4d) | 46.8 | 59.8 | 69.5 |
| 3 (14d) | 45.6 | 118.5 | 50.2 |
| 4 (9 d) | 45.3 | 66.1 | 54.1 |
| Overall | 38.9 | 70.9 | 50.6 |
| Treatment Period | (6) Organic Alkalinity Generated ( $\mathrm{mg} / \mathrm{L}$ ) | (7) Sulfate Reduction Alkalinity (mg/L) | (8) Alkalinity Generation Rate (g/d-m ${ }^{2}$ ) |
| 1 (14d) | 0.2 | 368.6 | 14.0 |
| 2 (4 d) | -9.7 | 179.4 | 29.0 |
| 3 (14d) | 68.3 | 519.8 | 35.9 |
| 4 (9 d) | 12.0 | 105.1 | 23.8 |
| Overall | 20.3 | 318.7 | 25.1 |

The treatment intervals between each of the four significant runoff events ranged from 4 to 14 days. Within each of these treatment periods, the pump flows may range from 0 to 75 gpm , which also affects the retention of water within the RAPS ( $\left.\tau_{u}, \mathrm{hr}\right)$. The average net alkalinity produced by the RAPS (N5) for each of the CPR events ranged from 26.2 to $\mathbf{4 6 . 8} \mathbf{~ m g} / \mathrm{L}$. The average RAPS alkalinity generation rates for each of the CPR events ranged from 14 to $35.9 \mathrm{~g} / \mathrm{d}-\mathrm{m} 2$. The concentrations of $\mathrm{Ca}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ at nodes N 2 and N 4 indicate possible supersaturation with respect to gypsum ( $\mathrm{CaSO}_{4}$ $\bullet 7 \mathrm{H}_{2} 0$ ). Therefore, the types of alkalinity generation with respect to $\mathrm{Ca}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ concentration changes are not reliable estimates of alkalinity generation. Based on the previous stoichiometric assumptions, a large amount of $\mathrm{SO}_{4}{ }^{2-}$ loss within the RAPS substrate is not contributing alkalinity. Significant $\mathrm{SO}_{4}{ }^{2 \cdot}$ changes exist within the substrate which potentially could yield an average of $318 \mathrm{mg} / \mathrm{L}$ of alkalinity as $\mathrm{CaCO}_{3}$. However. only $20.3 \mathrm{mg} / \mathrm{L}$ can be accounted for as generated bacterially-derived alkalinity. It is likely that a significant amount of $\mathrm{SO}_{4}{ }^{2-}$ is forming mineral deposits or is absorbed within the substrate. The overall alkalinity generation rate of $25.1 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$ compares favorably with the rate of $23 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$, which was measured during the winter of 2000 (Garrett et al., 2001) (Appendix A). These rates are also comparable to RAPS that receive partially treated AMD. Watzlaf et al. (2000) found that for a second RAPS in a SAPS, generation rates ranged from $14-35 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$.

### 4.2.4 Factors Affecting Alkalinity Generation

Differences in the various forms of generated alkalinity. such as net effluent. total. limestone, and biologically induced alkalinity exist between the treatment events (Table 11). The SPSS (1999) statistical modeling software was used to evaluate factors
that may influence these differences in concentration for various forms of alkalinity generated in the RAPS component. Figures 29 to 32 present some of the other factors that may effect alkalinity generation, such as water temperature, DO, ORP, and flow rate (i.e.. retention). The flow rates presented in Figure 32 are a repeat of Figure 21 so that comparisons may be easily made between these parameters. As previously discussed, a total of four runoff events occurred with average daily flows of greater than 30 gpm (Section 4.2.1). Water temperature in the ReRAPS generally increased as the 41-day treatment period progressed from the winter into the spring season (Figure 26). The temperature of the discharge from the RAPS component (N5) was moderated by the ground temperature while the greater variability of the other nodes was likely affected by changing air temperatures (Figure 29). DO concentrations were similar among all nodes except N5 and varied according to the temperature dependent DO saturation concentration (Figure 30). A concurrent decrease in DO and ORP occurred at N5 as the number of treatment days increased (Figures 30 and 31). The gradual reduction in DO and ORP at N5 is likely due to the increased biological activity in the RAPS substrate. The increased water temperatures increased the metabolic activity of aerobic microbes thereby increasing the consumption of DO (Figure 29). A reduction in daily average flows through N5 was also evident during the later half of the 41 -day monitoring period (Figure 32). Daily average flows through N5 approached 70 gpm on two occasions during the first half of the 41-day monitoring period. The lower flows during the second half of the monitoring period increased retention in the RAPS substrates thereby limiting the available DO for microbial consumption which further reduced the DO concentrations.


Figure 29. Daily average flow-weighted temperature for the ReRAPS during the 41 -day CPR treatment period. The maximum daily runoff events that occurred on treatment days 1.15.19, and 33 are referenced using a dashed vertical line.


Figure 30. Daily average flow-weighted dissolved oxygen for the ReRAPS during the 41 day CPR treatment period. The maximum daily runoff events that occurred on treatment days 1. 15. 19. and 33 are referenced using a dashed vertical line.


Figure 31. Daily average flow-weighted ORP for the ReRAPS during the 41-day CPR treatment period. The maximum daily runoff events that occurred on treatment days 1.15. 19. and 33 are referenced using a dashed vertical line.


Figure 32. Daily average flows for the ReRAPS during the 41-day CPR treatment period. The maximum daily runoff events that occurred on treatment days 1. 15.19. and 33 are referenced using a dashed vertical line.

A multivariate stepwise regression technique (Section 3.12.1) was used to evaluate the effects of the water quality parameters presented in Figures 29 through 32 on the generation of alkalinity in the RAPS and on the concentration of alkalinity produced at the RAPS discharge (net effluent alkalinity at N5). The average flow-weighted total alkalinity generated in the RAPS were best explained by the influent acidity, DO, and the log-transformed hourly retention ( $\tau_{u}$ ) within the substrate. The largest influence appears to be influent acidity (partial $\mathrm{r}=0.979, \mathrm{p}<0.001$ ); however, the addition of DO ( $\mathrm{p}<0.001$ ) and retention time ( $\mathrm{p}=0.01$ ) improved the model significantly ( $R^{2}=0.971, \mathrm{p}<0.001$ ). The net effluent alkalinity which would be available for recirculation in a ReRAPS were best explained by the $\mathrm{DO}(\mathrm{p}<0.001)$ and the log transformed hourly retention ( $\mathrm{p}=0.002$ ). Only $56 \%$ of the variability associated with the net effluent alkalinity could be explained using a model which included these variables ( $R^{2}=0.557$. $\mathrm{p}<0.001$ ).

For the range of parameters presented in this study, the following models were selected for predicting the total alkalinity generated in. and discharge from. the RAPS:

> Total Alk. Gen. $=$
> $39.932+1.047(\operatorname{lnf}$. Net Acid. $)-5.160(\mathrm{DO})+7.946\left(\log \tau_{u}\right)($ Equation 30$)$

Net Alk. Produced $=38.949-4.438(\mathrm{DO})+9.314\left(\log \tau_{u}\right) \quad($ Equation 31$)$

Where:
Total alkalinity generated in the RAPS is a concentration ( $\mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ )
Net alkalinity produced or discharged from the RAPS is a concentration ( $\mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ )
Influent net acidity = hot peroxide acidity less any total alkalinity, $\mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$
DO = dissolved oxygen as $\mathrm{mg} / \mathrm{L}$
$\tau_{a}=$ hourly water retention in the compost/ limestone voids, assumed $50 \%$

Both models are consistent with how these factors have been reported to influence alkalinity generation. Watzlaf et al. (2000) has determined that the alkaline addition in RAPS is often dominated by the limestone dissolution pathway. Both models predict alkalinity values consistent with the lower range of alkalinity production values reported by Watzlaf et al. (2000). An increase in DO indicates that the chemical reduction due to microbial activity may be slowing and, therefore, would lower alkalinity production. An increased retention ( $\tau_{u}$ ) would optimize microbial alkalinity production and dissolution and therefore would increase alkalinity production. The log transformation of the hourly retention time was used due to the limited effect of retention on dissolution beyond a 48 h contact period using high grade limestone (Watzlaf \& Hedin. 1993). The Plant Gorgas RAPS component was constructed using a high grade of limestone with $\mathbf{> 9 0 \%}$ $\mathrm{CaCO}_{3}$ (Gariett et al., 2001).

### 4.2.5 Detention Pond Performance

The reduction of contaminant concentrations clearly occurred between N2 and N12/13. most markedly in the detention pond (Figures 27 and 28). The highly significant differences between events for contaminant concentrations at all of the wetland nodes indicate that the performance of the detention pond is the primary factor controlling
contaminant concentrations in the downstream components (Section 4.2.2). However. it is not clear how much of the reduction in the detention pond was due to actual removal and how much was an artifact of dilution by recycled-treated water and possible seepage. Performing a mass balance for chemical constituents that enter (N1 and N12) and leave the detention pond ( N 2 ) would confirm the occurrence of removal for non-conservative constituents (e.g., Al and Fe ) and would close the mass balance for constituents that behave conservatively (e.g., Mn and net alkalinity).

The outlet concentrations at the detention pond (N2) are dependent on the inlet(s) and outlet mass balances and any removal processes that may be occurring. The mass balance relationship for determining concentrations at any time ( $t$ ) in a "well-mixed" detention pond with recirculation can be described using the following equations:

$$
\begin{gather*}
\left(S_{D P 1} C_{D P i}+Q_{N 1 t} C_{N 1 t}+Q_{N 12 t} C_{N 12 t}-Q_{N 2 t} C_{N 2 t}\right) / S_{D P t}=C_{D P t}  \tag{Equation32}\\
S_{D P 1}=S_{D P 1}+Q_{N 1 t}+Q_{N 12 t}-Q_{N 2 t} \tag{Equation33}
\end{gather*}
$$

Where:
$\mathrm{S}_{\mathrm{DP}}, \mathrm{S}_{\mathrm{DP}}=$ detention pond storage $\left(\mathrm{m}^{3}\right)$ at initial time and at time $=\mathrm{t}(\mathrm{hr})$
$\mathrm{C}_{\mathrm{DP}}, \mathrm{C}_{\mathrm{DP}}=$ detention pond concentration at initial time and at time $=\mathrm{t}(\mathrm{hr})$
$\mathrm{Q}_{\mathrm{NII}}=\mathrm{CPR}$ flow $\left(\mathrm{m}^{3} / \mathrm{hr}\right)$ at time $=t(\mathrm{hr})$
$\mathrm{C}_{\mathrm{Nit}}=\mathrm{CPR}$ concentration $(\mathrm{mg} / \mathrm{L})$ at time $=t(\mathrm{hr})$
$\mathrm{Q}_{\mathrm{N} 12 \mathrm{t}}=$ Recycle flow ( $\mathrm{m}^{3} / \mathrm{hr}$ ) at time $=\mathbf{t}(\mathrm{hr})$
$\mathrm{C}_{\mathrm{N} 12 \mathrm{t}}=$ Recycle concentration ( $\mathrm{mg} / \mathrm{L}$ ) at time $=\mathrm{t}(\mathrm{hr})$
$\mathrm{Q}_{\mathrm{N} 21}=$ Pump discharge flow ( $\mathrm{m}^{3} / \mathrm{hr}$ ) at time $=\mathrm{t}(\mathrm{hr})$
$\mathrm{C}_{\mathrm{N} 2 \mathrm{t}}=$ Pump discharge concentration $(\mathrm{mg} / \mathrm{L})$ at time $=\mathrm{t}(\mathrm{hr})$

Close agreement between the "predicted" concentration in the pond ( $\mathrm{C}_{\mathrm{DP}}$ ) at any time. $t$. and the measured concentrations at the pump discharge ( $\mathrm{C}_{\mathrm{N} 2 \mathrm{t}}$ ) would establish a mass balance and confirm that the modeled parameter behaves conservatively. This analysis was performed for net alkalinity (calculated; total alkalinity - hot peroxide acidity), $\mathrm{Al}, \mathrm{Fe}, \mathrm{Mn}, \mathrm{Ca}$, and $\mathrm{SO}_{4}$ using time step spreadsheet calculations based on Equations 32 and 33. Correlations between the concentration predicted for the pond ( $\mathrm{C}_{\mathrm{DP}}$ ) and those measured at the pump discharge $\left(\mathrm{C}_{\mathrm{N} 21}\right)$ were found for $\mathrm{Mn}\left(R^{2}=0.73\right)$ and net alkalinity ( $R^{\mathbf{2}}=0.48$ ). Figures 33 and 34 compare the predicted concentrations in the detention pond to the actual (including interpolated tabular) values at the pump outlet (N2). Both Mn and net alkalinity behave conservatively and tend to validate the monitored hydrological values from the ReRAPS (Figures 33 and 34). The improved predictions for Mn when compared to net alkalinity may be due to sampling frequency. Total metals were sampled 328 times ( 3 h interval, 8 samples per day $\times 41$-days) at nodes N1. N2. and N12. Total alkalinity and acidity were measured on a daily basis at each of these nodes. Daily sampling for acidity and alkalinity is not a sufficient frequency for determining the total mass of net alkalinity entering the detention pond during each CPR event. The low sampling frequency at N 1 is likely responsible for the deviations between the actual and predicted net alkalinity concentrations during the first 400 hours of the 41day monitoring period. The mass balance for $\mathrm{Al}, \mathrm{Fe}, \mathrm{Ca}$. and $\mathrm{SO}_{4}$ entering ( N 1 and N 12 ) and leaving ( N 2 ) the detention pond could not be established. The inability to predict the concentrations of the these parameters are either due to non-conservative behavior (i.e.. removal) or due to small differentials in concentrations between the inlet and outlet nodes of the detention pond.

## Pump Oischarge Net Alralinily



Figure 33. Predicted pond versus actual pump net alkalinities during the 41-day treatment of CPR.


Figure 34. Predicted pond versus actual pump manganese during the 41 -day treatment of CPR.

As previously discussed, the concentrations for Al and Fe were significantly different between events at the pump discharge (N2). Removals of Fe and Al varied by 23 and $34 \%$, respectively. Figures 35 and 36 present the concentrations of Al and Fe at N2 with respect to pH and net alkalinity during the 41 -day treatment period. Based on Figures 35 and 36 , the optimal pH and net alkalinity for Al removal are 5.5 and $-20 \mathrm{mg} / \mathrm{L}$. respectively. The optimal pH and net alkalinity for Fe removal are 4.5 and $\mathbf{- 8 0} \mathbf{m g} / \mathrm{L}$. respectively. The optimal net alkalinity ( $-20 \mathrm{mg} / \mathrm{L}$ ) for Al and Fe removal in the detention pond represents the acidity that remains after all of the Fe and Al acidity has been consumed due to the recycled alkalinity. Therefore, the optimal ReRAPS/detention pond performance should be based on the consumption of nen-Mn acidity.


Figure 35. Concentrations of Total Al and Fe at N 2 with respect to pH during the 41 -day treatment period


Figure 36. Concentrations of Al and Fe at N 2 with respect to net alkalinity (calculated: total alkalinity - hot peroxide acidity) during the 41 -day treatment period

Theoretically, the avoidance of all AI and Fe precipitate plugging in the RAPS substrate is possible if the optimal net alkalinity and retention for Al are maintained in the detention pond. Batch tank studies performed by Garrett et al. (2001) (Appendix A) have determined that a 48 h retention is sufficient for the removal of the metal hydroxides.

In a ReRAPS, it is the ratio of recycle flow to runoff flow or "recycle ratio" that dictates the net alkalinity of the pond. It is the pump to runoff flow, or "retention ratio." that dictates the minimum size of the ReRAPS components. Assuming a steady-state flow and mixing condition. the "recycle ratio" is derived from the mass balance relationship where:

$$
\begin{equation*}
\text { Recycle Ratio, } \mathrm{R}_{\text {recycle }}=\mathrm{Q}_{\text {recycle }} / \mathrm{Q}_{\mathrm{CPR}} \tag{Equation34}
\end{equation*}
$$

Where:
$Q_{\text {recyck }}=$ Flow of treated water recycled into detention pond (N12)
$\mathbf{Q}_{\text {CPR }}=$ Flow of contaminated coal pile runoff (CPR) into detention pond (N1)

And the mass balance is:

$$
\mathrm{Q}_{\mathrm{CPR}} \mathrm{C}_{\mathrm{CPR}}+\mathrm{Q}_{\mathrm{rcxycle}} \mathrm{C}_{\text {recycle }}=\left(\mathrm{Q}_{\mathrm{CPR}}+\mathrm{Q}_{\mathrm{recyccte}}\right)\left(\mathrm{C}_{\mathrm{DP}}\right)
$$

(Equation 35)

Where:
$Q_{\text {recycle }}=$ Flow of treated water recycled into detention pond (N12)
$Q_{\text {CPR }}=$ Flow of contaminated coal pile runoff (CPR) into detention pond (N1)
$\mathrm{C}_{\text {recycle }}=$ Concentration of net alkalinity in $\mathrm{Q}_{\text {recycle }}$
$\mathrm{C}_{\mathrm{CPR}}=$ Concentration of net alkalinity in $\mathrm{Q}_{\mathrm{CPR}}$
$C_{D P}=$ Concentration of net alkalinity in well mixed detention pond

Therefore, the mass balance relationship can be rearranged to solve for the recycle ratio using only the concentration values at the two detention pond inlets and the desired detention pond concentration:

$$
\begin{equation*}
\mathrm{Q}_{\text {recycle }} / \mathrm{Q}_{\mathrm{CPR}}=\left(\mathrm{C}_{\mathrm{DP}}-\mathrm{C}_{\mathrm{CPR}}\right) /\left(\mathrm{C}_{\text {rececle }}-\mathrm{C}_{\mathrm{DP}}\right)=\mathrm{R}_{\text {rececle }} \tag{Equation36}
\end{equation*}
$$

The retention ratio, the ratio of pump to runoff flow is therefore derived using Equations 35 and 36 as follows:

$$
\begin{gather*}
\mathrm{R}_{\text {recmion }}=\mathrm{Q}_{\text {pump }} / \mathrm{Q}_{\mathrm{CPR}}= \\
\left(\mathrm{Q}_{\text {rexycle }}+\mathrm{Q}_{\mathrm{CPR}}\right) / \mathrm{Q}_{\mathrm{CPR}}=\mathrm{R}_{\text {receclc }}+1 \tag{Equation37}
\end{gather*}
$$

Where:

$$
\mathrm{Q}_{\text {pump }}=\text { Pump flow (N2) }
$$

Based on the average flow-weighted net alkalinity for nodes N1, N2, and N12, the recycle and retention ratios required to achieve optimal Al removal are calculated using Equation 38:

$$
\begin{equation*}
R_{\text {recycle }}=(-20-(-178)) /(43-(-20))=2.5 \tag{Equation38}
\end{equation*}
$$

Where:
$\mathrm{C}_{\mathrm{cpr}}=\mathrm{C}_{\mathrm{N} 1}=-178 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}, 41$-day flow-weighted average
$\mathrm{C}_{\text {recycle }}=\mathrm{C}_{\mathrm{N} 12}=43 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}, 41$-day flow-weighted average
$\mathrm{C}_{\mathrm{DP}}=-20 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$, desired

Therefore, using Equation 39

$$
\begin{equation*}
\mathrm{R}_{\text {retemion }}=\mathrm{R}_{\text {recycle }}+1=3.5 \tag{Equation39}
\end{equation*}
$$

The overall average recycle and retention ratios for the ReRAPS. during the 41-day CPR treatment are calculated as follows:

$$
\begin{align*}
& \text { Actual Operating } R_{\text {recycle }}=Q_{\text {recycle }} / Q_{C P R}=2.0  \tag{Equation40}\\
& \text { Actual Operating } R_{\text {recention }}=Q_{\text {pump }} / Q_{C P R}=2.8 \tag{Equation41}
\end{align*}
$$

Where total flows for the entire 41-day CRP treatment period were:

$$
\begin{aligned}
& Q_{\text {recycle }}=6192 \mathrm{~m}^{3} / 41 \text { days } \\
& Q_{\text {CPR }}=3044 \mathrm{~m}^{3} / 41 \text { days } \\
& Q_{\text {pump }}=8473 \mathrm{~m}^{3} / 41 \text { days }
\end{aligned}
$$

If the total flows at N1. N2, and N12 were routed during steady-state conditions the actual operating recycle and retention ratios were $20 \%$ lower than what would be
required to achieve the targeted net alkalinity of $-20 \mathrm{mg} / \mathrm{L}$. However. the treatment of runoff does not provide for steady-state opportunities. Therefore, the design of ReRAPS must consider peak runoff flows if optimal removal of Fe and Al are desired prior to the RAPS component.

A recomputation of the actual recycle and retention ratios using the 1-day peak runoff period (Event \#2, day 14, February 13, 2001) is as follows:

$$
\text { Actual Operating } R_{\text {recycle }}=Q_{\text {recycle }} / Q_{C P R}=0.19
$$

$$
\begin{equation*}
\text { Actual Operating } R_{\text {retention }}=Q_{p u m p} / Q_{C P R}=0.24 \tag{Equation43}
\end{equation*}
$$

Where the peak one-day CPR flow and concurrent recycle and pump flows are:

$$
\begin{aligned}
& Q_{\text {recycle }}=180 \mathrm{~m}^{3} / \text { day } \\
& Q_{C P R}=932 \mathrm{~m}^{3} / \text { day } \\
& Q_{\text {pump }}=226 \mathrm{~m}^{3} / \text { day }
\end{aligned}
$$

The operating ratios based on the one-day peak flows are much lower than the 2.5 recycle and 3.5 retention ratios required to achieve the $-20 \mathrm{mg} / \mathrm{L}$ targeted net alkalinity. It was after this one day peak runoff during Event \#2 that the detention pond pH began to drop and did not recover until after the peak flows of Event \#3 occurred (Figure 20). Assuming that the detention pond net alkalinity was maintained at $-20 \mathrm{mg} / \mathrm{L}$ ( $\mathrm{R}_{\text {recycle }}=$ 2.5. $\mathrm{R}_{\text {retention }}=3.5$ ), the one day recycle and pump flow required to treat the one-day peak CPR flow of $932 \mathrm{~m}^{3} /$ day and maintain the targeted net alkalinity are calculated as follows:

> Required $Q_{\text {recycle }}=R_{\text {recycle }} Q_{\text {CPR }}=$ $\left(932 \mathrm{~m}^{3} /\right.$ day $)(2.5)=2.330 \mathrm{~m}^{3} /$ day or 427 gpm

$$
\begin{gathered}
\text { Required } Q_{\text {pump }}=R_{\text {retemion }} Q_{C P R}= \\
\left(932 \mathrm{~m}^{3} / \text { day }\right)(3.5)=3,262 \mathrm{~m}^{3} / \text { day or } 600 \mathrm{gpm}
\end{gathered}
$$

Flow rates such as these are not cost effective for treating runoff from a 4.5ha coal pile. A 600 gpm pump (Equation 45) would be required in order to provide optimal net alkalinity concentrations for Al removal when treating this typical peak flow originating from a 2.5 cm rain.

Equalization of CPR flow will dramatically reduce the flow requirements ( $\mathrm{Q}_{\text {rocycle }}$ and Qpump) of the ReRAPS. Assuming the $3044 \mathrm{~m}^{3}$ CPR flow (Equation 41) was equalized throughout the 41 -day treatment period, only $74 \mathrm{~m}^{3} /$ day ( 14 gpm ) of CPR would require treatment on a daily basis. Only $186 \mathrm{~m}^{3} /$ day ( 34 gpm ) would require recycling and $259 \mathrm{~m}^{3} /$ day ( 48 gpm ) would require pumping. These flow rates are within the present operational parameters of the Plant Gorgas Wetland. Based on these analyses. further optimization of the Plant Gorgas Wetland may best be achieved through the use of a well designed equalization basin which would retain and limit the maximum discharge of acidic runoff to the detention pond.

### 4.3 Identification and Removal of Toxicity

A weight-of-evidence approach was used to identify the primary toxic agents and evaluate the removal of toxicity in the CPR as it was routed through the ReRAPS. The weight-of-evidence approach used in this study is as follows:
a The possibility of trace metal toxicity is determined by evaluating the 41 -day 2001 monitoring data for cumulative TUs based on the total trace metal concentrations and the EPA CCC (Section 4.3.1).

- The possibility of non-metal toxicity is minimized when concentrations for all of the non-metal priority pollutants are less than their respective EPA CCC (Section 4.3.2).
- Evidence for the presence and removal of aquatic toxicity in the ReRAPS is confirmed using two test species (Section 4.3.3).
- Trace metal-based logistic regression models best explained the toxicity variability associated with the two test species and identified the predominant toxic agents. Other water quality factors that may effect toxicity were also identified (Section 4.3.4).
- The wetland water contains a mixture of major and minor ions. which can exert toxic effects on the test species. The potential for major ion toxicity in the mixed wetland waters are minimized after re-evaluating the water quality of the toxicity testing samples using the GRI model (Section 4.3.5).


### 4.3.1 Removal of Toxic Metals During Intensive Monitoring

Most RAPS-based wetlands have been designed to remove Fe to concentrations below $3 \mathrm{mg} / \mathrm{L}$ and Mn to concentrations below $2 \mathrm{mg} / \mathrm{L}$. These concentrations are the typical monthly average NPDES limitation. Although Mn is not listed as a toxicant to aquatic life (EPA. 1999), it is used as a surrogate for the presence of priority pollutants such as As. $\mathrm{Cd} . \mathrm{Cr}, \mathrm{Cu}, \mathrm{Pb}, \mathrm{Hg} . \mathrm{Ni} . \mathrm{Se}, \mathrm{Ag}$. and Zn . As a result, there has been very little information concerning RAPS-based wetland removal of specific toxic metals to levels that are considered non-toxic to aquatic life. The Criterion Continuous Concentrations (CCCs) recommended by the EPA for the protection of aquatic life have been presented in Table 2. As previously described, the hardness dependent EPA CCC calculations were
performed using the $400 \mathrm{mg} / \mathrm{L}$ maximum hardness value because the wetland waters typically exceed the level (Figure 37, see Section 4.1 for box plot interpretations).


Figure 37. Box plot of calculated hardness values ( $\mathrm{mg} / \mathrm{L}$ as CaCO ) for nodes $\mathrm{N} 1-\mathrm{N} 10$ during the 200141 -day monitoring. The $400 \mathrm{mg} / \mathrm{L}$-reference line is the maximum value that can be used in the EPA CCC calculation for hardness dependent priority pollutants.

Previous analyses using the Wilcoxon Signed Rank test found significant reductions among successive nodes for the metallic parameters ( $\mathrm{Al}, \mathrm{Fe}$, and Mn ) that are commonly used to design wetlands. Figure 38 presents a box plot of the $\log$ concentrations for Al , Fe, and Mn during the 41-day monitoring period at each of the wetland nodes. See Section 4.1 box for box plot interpretations. Significant removals were also found for all of the priority pollutants detected in the CPR. Table 13 presents the results of the Wilcoxon Signed Rank Tests which were used to determine if differences existed between the wetland minor ion concentration and the minimum detectable levels (MDL),

CCC, and the NPDES limitation, when applicable. The MDLs for the analytical instrumentation are lower than or equal to the respective CCCs.

The concentration for five ( $\mathrm{As}, \mathrm{Pb}, \mathrm{Se}, \mathrm{Ag}$, and Hg ) of the 12 metal pollutants in the CPR were significantly lower than the MDL (Table 13). Although the analyses of $\mathbf{H g}$ was not included in the routine monitoring design, periodic analyses of CPR ( $\mathrm{n}=5$ ) yielded non-detectable results (MDL $=0.02 \boldsymbol{\mu g} / \mathrm{L}$ ). Although significantly lower than their respective MDLs, Pb , and Se were detectable in a few samples. Box plots of the pollutants $(\mathrm{Zn}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Cr}, \mathrm{Se}, \mathrm{Cd}, \mathrm{Pb}, \mathrm{Al}, \mathrm{Fe}$, and Mn ) that were detected in the CPR (N1) are presented in Figures 39 through 41 for all of the primary nodes (N1, N2, N4, N5, N7, and NI0). The seven priority metal pollutants detected in the CPR in decreasing concentrations are $\mathrm{Zn}>\mathrm{Ni}>\mathrm{Cu} \gg \mathrm{Cr} \gg(\mathrm{Cd}, \mathrm{Pb}, \mathrm{Se})$.


- igure 38 . Box plot of $\log$ concentrations for $\mathrm{Al}, \mathrm{Fe}$ and Mn in the primary nodes (N1, N2, N4, N5, N7, and N10) during the 41 -day CPR treatment in 2001. Reference lines represent any applicable NPDES regulatory limits and EPA CCC levels for aquatic life.


## Table 13

Results of the Wilcoxon Signed Rank Analyses to Determine Significant Differences
between the Pollutant MDL, CCC. or NPDES Limitation

| Pollutant | MDL ( $\mu \mathrm{g} / \mathrm{L}$ ) | CCC ( $\mu \mathrm{g} / \mathrm{L}$ ) | NPDES ( $\mu \mathrm{g} / \mathrm{L}$ ) |
| :---: | :---: | :---: | :---: |
| Priority Pollutants |  |  |  |
| Total As (ug/L) | CPR < 5 ** | CPR < 150 *** | --- |
| Total Cd (ug/L) | N2<2 *** | CPR<7.3 *** | --- |
| Total Cr (ug/L) | N1-N10>1 ${ }^{* * *}$ | CPR<268 ${ }^{\text {a }}$ *** | --- |
|  |  | N2<11 ${ }^{\text {b *** }}$ |  |
| Total Cu (ug/L) | N $5<5^{* *}$ | $\mathrm{N} 2<30.5{ }^{* * *}$ | --- |
| Total $\mathrm{Hg}(\mathrm{ug} / \mathrm{L})^{\text {c }}$ | CPR < 0.2 | CPR < 0.77 | --- |
| Total $\mathrm{Pb}(\mathrm{ug} / \mathrm{L})$ | CPR < 4 *** | CPR<18.6 *** | --- |
| Total $\mathrm{Ni}(\mathrm{ug} / \mathrm{L})$ | N10<4*** | N2<168*** | --- |
| Total Se (ug/L) | CPR $<5$ *** | CPR < $5^{* * *}$ | --- |
| Total Ag ( $u g / L$ ) | CPR < 6 *** | CPR < 44 *** | --- |
| Total Zn (ug/L) | N1-N10>4*** | N2<380 *** | --- |
| Non-Priority Pollutants |  |  |  |
| Total Al (ug/L) | N1-N10 ${ }^{18} 8^{* * *}$ | N10<87** | --- |
| Total Fe (ug/L) | N1-N10>3*** | N2 $<1000$ * | N2<3000*** |
| Total Mn (ug/L) | $\mathrm{N} 1-\mathrm{NIO}>4 * * *$ | -- | N2<2000 *** |
| Note. The first upstream node where significantly lower values were found is indic Analyses performed using daily average total metal values. <br> Wilcoxon Signed Rank Paired Test for differences in node concentration <br> ns $=$ Not significant. $p>0.05$, one tailed <br> * $=$ Significant concentration change, $p<0.05$. one tailed <br> ** = Significant concentration change, $p<0.01$, one tailed <br> *** $=$ Significant concentration change, $p<0.001$. one tailed |  |  |  |
|  |  |  |  |
| ${ }^{2} \mathrm{Cr}$ (III) CCC. <br> ${ }^{6} \mathrm{Cr}(\mathrm{VI}) \mathrm{CCC}$ <br> ${ }^{c} \mathrm{Hg}$ only measured | PR ( $\mathrm{n}=5$ ), all values | n-detectable. |  |



Figure 39. Box plot of log concentrations for Zn and Ni in the primary nodes ( $\mathrm{N} 1, \mathrm{~N} 2, \mathrm{~N} 4$, N5, N7, and N10) during the 41-day CPR treatment in 2001. Reference lines represent any applicable NPDES regulatory limits and EPA CCC levels for aquatic life.


Figure 40 . Box plot of $\log$ concentrations for $\mathrm{Cu}, \mathrm{Cr}$, and Se in the primary nodes (N1, N2, N4, N5, N7, and N10) during the 41 -day CPR treatment in 2001. Reference lines represent any applicable NPDES regulatory limits and EPA CCC levels for aquatic life.


Figure +1. Box plot of $\log$ concentrations for Cd and Pb in the primary nodes (N1, N2, N4. N5, N7, and N10) during the 41-day CPR treatment in 2001. Reference lines represent any applicable NPDES regulatory limits and EPA CCC levels for aquatic life.

Only six of the detectable pollutants $(\mathrm{Cr}, \mathrm{Cu}, \mathrm{Ni}, \mathrm{Zn}, \mathrm{Al}$, and Fe$)$ were found in concentrations that were greater than the CCC during the 2001 41-day treatment period (Table 13). With the exception of AI, all were treated to levels that were significantly lower than the CCC within the detention pond (N2) (Table 13). Aluminum required the entire wetland (N10) in order to reduce concentrations below the CCC (Table 13)

The total Al concentration ( $0.12 \mathrm{mg} / \mathrm{L}$ average) at the Drains and Basins outlet (N10) may be much lower than the actual toxic concentration for Al because the EPA recommended CCC for Al is not adjusted for hardness (EPA, 1999). The EPA suggests the use of the Water-Effect Ratio (WER) test to determine site-specific toxicity in situations where moderate to high hardness levels and higher pH may mitigate for toxic effects to aquatic life (EPA, 200 lb ). At NIO, the hardness ( $464 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$. average) and the pH (7.3, average) are greater than the level from which the AlCCC is
based on (EPA, 1999). Typically, only the dissolved form of the metal is toxic. However, the total recoverable Al is appropriate for Al toxicity monitoring because the hydroxide particles are toxic to fish (EPA, 1999; Henry et al., 1999). The total recoverable analytical procedure for metals may be measuring aluminum associated with the suspended clay particles from the ReRAPS liner and, therefore, could be a biased estimate of the suspended Al hydroxide.

The removal of the predominant priority metal pollutants (i.e., $\mathrm{Cu}, \mathrm{Ni}$, and Zn ) was correlated with the removal of AI, Fe. and Mn. Figure 42 presents a matrix scatter plot for all of the detectable metal pollutants present in the CPR and ReRAPS during the 41day monitoring period. A matrix scatterplot presents all possible simple (bivariate) scatterplots in a square matrix for all pairs of variables requiring analyses. Of the three non-priority metal pollutants, total manganese was most highly correlated ( $\mathbf{p}<\mathbf{0 . 0 0 1 \text { ) with }}$ $\mathrm{Cu}\left(R^{2}=0.83\right) \mathrm{Ni}\left(R^{2}=0.98\right)$ and $\mathrm{Zn}\left(R^{2}=0.97\right)$. Therefore, the use of the nonpriority metals ( Al and Fe ) and Mn as surrogates for the removal of the priority pollutants seems to have merit in a RAPS-based application.

As presented in Section 2.2.4 and using Equation 13. the cumulative toxicity due to the priority metals was estimated by summing the normalized concentrations based on the EPA CCC. The normalized toxicity value is expressed as toxicity units (TUs). Figure 43 presents the cumulative toxicities at each of the wetland nodes using the overall average metal concentration. The cumulative TUs in Figure 43 were calculated for the priority metals that were measured at concentrations that were significantly greater than their respective MDL (Table 13). Based on Figure 43 the metals which may contribute toxicity, in decreasing order. are $\mathrm{Cu}>\mathrm{Ni}>\mathrm{Zn} \gg \mathrm{Cd}>\mathrm{Cr}$.


Figure $\ddagger$ 2. Correlation matrix for $\mathrm{Al}, \mathrm{Fe}, \mathrm{Mn}, \mathrm{Cu}, \mathrm{Ni}$, and Zn .


Figure 4 . Cumulative toxicity units (TUs) for priority pollutants in the ReRAPS wetland during 2001.

Due to the high correlation among metals in the wetland. it is justified to further evaluate the relationship between the use of non-priority pollutant monitoring as a surrogate for chronic toxicity using an assumed additive effect. Figure 44 presents analyses of the predictive values for Mn and Al . This analysis also found that the predictive value of using total Al and total Mn as surrogates for priority pollutant monitoring was improved when only aerobic waters (ORP>100 mv) were evaluated (N5 omitted). It is not reasonable to use Mn as a surrogate in mixed partially reduced conditions. N5 was omitted because poor relationships exist between the major metal cations and the minor metal ions in the chemically reduced effluent of the RAPS component (N5). Therefore, the predictive models for Al and Mn in Figure 44 do not include data from the RAPS component effluent (N5). The simple regression analyses using quadratic models found that $\mathrm{Mn}\left(R^{2}=0.89, \mathrm{p}<0.001\right)$ and $\mathrm{Al}\left(R^{2}=0.84 . \mathrm{p}<0.001\right)$ were good predictors of "cumulative toxicity" due to the priority pollutants. Fe ( $R^{2}=$ 0.47. $\mathrm{p}<0.001$ ) was not found to be as good a predictor of potential priority metal toxicity. Based on Figure 44, the commonly used limit of $2 \mathrm{mg} / \mathrm{L}$ total Mn may not eliminate "chronic" toxicity to aquatic life in the whole water effluent of the ReRAPS. Removal to less than $1 \mathrm{mg} / \mathrm{L}$ of Mn would be required (assuming that no toxicity exists due to AI). Based on this analysis, the first two components of the Plant Gorgas ReRAPS wetland (i.e.. detention pond and RAPS) may have removed the metal pollutants in the whole water effluent to levels that would not be chronically toxic to aquatic organisms.


Figure 4 f. Best-fit model for predicting and actual toxicity units (TUs) in aerobic water using total Al and total Mn in the ReRAPS wetland during 2001. The $95 \%$ confidence interval for the means of the prediction lines is presented.

### 4.3.2 Toxicity Testing Chemistry

The toxicity of the ReRAPS water that was collected from various nodes was evaluated to test the hypothesis that the treatment system was removing all of the chronically toxic agents. Water samples collected for toxicity testing were chemically analyzed and tested for chronic toxicity to the larval fathead minnow and Ceriodaphnia duhia. The predominant constituents of toxicity in the CPR and in the ReRAPS wetland are the dissolved trace metals. Therefore. a total and dissolved trace metal TU for each of the samples was calculated to determine a semi-qualitative "cumulative" toxicity assessment of the samples. The samples were also analyzed for the presence of other toxic agents such as. ammonia. along with semi-volatile and volatile organic compounds.

Conductivity levels and the GRI model were also used to determine if major ion toxicity was possible.

Results of the water chemistry and toxicity testing analyses for the 17 grab samples collected from the wetland nodes are presented in Appendix G. As previously described. the toxicity units (TUs) that were calculated based on the total priority metal pollutant concentrations from the 41-day 2001 monitoring period, indicate that chronic levels of trace metal toxicity should exist upstream from the RAPS component (<N5). An evaluation of the total and dissolved TUs for the 17 toxicity testing samples, also indicates that chronic toxicity effects may be expected in the upstream portion of the wetland (<N5). The maximum calculated TU value among the toxicity testing samples was in a sample collected from the detention pond outlet (N2). The total (unfiltered) TU was 3.9 and the dissolved ( $0.45 \mu \mathrm{~m}$ filter) TU was 0.9 . The availability of the free trace metal ion is expected to affect the toxicity of the wetland water. Therefore, the semiqualitative TUs for both the dissolved fraction and total metal in the water column represents a possible range of toxicity that may be bracketed by these values. As expected, the total and dissolved TUs values are correlated ( $R^{2}=0.81, \mathrm{p}<0.01$. Figure 45) due to the predominance of the dissolved fraction over the suspended fraction in the wetland. Figure 45 also indicates that four of the samples may contain chronically toxic trace metals that approach or exceed $1.0 \mathrm{TU}(\mathrm{TU}>\approx 0.4$. based on total or dissolved cumulative trace metal concentrations).


Figure 45. Scatter plot correlating dissolved and total toxicity units measured in the 17 toxicity testing samples. The best-fit line and $95 \%$ confidence interval of the mean are provided.

Laboratory and field measurements indicate that the non-metallic parameters in the CPR and ReRAPS were not toxic to aquatic life. Conductivity values in the toxicity testing samples were less than $1037 \mu \mathrm{~S} / \mathrm{cm}$. indicating that the major ions are not approaching levels ( $>2000 \mu \mathrm{~S} / \mathrm{cm}$ ) that would be acutely toxic (Goodfellow et al., 2000). The ammonia levels in the toxicity testing samples are all considered non-toxic. The measured total ammonia concentrations in all of the toxicity samples collected were less than $0.24 \mathrm{mg} / \mathrm{L}$ as N at pH of 8.9. The calculated EPA CCC at pH 8.9 is $0.29 \mathrm{mg} / \mathrm{L}$ as N (EPA. 1999: Stephen et al.. 1998). The analyses of 116 volatile and semi-volatile organic
compounds in five of the samples submitted for toxicity testing did not detect any organic compounds, even with MDLs ranging from 0.5 to $8 \mu \mathrm{~g} / \mathrm{L}$.

### 4.3.3 Chronic Toxicity Testing

Evaluations of the survivability of the test species along with the growth and reproduction measurements were used to determine if the wetland was removing toxic constituents from the CPR. Finally, after a series of statistical routines. a logistic regression model was developed from all of the chemical data, including various transformations, to determine which factors may be controlling the removal of toxicity in the ReRAPS wetland.

Direct toxicity testing of the 17 water samples indicated that the water within the treatment wetland was always acutely toxic upstream from the RAPS component (N1 and N2. I sample per node). However, some residual chronic toxic effects still existed in some of the treated water downstream from the RAPS component ( $>$ N5. 8 toxic samples of 14). As described in Section 3.15, these test were performed according to EPA protocol (EPA, 1994b).

Chronic C. dubia toxicity data were collected for 17 samples and chronic fathead minnow toxicity data were collected for 11 samples. The chronic toxicity data are presented in Tables 14 and 15, along with the respective test group controls which were performed using laboratory dilution water. During each of the tests. 4 replicate fathead minnow treatments and 10 replicate $C$. dubia treatments were evaluated to determine the effects of the whole wetland water ( $100 \%$ ) on the organisms.

Table 14
Mean Fathead Minnow Survival (\%) and Growth (g) in II Water Samples (4 replicates per sample) used to Test for Toxicity in the ReRAPS Wetland

|  | Test Groups |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 12 March 2001 |  |  | 25 April 2001 |  |  |
|  | Minnow Survival (\%) | Wgt, g/surv. \# <br> (g) | Wgt, g/initial \# (g) | Minnow Survival (\%) | Wgt, g/surv. \# (g) | Wgt, g/initial \# <br> (g) |
| Control | 86.67 | 0.3233 | 0.2975 | 98.33 | 0.4103 | 0.4033 |
| N1 | 6.67 | 0.0250 | 0.0067 | . |  |  |
| N2 | 0 | . | 0.0000 |  |  |  |
| N6 | . | - | . | 93.33 | 0.4049 | . 3766 |
| N7 | 80.00 | 0.3566 | 0.3070 | 43.33 | 0.4893 | 0.1983 |
| N8 |  | . | . | 28.33 | 0.4523 | 0.1300 |
| N9 | . | . | . | 43.33 | 0.4999 | 0.2183 |
| N10 |  | . |  | 48.33 | 0.3469 | 0.1683 |
| N11 |  | . |  | 66.67 | 0.5168 | 0.3183 |
| N12 | 85.00 | 0.4150 | 0.3686 | 71.67 | 0.4160 | 0.3033 |
| Note. Two fathead minnow growth metrics are measured: the final dry weight of surviving larvae divided by the surviving number of larvae ( $\mathrm{Wgt} . \mathrm{g} /$ surv. \#) and the final dry weight of surviving larvae divided by the number of larvae used to start the testing (Wgt. g/initial \#). |  |  |  |  |  |  |

Table 15
Mean Ceriodaphnia dubia Survival (C.d. Surv.) and Reproduction (C.d. Repr.) for 17 Samples ( 10 replicates per test) used to Test for Toxicity

|  | Test Groups |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 12 Mar | h 2001 | 2 April 2001 |  | 25 April 2001 |  | 17 May 2001 |  |
|  | C.d. Surv. (\%) | C.d. <br> Repr. <br> ( ${ }^{(1)}$ | C.d. Surv. (\%) | C.d. Repr. (H) | C.d. Surv. (\%) | C.d. Repr. <br> (\#) | C.d. Surv. (\%) | C.d. Repr. (\#) |
| Control | 100.0 | 18.9 | 100.0 | 20.6 | 100.0 | 20.8 | 100.0 | 18.4 |
| N1 | 0.0 | 0.8 | . | . | . | . | . |  |
| N2 | 0.0 | 0.0 | . | . | . | . | . |  |
| N4 | - | - | - | - | . | . | 100.0 | 14.3 |
| N6 | . | . | . | . | 100.0 | 22.0 | 100.0 | 5.3 |
| N7 | 100.0 | 15.5 | . | - | 100.0 | 11.7 | 100.0 | 16.6 |
| N8 | . | - | - | - | 100.0 | 0.4 | . | . |
| N9 | . | - | - | - | 100.0 | 19.5 | 90.0 | 10.2 |
| N10 | . | - | . | - | 100.0 | 13.0 | . | . |
| N 11 |  | - | - | . | 100.0 | 17.5 | . |  |
| N12 | 100.0 | 7.1 | 100.0 | 1.0 | 90.0 | 21.7 | 100.0 | 19.5 |

Three chronic toxicity testing metrics were measured during the fathead minnow testing (Table 14). Fathead minnow survival (\%) is based on the average survivability of 15 larvae among 4 replicate tests. Fathead minnow growth (grams dry weight) was evaluated using two different metrics which are presented in Table 14; (1) based on the number of surviving larvae ( $\mathbf{W g t}, \mathrm{g} /$ surv. \#) and (2) based on the initial 15 larvae used in each of the test replicates (Wgt, g/initial \#). The measure of growth that is based on the initial number of organisms would reflect the effects of both survivability and weight loss, whereas a growth measure based on the number of surviving larvae would reflect the effects on weight loss alone.

Ceriodaphnia survival is based on the overall survivability of 10 adults per test. One adult was placed in each of the 10 test containers and were evaluated for survivability over the 7 day test period. C. dubia reproduction was evaluated by counting the number of neonates produced by each adult. One adult was used in each of the 10 test replicates.

Testing of differences for C. dubia survival was performed using the Non Parametric Fishers Exact Test (SPSS, 1999) because only one adult was used in each of the test replicates. Results of the Fisher Test clearly indicate ( $p<0.001$ ) that the samples from the CPR (N1) and detention pond outlet (N2) were toxic to C. duhia survival (Figure 46). whereas C. dubia survival was $95 \%$. or greater. further downstream (N4-N12).

Control results were not significantly different among the test groups for fathead minnow survival, fathead minnow growth, or for C. dubia reproduction. Therefore, the results are combined based on the control and the node where the samples were collected in order to evaluate the relative reduction of toxicity as the treated water was routed through the wetland nodes. The Levene's Test (SPSS. 1999) for equality of variance
determined that the spread of the nodes and of the control were significantly different ( $p<0.05$ ) for the remaining metrics. Therefore, a Dunnetts T3 nonparametric analyses was performed to evaluate fathead minnow survival, fathead minnow growth, and $C$. dubia reproduction at each of the sampled nodes relative to the pooled control values.


Figure 16. C. dubia survival pooled by sample node and control group for 17 wetland samples.
C. dubia reproduction was reduced from 19.6 neonates per adult (control) to 14.0 neonates per adult in the downstream nodes (N4-N12) (Figure 47). Significant reductions were observed at N7 $(p=0.012)$, N8 ( $p=0.003$ ), and N12 ( $p<0.001$ ). Spurious reproduction results were thought to be associated with the N8 sample when it is observed that the three samples from N7 and two samples from N9 experienced only slight decreases in reproduction. However, upon further examination, which will be discussed later, it was determined that the toxicity results from N8 were valid.


Figure 47. C. dubia reproduction pooled by sample node and control group for 17 wetland samples. The dashed horizontal line represents the control mean.

Results of the Dunnets T 3 analyses clearly revealed that the $\mathrm{CPR}(\mathrm{N} 1)$ and the detention pond outlet ( N 2 ) were highly toxic to fathead minnow survival when compared to the control ( $\mathbf{p}<0.001$, Figure 48). As with C. dubia (Figure 46), there was no survival of fathead minnows in either of these two samples. A reduction (although not significant) in fathead minnow survival in the downstream portions of the wetland was evident. It should be noted that significant fathead minnow survival reductions in the downstream portions of the RAPS were only observed at $\mathrm{N} 8(\mathrm{p}=0.001)$. As with the C. dubia reproduction. these results were thought to be spurious in nature but were later found to be valid. Significant reductions in the growth of surviving fathead minnows (Figure 49) in the downstream portions of the ReRAPS (N6-N12) were not detected.


Figure 48. Fathead minnow survival for the eleven samples (4 replicate tests per sample). Means and $95 \%$ confidence intervals are presented for test replicates which are pooled by control and sample node. Dashed reference lines denote the control mean.


Figure 49. Fathead minnow growth metrics (average weight of surviving larvae and average weight based on initial number of larvae in test) for the eleven samples ( 4 replicate tests per sample). Means and $95 \%$ confidence interval are presented for the test replicates. which are pooled by control and sample node. Dashed reference lines represent the control means for the two growth metrics.

### 4.3.4 Factors Explaining ReRAPS Toxicity Variability

A matrix scatter plot presented in Figure 50 correlates the toxicity parameters for the sixteen C. dubia and eleven fathead minnow chronic toxicity tests (Section 4.2 .6 for scatterplot explanation). An obvious correlation ( $R^{2}=0.98, p<0.01$ ) with fathead minnow survival occurs with fathead minnow growth when growth is normalized using the initial number of larvae used in each test replicate ( $\mathrm{n}=15$ ). Without normalization. a poorer correlation exists between fathead growth of the surviving larvae and fathead minnow survival ( $R^{2}=0.59 . \mathrm{p}<0.05$ ).


Figure 50. Matrix scatter plot for the chronic toxicity metrics: C. dubia survival (C.d. Surv). C. dubia reproduction (C.d. Repro), fathead minnow survival (FHM Surv), fathead minnow growth of surviving larvae (Wgt./Surv.\#). and fathead minnow growth normalized for the initial number of larvae used in the test (Wgt./Initial\#, $n=15$ ).

An apparent cross species correlation exists concerning the toxic effects of the whole water samples. Fathead minnow survival is significantly correlated with C. duhia reproduction ( $R^{2}=0.78, \mathrm{p}<0.01$ ). When one assumes that the energy requirements for
fathead minnow survival are greater than those for $C$. dubia reproduction, then these results would indicate that the fathead minnow is more sensitive to the toxic effects of the water samples than C. dubia.

Another evaluation of the apparent toxic effects to fathead minnow survival and C. dubia reproduction reveal that the correlated effects are gradual and are indicative of a possible dose response. Average fathead minnow survivals ranged from 0 to approximately $100 \%$ and C. dubia reproduction ranged from 0 to approximately 20 neonates.

Therefore, based on the possibility of a dose response effect. hierarchical cluster analyses was used to examine complex associations between the correlated chronic toxicity metrics and the chemical parameters which were measured in the water samples used for the toxicity testing. A tree diagram (dendogram) produced by SPSS (1999) is presented in Figure 51. Factors or parameters, which are linked to each other by short branches. are more correlated than those linked by longer branches. The shortest branches are signifying correlation coefficients that are close to 1 . Connected vertical lines designate joined variables. which form a cluster of correlated variables. Based on the results of the cluster analyses. a simple relationship between the toxicity metrics and the chemistry does not exist and suggests that any cause and effect relationship would be multivariate in nature.


Figure 51. Dendogram (SPSS, 1999) for clustering of the chronic toxicity metrics C. duhia reproduction (C.d. Reproduction). C. dubia survival (C.d. Survival). and fathead minnow survival (FHM Survival) with the water chemistry variables and select transformations.

Another set of cluster analyses were performed so that similar water samples may be grouped according to their respective toxicity testing metrics and according to their respective water quality. The sample from N8 was eliminated from the cluster analyses due to the assumed spurious toxicity results. The results of the sample grouping based on toxicity ( $\mathrm{n}=11$, Cd reproduction, FHM survival, FHM survival growth, and FHM growth based on initial number of larvae per test replicate) are presented in Figure 52. The grouping of samples based on water quality parameters (Figure 53) used the same variables as those used to produce the results in Figure 51.


Figure 52. Dendogram for clustering of samples based on toxicity metrics. Only samples where both species were evaluated are combined in this analysis.


Figure 53. Dendogram for clustering all of the samples based on the water quality variables used in Figure 51.

The results of the sample clustering based on toxicity (Figure 52) and water quality (Figure 53) reveal that the samples from nodes N 1 and N 2 were separately grouped from the downstream nodes. This similar grouping presupposes that differences in the toxicity among the samples can be explained by the differences in the sample contents.

Intuitively the differences in toxicity between the upstream ( N 1 and N 2 ) and downstream portions (>N5) of the wetland were likely due to differences in the metal content of the water. However, the variability in toxicity within the downstream portion of the wetland ( $>\mathrm{N} 5$ ) was difficult to ascertain. A principal component factor extraction method was used to develop nonlinear combinations of water quality variables, which could be used to generate hypotheses regarding causal mechanisms for the toxicity. Discriminant analyses were performed to develop water quality factors that would best explain the variability within samples grouped by toxic effects (acute vs. chronic) or by wetland location (upstream vs. downstream). Neither of these methods was successful. Finally, a logistic stepwise multiple regression technique was used to select the water quality variables that best explain the toxicity associated with the 11 samples where both the fathead minnow and C. dubia were tested. The cluster analyses techniques were helpful in determining which variables to evaluate without violating the non-linearity assumptions in the final models.

The regression technique found that dissolved Zn , total Mn . and dissolved K best explained the variability ( $R^{2}=0.95$. $p<0.001$ ) associated with fathead minnow survival. A separate analyses found that the natural $\log$ transformation of dissolved TU (cumulative dissolved Zn and Ni toxicity units) and dissolved Mn best explained the variability ( $R^{2}=0.78, \mathrm{p}=0.003$ ) associated with $C$. dubia reproduction.

Figure 54 presents the relationship between the best-fit water quality variables and the toxicity metrics (Section 4.2 .6 for scatterplot explanation). Based on the cluster analyses presented in Figure 51, the initial variables selected to explain the chronic toxicity for both species are related. As expected, dissolved TU is highly correlated with the dissolved priority metal pollutants (i.e., dissolved Zn and Ni ) and both forms of Mn (total and dissolved) are highly correlated because most of the Mn exists in the dissolved state. Collinearity between the two predictor variables, transformed TUs and Mn. is not a problem because the correlation between the predictor variables are $R^{2}<0.9$ (Kleinbaum et al., 1998).


Figure 5t. Scatter plot for $\ln$ (dissolved TUs), dissolved Zn . dissolved Ni, total Mn. dissolved Mn . and dissolved K versus fathead minnow survival and C. duhia reproduction.

Therefore, the water quality variables in Figure 54 were applied to the development of a logistic regression model which could be used to predict the probability of fathead minnow survival and C. dubia reproduction. The probability of fathead minnow survival was based on the initial number of larvae ( $\mathrm{n}=15$ as $100 \%$ survival) per test. The probability of C. dubia reproduction was based on the average number of neonates produced in each of the test controls (test control $=100 \%$ reproduction). If the average neonate production from the water samples exceeded the test control, the reproductive probability value was therefore assigned $100 \%$. Subsequent analyses found that including K (dissolved potassium) in the model improved the $R^{2}$ by only $7.7 \%$. Given the small sample size, a two variable model based on the log-dissolved TU and dissolved Mn was developed for the final equation (Table 16). $R^{2}$ for the final regressions were 0.861 for $C$. dubia reproduction and 0.838 for fathead minnow survival.

Table 16
Regression coefficients for final logistic regression equations

|  | 7 Day C. dubia <br> Reproduction | 7 Day Fathead <br> Minnow Survival |
| :--- | ---: | :---: |
| Constant | -15.44768 | -7.03116 |
| LN(D-TU) | -3.01943 | -1.42793 |
| D-Mn | 12.95287 | 3.67786 |
| Model $R^{2}$ | 0.861 | 0.838 |

Note. The units for the dissolved metals are $\mathrm{mg} / \mathrm{L}$.

As a means to visually evaluate the fit of the data sets to the regression equations, the predicted survival and reproduction values were plotted against the actual values (Figure 55). Jackknife residual plots indicate good overall quality of fit (random pattern with no obvious trends) for both models with reasonable residuals (Figure 56). The graphical analyses of the residuals between the observed and predicted values for both models indicate the there are no systematic residual trends or patterns for the limited number of data points used (Kleinbaum et al., 1998).


Figure 55. Scatter plot comparing the predicted fathead minnow survival and C. dubia reproduction to the actual test values. The sample nodes are also labeled.


Figure 56. Scatter plot comparing the predicted fathead minnow survival and C. dubia reproduction to the residuals associated with each model. The sample nodes are also labeled.

### 4.3.5 Evaluation of Toxicity Testing Chemistry Using the GRI Model

The elimination of $K$ from the model is supported by the application of the GRI (major ion) model. Figure 57 presents the average percentage of the major ions which contribute toxicity according to the model (Table l) in the toxicity testing samples collected upstream and downstream from the RAPS component outlet (N5). Note that K represents only a small percentage of the ionic composition and that $\mathrm{Ca} . \mathrm{Na}$. and Mg are the predominant cations. An increase in the bicarbonate ion $\left(\mathrm{HCO}_{3}\right)$ downstream from the RAPS is due to the dissolution of limestone.


Figure 57. Molar composition for the major ions in the toxicity testing samples.

Using the molar composition of the wetland water the GRI model was used to determine if acute toxicity due to osmotic stress was possible. The application of the model is presented in Figure 58. The model was applied using a consistent molar ratio (Figure 57, N6-N12) of major ions but at increasing concentration. thereby increasing the total dissolved solids, which represent the cumulative total of the major ions. The model predictions for $C$. dubia survival were performed using a 1 and 2 cation model. Model predictions for both species were evaluated by doubling the actual major ion concentrations in an attempt to estimate any long-term chronic effects. The cumulative concentrations of major ions in the ReRAPS wetland are also indicated. The application of the model would suggest that major ion toxicity in the wetland does not exist. The removal of any protective effects due to the presence of multiple cations fails to predict acute toxicity in the ReRAPS. Doubling the ionic concentrations in an attempt to mimic any chronic effects also fails to predict any toxicity. Furthermore the model also
suggests, when using the ionic composition of the toxicity testing samples (Figure 57, N6-N12), that C. dubia would be more sensitive to the wetland water than the fathead minnow (Figure 58). This is in contrast to the results of the eleven concurrent tests, which reveal that in the later portions of the wetland (N4-N12), fathead minnows experienced greater toxicity sensitivity to the water. As previously discussed, fathead minnow survival is correlated with $C$. dubia reproduction (Section 4.3.2, Figure 50) and the energy requirements for fathead minnow survival are greater than $C$. dubia reproduction. Therefore, the application of the GRI model has indicated that the ionic composition of the ReRAPS is not toxic and that the greater sensitivity of the fathead minnow is indicative of toxicity that is not attributable to the major ions.

$\longrightarrow C . d ., 48 \mathrm{hr}, 2$ Cations
$\multimap$ C.d., 48 hr, 1 Cation
$\longrightarrow-C . d ., 48 \mathrm{hr}, 2 \times$ ion Conc., 1 Cation ——C.d., $48 \mathrm{hr}, 2 \times$ ion Conc., 2 Cations
——FHM, 96 hr
_- N6-N12 Chemistry
$\longrightarrow$ FHM, $96 \mathrm{hr}, 2 \times$ Conc.

- -N1-N4 Chemistry

Figure 58. Application of the GRI model for predicting major ion toxicity to (. chubia (C.d.) and fathead minnow (FHM) in the ReRAPS wetland at various cumulative dissolved ion concentrations. Vertical reference lines represent the average major ion concentration in the upstream (N1-N4. $470 \mathrm{mg} / \mathrm{L}$, right line) and downstream portion of the wetland (N6$\mathrm{N} 12,400 \mathrm{mg} / \mathrm{L}$, left line).

For the following reasons the weight-of-evidence would therefore suggest that the primary agents of toxicity in the ReRAPS are the dissolved priority metal pollutants, Zn and Ni .

- The concentrations of other constituents that are known to cause toxicity to aquatic life were either not detected (i.e., organic compounds) or were found to exist at levels below the EPA CCC (i.e., nonionized ammonia) (EPA, 1999).
- Application of the GRI model (Mount et al., 1997) has determined that major ion toxicity does not exist in the wetland (Figure 58).
- The free trace metal ions are toxic and additivity among individual ion toxicities is acceptable when describing the trace metal mixtures, at least from an empirical standpoint (Figure 43).
- Detectable levels of dissolved Cu were not detected in the toxicity testing samples. However, it is reasonable to assume that the LN(dissolved TU) variable may be appropriately applied if dissolved Cu were present. based on the previous finding.
- The selection of the LN (dissolved TU ) factor in the logistic regression model that predicts toxicity in the ReRAPS is consistent with the Biotic Ligand Model(BLM. Figure 2. Table 16).
- The apparent amelioration of trace metal toxicity by $\mathbf{M n}$ is also consistent with the BLM and has been determined to be additive in nature. Mn may be considered a competing ion in the BLM (Figure 2). Using logistic regression techniques. Mn has been shown to reduce the chronic toxicity of Ni and Zn to two


## different test species in a treatment wetland environment (Figure 55).

- No other water quality factors (including TDS) were able to explain the variability associated with $C$. dubia reproduction and fathead minnow survival in the downstream portion of the wetland (>NS).

It should also be noted that the development of the logistic regression model was initially developed without the "apparent" spurious toxicity results from N8. Further development of the model using the transformed dissolved TU and dissolved Mn allowed for the explanation of the apparent spurious results from N8. This further supports the concept that some type of relationship exists where dissolved Mn in the water may have a protective effect against the trace metals.

An extrapolation of the trace metal/Mn model was performed within the limits of the toxicity testing water quality conditions (Figure 59). The natural $\log$ transformed values for dissolved TU ranged from -5.3 to -0.13 , and dissolved Mn ranged from 0.0 to $0.98 \mathrm{mg} / \mathrm{L}$. Based on these model results, dissolved TUs as low as $1 / 100^{\text {th }}$ of the respective EPA CCC were found to be toxic to the test organisms. However, $1 / 100^{\text {th }}$ of the respective EPA CCC is predicted to be non-toxic in the presence of dissolved Mn at levels of $0.5 \mathrm{mg} / \mathrm{L}$.

The development of these models presented in Table 16 are based on very limited field data. Because of the low number of samples used to develop the model. both field tests and laboratory tests are required to confirm the possible protective effects of Mn against trace metal toxicity at the chronic levels.


Figure 59. Application of the dissolved $\mathrm{TU}+\mathrm{Mn}$ model for predicting the 7 d chronic toxicity to C. dubia (C.d.) and fathead minnow (FHM) in the ReRAPS wetland.

The influence that Mn may have on the combined toxicity of the trace metals was discovered with little precognition. However, the non-toxic nature of Mn (relative to the trace metals) to aquatic life is well known. For Mn to behave as a protective influence in very hard water was totally unexpected. The protective effects of competing non-toxic ions are consistent with the Biotic Ligand Model (BLM) and the major ion model (GRI model). It is ironic that Mn . may be responsible for reducing the toxicity effects of the agents for which it serves as a monitoring surrogate.

Dave Mount of the EPA (personal communicaton) hypothesized that based on the concepts in the BLM model, that it may be possible for Mn to compete with other metals for binding sites. However, he cautions "That performing and properly interpreting chronic toxicity work with metals and daphnids is really tricky because of the influence
of the food on metal speciation." Ray Arnold of the Copper Development Association. Inc. (per. Com.) suggests that "from a competition stand point one would not expect Mn to be a player but it might be involved in some redox reactions that influence speciation and ultimately bioavailability." He also states, "It is not too surprising that the daphnid and minnow data correlate." He also would expect that the high hardness should reduce zinc toxicity but that it may have less of an effect on Ni . Sulfate may be involved in some redox reactions catalyzed by Mn.

### 4.4 Summary of Results

### 4.4.1 ReRAPS Performance

An evaluation of the long term monitoring data determined that the CPR remained contaminated over the four-year period (Section 4.1) and that the ReRAPS system had begun to perform at equilibrium with respect to alkalinity production during the third year of operation (Section 4.1.2). Alkalinity production concentrations of over $200 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ were achieved during the first 2 years of operation.

Significant differences existed during the intensive 41-day monitoring period with contaminant removal, alkalinity generation. and contaminant loading within the wetland between stormwater runoff events (Section 4.2.1). Based on the evidence of significant contaminant and alkalinity differences, the contaminant removal and alkalinity generation rates were determined for the major wetland components (Section 4.2.2). Approximately $35 \%$ of the CPR acidity, $59 \%$ of the AI. and $\mathbf{8 2 \%}$ of the Fe were removed in the detention pond. The remaining acidity and AI were primarily removed in the RAPS component. Most of the Mn was removed in the settling basin (71\%) with the remaining amounts being removed further downstream in the drains and basins. RAPS alkalinity generation
( $25.1 \mathrm{~g} / \mathrm{d}-\mathrm{m}^{2}$ ) was similar to other systems where influent acidity levels were relatively low (Section 4.2.3). The influent acidity had the greatest affect on alkalinity generation, therefore, any acidity entering the RAPS component was neutralized (Section 4.2.4). Other factors such as increased water retention and increased oxygen consumption (i.e., lower DO) also improved alkalinity generation in the RAPS component. As expected, the neutralization of CPR acidity and the concomitant increase in pH were the primary factors affecting Fe and Al removal in the detention pond (Section 4.2.5). Therefore, a net alkalinity value of $\mathbf{- 2 0}$ to 0.0 can be used along with sufficient retention ( $>48 \mathrm{~h}$ ) when designing a recirculating detention pond for optimal Fe and Al removal. The mass balance of net alkalinity in the detention pond suggests that the design of the entire ReRAPS wetland is controlled by the ratio of the mass loading of CPR acidity and the recirculated alkalinity.

### 4.4.2 Toxicity Removal

The seven priority metal pollutants detected in the CPR in decreasing concentrations are $\mathrm{Zn}>\mathrm{Ni}>\mathrm{Cu} \gg \mathrm{Cr} \gg(\mathrm{Se}, \mathrm{Cd}, \mathrm{Pb})$ (Section 4.3.1). After normalizing the concentrations based on the EPA Criterion Continuous Concentration (CCC) the metals (unfiltered) which were present at concentrations greater than the MDL may contribute to the toxicity of the wetland water in the following decreasing order: $\mathrm{Cu}>\mathrm{Ni}>\mathrm{Zn} \gg \mathrm{Cd}$ >> Cr (Figure 43). Contrary to what has been reported. Mn was found to be a good predictor of trace metal toxicity in the aerobic ReRAPS water based on a highly significant correlation with the total (unfiltered) trace metal TUs (Figure 44).

The acute toxicity of CRP was significantly reduced by the ReRAPS treatment to near non-toxic levels. Water quality analyses of the toxicity testing samples found no
indication of potential non-metallic toxicity in the ReRAPS (Section 4.3.2). Toxicity testing using Ceriodaphnia dubia and fathead minnow found that the chronic toxicity effects were variable in the latter portion of the ReRAPS (Section 4.3.3). A logistic regression analysis found that the cumulative TUs (natural $\log$ transformed) based on the dissolved concentrations of Zn and Ni best explained the toxicity variability in both species when adjusted for Mn concentrations (Section 4.3.4). An evaluation of the toxicity testing samples using the GRI model (Section 4.3.5) and measurements of conductivity (Section 4.3.2) both indicate that the major ions have relatively little effect on the short term chronic toxicity. Therefore, the "weight-of-evidence" suggests that the priority metal pollutants. Zn and Ni . are primarily responsible for the toxicity. Although Mn was found to behave as a surrogate for the trace metals, Mn ironically was determined through a series of cluster analyses, and logistic regression techniques. to have a possible protective effect against trace metal toxicity in the later portions of the wetland. Further field and laboratory toxicity tests should be performed to confirm the protective effects of Mn .

## CHAPTER 5 CONCLUSIONS

Many full-scale RAPS-based systems have been built and are successfully treating AMD. However, few, if any, have been constructed to treat CPR, and none have been as extensively studied as Alabama Power's Plant Gorgas constructed wetland. Specifically, intensive studies were conducted to better understand metal removal and the concomitant reduction in toxicity. Over 1,800 water samples from the CPR and wetland including over $\mathbf{8 0 , 0 0 0}$ individual laboratory and field measurements, have been analyzed during the research into the performance of this ReRAPS wetland.

Most RAPS-based systems have been constructed with partial contaminant removal as a goal. However, this system has surpassed the typical $3 \mathrm{mg} / \mathrm{L} \mathrm{Fe}$ and $2 \mathrm{mg} / \mathrm{L} \mathrm{Mn}$ NPDES limitation and achieved near complete removal of the EPA priority pollutants from CPR, with only minimal chronic levels of toxicity remaining in the whole water effluent. The extensive monitoring and the gradual treatment processes associated with this constructed wetland allowed for an evaluation of the predominant contaminant and toxicity removal factors associated with the performance of this treatment system.

The pumping and recirculation of treated water to a detention pond prior to a RAPS component defines the ReRAPS (Recirculating-Reducing and Alkalinity Producing System) design concept. Intensive water quality and hydrologic monitoring results prove that the ReRAPS design shifts the primary component for contaminant removal from the RAPS. upstream to a detention pond (Figures 1 and 27). Complete removal of the trace metal toxicity associated with the CPR seems possible with ReRAPS treatment.

Ironically, the complete removal of the trace metals surrogate, Mn. may have undesirable toxicity enhancing effects in the later portion of the wetland and requires further study (Section 4.3.4). It should also be emphasized that this relationship was found in this study alone and the relationship between Mn and other trace metals in mixed waters with high hardness has not been established in other studies. It is recognized, however. that the interpretation of chronic toxicity results with metals is fraught with uncontrollable variables such as the influence of the food on metal speciation, disease effects, and proper controls. Further field and laboratory testing is required to confirm the protective effects of Mn .

The treatment successes of the Plant Gorgas ReRAPS wetland treatment system along with results from the extensive monitoring effort and the operational experience are combined to provide some concluding recommendations concerning the applicability of the ReRAPS for treating various acidic waste streams and runoff (Section 5.1). Section 5.2 presents a list of topics that require research and will enhance the development of constructed wetland technology. Finally, specific ReRAPS design calculations for treating various amounts of acidic runoff are presented in Section 5.3. The design recommendations and calculations should be interpreted in the context that the ReRAPS wetland is a stormwater treatment system. which operates primarily during the winter and spring months when runoff from the coal pile occurs. However, the level of contaminants can be compared to other coal related acidic runoff requiring treatment. The average CPR concentrations were $12.8 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Fe} .24 .9 \mathrm{mg} / \mathrm{L}$ of aluminum. $2.9 \mathrm{mg} / \mathrm{L}$ of manganese. and $178.0 \mathrm{mg} / \mathrm{L}$ of acidity during the fourth year of operation. The treatment of the Plant Gorgas CPR would be comparable to the treatment of
continuously flowing AMD ( 30 gpm ) with similar concentrations. Also, it should be emphasized that data presented in this study is based on treatments performed during some of the cooler months of the year. The RAPS water temperatures ranged from 9 to $15^{\circ} \mathrm{C}$ and therefore represent an accurate assessment of the ReRAPS applicability during the winter in the southeastern United States.

### 5.1 ReRAPS Design Recommendations

### 5.1.1 Recommendations for Characterization of CPR

The optimal ReRAPS design requires an accurate acidity characterization of the runoff or waste stream requiring treatment. The characterization of the CPR acidity prior to the construction of the Plant Gorgas ReRAPS treatment wetland was woefully inadequate and over-predicted the severity of the contaminated runoff that would require treatment (Section 3.3). The design of treatment systems for CPR must consider the possibility of acidic salt accumulations within the coal pile area. Coal storage facilities traditionally use some form of containment for maintaining the coal pile. However, a bowl shaped containment area may encourage the development of evaporative pools. which over time, contribute to the build up of acidic salts. If the containment area is properly drained for constructed wetland treatment, the accumulated salts will quickly diminish. The amount of acidity produced would then be in equilibrium with factors affecting pyrite oxidation in the coal pile.

The proper evaluation of the CPR loading requires frequent sampling ( $\sim 1 /$ hour) so that the true contaminant loading can be accurately assessed. Samples collected from stagnant pools at the base of a coal pile will over-estimate the loading of contaminants
requiring treatment. Grab samples collected during stagnant (pooled) time periods may represent only a small portion of the overall runoff volume.

### 5.1.2 Monitoring Required for Proper Performance Evaluation

An accurate assessment of the wetland performance requires long term multi-year monitoring of the treatment system and frequent sampling. Based on the alkalinity monitoring, the performance of the ReRAPS had come into equilibrium or had stabilized after two years of operation (Section 4.1.2). These results indicate that evaluations of RAPS-based treatment systems should include long term monitoring ( $>3$ years). The samples should continue to be collected until after a stable performance period has been identified. Sample collection should be performed more frequently in the upstream nodes during active flowing events with a continuous measurement of the flows.

### 5.1.3 Recommendations for Occasional Compost Additions

All contaminant removal processes are directly or indirectly related to the generation of alkalinity in the RAPS. The RAPS component was constructed based on conventional designs, which recommend a minimum 15 hours of retention (Kepler \& McCleary, 1994: Skovran \& Clouser, 1998). The RAPS component generally remained stagnant and full during the summer and fall months due to infrequent runoff events and direct precipitation. Results from the winter and spring long-term monitoring have clearly determined that bacterially-derived alkalinity production is limited and decreases with operational age (Section 4.1.2). The bacterially-derived alkalinity generation would likely be enhanced by occasional additions of compost augmented with limestone sand. Augmentation with limestone sand creates an optimal microhabitat for the reducing
bacteria. Further evaluation of alkalinity generation using occasional compost additions is needed to determine the operational benefits of the technique.

### 5.1.4 RAPS Retention and Alkalinity Production Recommendations

Without the potential benefits of regular compost additions, alkalinity generation is primarily dependent on the dissolution of limestone in a mature (>3year old) system and the dissolution of limestone is affected by the RAPS influent (non-Mn) acidity. The production of excess alkalinity from the RAPS is primarily affected by the production of bacterially-derived alkalinity (Section 4.2.4). Therefore, the production of alkalinity in a ReRAPS would be improved during the cooler months if the minimum retention were increased from 15 hours to approximately 24 hours. Given sufficient retention a RAPS component can produce $>40 \mathrm{mg} / \mathrm{L}$ of alkalinity when limestone dissolution predominates and bacterially derived alkalinity is minimal. It should be noted that this value is based on the use of high grade limestone ( $>\mathbf{9 0 \%}$ ).

### 5.1.5 Detention Pond Retention and Morphology Recommendations

It is especially noteworthy, that the modification to this wetland (i.e., partial recirculation of treated water) improved Fe and Al removal prior to the RAPS component. The removal of Fe and Al in the detention pond lessens the amount of metal hydroxides that could precipitate in the RAPS substrate. thereby extending the operational lifetime of the component. The detention pond removed $82 \%$ of the total Fe . $59 \%$ of the AI, and $35 \%$ of the acidity loading prior to the RAPS component (Section 4.2.2). Increasing the recycle rate to pumping ratio would likely increase the removal of Fe and Al in the detention pond by increasing the amount of alkalinity recycled to the detention pond. The recycle rate should be maintained so that net
alkalinity is greater than the non-Mn acidity. For the Plant Gorgas ReRAPS the optimal net alkalinity for detention pond treatment was $-20 \mathrm{mg} / \mathrm{L}$ (Section 4.2 .5 ). This, however, would require an increased pumping rate, which would reduce the retention time in the detention pond. In order to maintain the recommended 2 days retention, an increase in detention pond storage would be required (Section 4.2.5).

Therefore, the detention pond in a ReRAPS is the primary treatment component which affects the overall performance of the system. The detention pond should be designed with excess storage capacity and should be shaped with a length-to-width ratio (L/W) of at least 10 to 1 to minimize short-circuiting (Tchobanoglous \& Burton, 1991).

### 5.1.6 ReRAPS Configuration and Area Optimization

Mass balance relationships for the detention pond determined that Mn was not removed and behaved conservatively in the detention pond. However, recognizing that Mn removal often occurs only after significant removal of Fe , the early removal of Fe in the detention pond moves the locale of Mn removal from the rock drains upstream into the settling basin (Figure 1).

Based on the near complete removal of $\mathrm{Fe}(80 \%$. Figure 27$)$ in the detention pond and the reported Mn removal rates for rock drains (limestone aggregate. Sikora et al. 2000). the area of the ReRAPS could be optimized by routing the RAPS discharge directly to a rock drain. Sikora et al. (2000) recommends a 5 to $10 \mathrm{~g} / \mathrm{m}^{2} / \mathrm{d}$ removal rate for 2 cm limestone aggregate (Section 2.4.4). Therefore a ReRAPS design that includes a detention pond. RAPS and rock drain configuration can produce compliance grade effluent with $6<\mathrm{pH}<9 . \mathrm{Fe}<3 \mathrm{mg} / \mathrm{L}$ and $\mathrm{Mn}<2 \mathrm{mg} / \mathrm{L}$.

It should be noted that the absence of Mn removal in the detention pond observed in 2001 does not suggest that Mn removal will not occur there under different conditions (e.g., increased retention time, increased pH or increased alkalinity).

### 5.1.7 Rock Drain Recommendations

Placement of the rock drain immediately downstream from the RAPS should include opportunities for maximum reaeration (e.g., turbulent flow, splash pad) before routing the water through the aggregate limestone material. Aerated near-neutral water is required for optimal biooxidation of Mn (Section 2.3.5).

### 5.1.8 ReRAPS Discharge Recommendations

Soon after the Plant Gorgas ReRAPS began operation. pH exceedances of $>\mathbf{9}$ occurred at the ReRAPS discharge (N13). These exceedances were caused by the photosynthetic activity of filamentous algae in the wetland storage basin (N11-N12/13). Relocating the wetland discharge immediately after the rock drains (N10) minimized the pH exceedances. The rock drain water is routed through (down inside) 6 inch deep aggregate limestone and is shaded from the sunlight thereby preventing any photosynthetic activity or $\mathrm{CO}_{2}$ consumption.

### 5.1.9 Prevention of Algae Plugging

Occasional plugging of PVC piping were experienced at various nodes during the study. The build-up and die-off of dense mats of filamentous algae caused the plugging. Node piping inlets were buried under 3-5 inch stone to prevent future plugging. The recommended PVC piping diameter for use in the ReRAPS system is 4 inches or greater.

### 5.1.10 Recirculation of Organics

Based on the weight-of-evidence approach, the predominant toxic agents in the wetland were determined to be dissolved Zn and Ni . It should be noted that dissolved Cu was not detected in the toxicity testing samples. The recirculation and availability of organic ligands in the ReRAPS may explain the absence of dissolved Cu in the toxicity testing samples. Therefore, another possible benefit to the use of compost, is the generation of total and dissolve organic matter (DOM), which can serve as ligands that bind with free trace metal ions, thereby eliminating the toxic effect. The benefits of recirculating organic matter and the possible removal of trace metal toxicity require further study.

### 5.1.11 Treatment Required for Toxicity Removal

The results of this research may be indicative of the level of treatment required when removing chronically toxic metal agents from acidic water associated with coal production, coal-handling processes or AMD.

The value of using total Mn as a trace metal surrogate was confirmed for the treatment of CPR in the Plant Gorgas ReRAPS. The removal of Mn in the ReRAPS correlated closely with the decrease in TUs. It seems likely, that the level of Mn required for achieving removal of TUs (i.e., dissolved Ni and Zn ) is site specific and is likely affected by the ratio of Mn to trace metals in the acidic runoff. Regardless. concentration reductions to $1 \mathrm{mg} / \mathrm{L}$ were required at the Plant Gorgas ReRAPS to achieve TUs $<1$. However. it should be recognized that although Mn may have behaved as a surrogate for the presence of trace metals, it may not be appropriate to use Mn as a regulatory monitoring tool for the removal of toxicity due to the potential protective effects it may
exhibit. In other words, it may not be beneficial to design a wetland that removes all of the Mn if the treatment goal is to remove toxicity. Again, the potential protective effects of Mn against trace metal toxicity will require confirmation through additional laboratory and field toxicity research.

### 5.1.12 Recycling and Increasing Salt Concentrations

The application of the ReRAPS treatment option should consider the potential effects of concentrating ions to the levels that may be toxic due to recycling. The acute toxicity model results indicate that C. dubia would be more sensitive, and that a $20 \%$ reduction in survival may occur, if the total dissolved solids were increased from approximately 400 to $2000 \mathrm{mg} / \mathrm{L}$ (Figure 58. C.d. 48 h Survival). This analyses indicates that the salts of the ReRAP waters may be concentrated by a factor of 4 without experiencing acute toxicity effects on C. dubia.

High recycle and retention ratios, required for the treatment of highly acidic and continuously flowing drainages, may be limited by the eventual build-up of gypsum in the RAPS component. Therefore, concentrations of salts in the wetland may not maintain the ionic composition as presented in Figure 54, should the recycle ratio increase. The $\mathrm{Ca}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ ions in the wetland may be limited by the solubility of gypsum. Calculations based on the solubility product of gypsum indicate that the ReRAPS water is saturated with respect to gypsum. Gypsum accumulation in the RAPS component may have long-term operational effects due to potential plugging. However. gypsum resolubilization and the flushing of $\mathrm{Ca}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ ions from the system may be possible using upland runoff with a relatively low dissolved solids content. The fate of $\mathrm{Ca}^{+2}$ and
$\mathrm{SO}_{4}{ }^{2-}$ in the RAPS, which may be supersaturated with anhydrite ( $\mathrm{CaSO}_{4}$ ), requires further study.

### 5.2 Summary of Recommended Studies

Based on the previous recommendations concerning the application of ReRAPS design option for the treatment of acidic runoff, the following topics require further study:

- Field and laboratory short term chronic toxicity testing concerning possible protective effects of Mn and organic ligands against trace metal toxicity in RAPS-based wetlands.
a Full-scale field-tests to evaluate the benefits of regular compost additions for increasing alkalinity production.
- Effects of high recycle ratios and potential accumulation of anhydrite $\left(\mathrm{CaSO}_{4}\right)$ on ReRAPS performance.


### 5.3 ReRAPS Design Application

Aluminum and Fe are retained in a passive RAPS-based (no pump) wetland. However, it is plausible that a ReRAPS wetland can be designed to treat even the most severe acidity and continue to minimize the amount of metal precipitate in the RAPS. This intensive study of the ReRAPS has provided dependable contaminant removal rates and alkalinity generation rates for various components commonly used in most RAPSbased systems (Figure 28 and Table 12). Alkalinity production from the RAPS and the CPR acidity (non-manganese) dictates the amount of recycling and retention required to achieve contaminant removal throughout the ReRAPS.

In a ReRAPS wetland, the RAPS component is not intended to retain metal precipitates such as Al-hydroxides or metal sulfides. Rather, this component must produce alkalinity and be maintained in a chemically reduced state to prevent the accidental coating of iron oxides on the limestone surface, should an upset or high loading event occur in the detention pond.

An analysis of the ReRAPS potential to treat various types of CPR and AMD reveals that the use of the ReRAPS may be best used where (1) electrical pumping is an option; (2) enough area is available to meet the recycle and retention requirements for metal hydroxide precipitation in the detention pond; and (3) sufficient alkalinity production occurs in the RAPS. Rock drains with aeration should be used as a final component if additional Mn removal is required.

### 5.3.1 ReRAPS Design Calculations

Based on the results of this study, the following procedure and calculations can be applied when developing a ReRAPS design. The recycle ratio (recycled alkalinity to CPR acidity) is the primary design factor that controls the size and operation of the ReRAPS wetland. Equalization of runoff flow is a critical factor for treating highly variable flows. Provided enough area is available, an equalization basin can be constructed upstream from the detention pond so that the recycle ratio may be maintained, insuring a consistent ratio of treated recycle water and contaminated influent is mixing and precipitating metals in the detention pond. Assuming a steady-state treatment condition. Equation 36 is simplified when the form of acidity requiring removal in the detention pond is completely neutralized (i.e., $\mathrm{C}_{\mathrm{DP}}=0$ ).

$$
\begin{equation*}
\mathrm{C}_{\mathrm{CPR}} / \mathrm{C}_{\text {recycle }}=\mathrm{R}_{\text {recyck }} \tag{Equation46}
\end{equation*}
$$

Where:
$\mathrm{C}_{\mathrm{CPR}}=$ specific concentration of the form of acidity to be neutralize
$\mathrm{C}_{\text {recycle }}=$ concentration of alkalinity recycled to the detention pond

The removal of Fe acidity promotes the early removal of Mn in the system and may eliminate the need for a settling basin. The additional removal of Al acidity will prevent the build up of Al precipitates within the RAPS component. Mn will behave conservatively in the RAPS component and is more efficiently removed downstream from the RAPS component, either in the settling pond or in the rock drain. Therefore, increasing the alkalinity to promote the "possible" removal of Mn is not necessary. The stoichiometric calculation for acidity (Equation 9) can be used to estimate the amount of Fe and Al acidity requiring neutralization (Rose \& Cravotta. 1998). The concentration of alkalinity that can be recycled back to the detention pond is dependent on the age of the RAPS component and the use of annual or semi-annual compost additions to maintain a relatively high level of alkalinity production. Compost additions require augmentation with limestone sand to improve the microhabitat for microbial reduction activity. Depending on the level of maintenance desired. alkalinity concentrations produced and recycled back to the detention pond will range from a low of $40 \mathrm{mg} / \mathrm{L}$ which represents limestone dissolution alkalinity to over $100 \mathrm{mg} / \mathrm{L}$. which would include the additional bacterially-derived alkalinity.

The recommended retention, the contaminated runoff flow, and the recycle ratio dictate the volumes of the components. The size of the system should also account for seepage, which can severely reduce the amount of alkalinity that can be recirculated. Care should be made to insure a good clay seal to minimize the amount of seepage. The loss of water flow between the pump discharge and the recycle node should be maintained to less than $10 \%$. Simplified volumetric requirements for the detention pond, RAPS, and settling basin are calculated based on the product of the retention ratio (Equation 37), the equalized influent flow (CPR), and the recommended retention for the wetland component. The maximum probable flow and non-Mn acidity is used if the contaminant influent is highly variable. The pumping and volumetric requirements are also adjusted for seepage. Adjustments for evapotranspiration, which would effectively concentrate alkalinity, are ignored due to an assumption that the mass of net alkalinity produced by the RAPS component would not be greatly effected. Average alkalinity at N5 ( $50.1 \mathrm{mg} / \mathrm{L}$ ) was $3.6 \mathrm{mg} / \mathrm{L}$ greater than $\mathrm{N} 10(46.5 \mathrm{mg} / \mathrm{L})$ during 2001 in January through March (Appendix B).

$$
\begin{gather*}
Q_{\text {pump }}=\left(R_{\text {recycle }}+1\right)\left(Q_{\text {CPR }}\right)\left(F_{\text {seep }}+1\right)  \tag{Equation47}\\
V=\left(Q_{\text {pump }}\right)\left(\tau_{n}\right)
\end{gather*}
$$

(Equation 48)

Where:
$Q_{\text {pump }}=$ Pumping requirements including excess capacity for seepage ( $\mathrm{m}^{3} / \mathrm{d}$ )
$V=$ Volumetric requirements of the wetland component ( $\mathrm{m}^{3}$ )
$\mathrm{R}_{\text {rececle }}=\mathrm{C}_{\mathrm{CPR}} / \mathrm{C}_{\text {reçcle }}($ Equation 46)
$\mathrm{Q}_{\mathrm{CPR}}=$ Equalized contaminated influent flow ( $\mathrm{m}^{3} / \mathrm{d}$ )
$\tau_{\mathrm{n}}=$ Retention required in wetland component (d)
$F_{\text {seep }}=$ Estimated ratio of water loss due to seepage relative to the required volume of recycled flow plus influent ( $\mathrm{Q}_{\text {recycle }}+\mathrm{Q}_{\text {CPR }}$ )

The volumetric requirements of the RAPS must incorporate the minimum recommended retention in the limestone as established by Equation 48. The bulk volume of limestone producing alkalinity over an established operational life of the system. the volume of the compost, and the volume of surface water over the compost dictates the additional volumetric requirements for the RAPS component. The recommended retention values and component depths based on the performance Plant Gorgas ReRAPS wetland for various components and sub-components are presented in Table 17. Using the following removal and influent criteria from the ReRAPS, the volumetric area requirements of the component can be calculated and are also presented in Table 17.

$$
\begin{aligned}
& Q_{\mathrm{CPR}}=74 \mathrm{~m}^{3} / \mathrm{d} . \\
& \mathrm{C}_{\mathrm{CPR}}=175 \mathrm{mg} / \mathrm{L} \mathrm{Fe} \text { and Al acidity }\left(\text { as } \mathrm{CaCO}_{3}\right) \\
& \left.\mathrm{C}_{\text {recycle }}=43 \mathrm{mg} / \mathrm{L} \text { (as } \mathrm{CaCO}_{3}\right) \\
& \mathrm{R}_{\text {receclc }}=4.1 . \text { complete } \mathrm{Fe} \text { and Al removal. Equation } 46 \\
& \mathrm{~F}_{\text {scep }}=0.1 \text { or } 10 \% \\
& \mathrm{Q}_{\text {pump }}=412.8 \mathrm{~m}^{3} / \mathrm{d} \\
& \text { Limestone } \mathrm{CaCO}_{3} \text { purity }=0.9 \text { or } 90 \% \\
& \text { Limestone } 3-5 \text { inch loose bulk density }=1.547 \mathrm{~kg} / \mathrm{m}^{3} \\
& \text { Bulk limestone void percentage }=0.5 \text { or } 50 \% \\
& \text { Bulk compost void percentage }=0.5 \text { or } 50 \%, \text { augmented with limestone sand }
\end{aligned}
$$

Therefore, based on Table 16, and assuming flow equalization, approximately $4.000 \mathrm{~m}^{2}$ of working surface area is required to treat the Plant Gorgas CPR. Fe and AI are completely treated within the detention pond when only 175 of the $180 \mathrm{mg} / \mathrm{L}$ of acidity is neutralized in the detention pond. Manganese is allowed to pass conservatively through the RAPS to be treated in the settling basin.

Table 17
Recommended Component and Sub-component Retention and Depth along with Calculated Volume and Area Requirements for a Recycle Ratio of 4.1 and Influent Flow of $7+\mathrm{m}^{3} / \mathrm{d}$

| Component | Sub-component | Retention $\tau_{n}$ (d) | $\begin{gathered} \begin{array}{c} \text { Volume } \\ \left(\mathrm{m}^{3}\right) \end{array} \\ \text { Equation } 47 \end{gathered}$ | Depth (m) | Area ( $\mathrm{m}^{2}$ ) Vol./Depth |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Detention Pond |  | 4 | 1.651 .3 | 1 | 1.651 .3 |
| RAPS | RAPS Surface Water | NA | 612.5 | 1 |  |
|  | RAPS Compost | NA | 183.7 | 0.3 |  |
|  | RAPS <br> Alkalinity <br> Producing <br> Limestone | NA | 93.1 | 1.5 | 612.5 |
|  | RAPS <br> Retention <br> Limestone | 1 | 825.6 |  |  |
|  | Total RAPS |  | 1.714 .9 |  |  |
| Setling Basin |  | 4 | 1.651 .3 | 1 | 1.651 .3 |
| Overall ReRAPS without Equalization Basin |  |  | 5.017 .5 |  | 3.915 .1 |

As demonstrated, the recycle ratio and contaminant inflow dictate the morphology of the ReRAPS. However, the production of alkalinity from the RAPS will effect the size by reducing the amount of required recycle alkaline water and therefore the amount of pumping. The effect of RAPS alkalinity production on the physical size of the ReRAPS wetland is demonstrated in Figure 60. The previous calculation is based on a recycled alkalinity of $43 \mathrm{mg} / \mathrm{L}$, representing a system that primarily relies on limestone dissolution. However, regular compost renewal should easily increase RAPS alkalinity production to $100 \mathrm{mg} / \mathrm{L}$, thereby reducing the required recycle ratio from 4.1 to 1.75 (Figure 60). The reduction in the recycle ratio reduces the working surface area of the system from 0.4 to 0.2 ha (Figure 60). As presented in Figure 60, the reduction in area is more dramatic at higher influent flow rates.

The use of the ReRAPS design is limited by the severity of the influent contamination. The Plant Gorgas CPR had a total acidity of $180 \mathrm{mg} / \mathrm{L}$. which may be typical of most AMD. Although the level of contaminant loading may not theoretically limit the ReRAPS design there are practical space limitations that must be considered. Rose and Cravatta (1998) have reported of AMD with acidity (-net alkalinity) values as high as $3000 \mathrm{mg} / \mathrm{L}$ with the majority having concentrations of less than $500 \mathrm{mg} / \mathrm{L}$.


Figure 60. Estimated volumetric and area requirements for the ReRAPS wetland at various CPR flows and recycle ratios. The circle is indicative of the Plant Gorgas ReRAPS assuming equalization of CPR flow.

### 5.3.2 Operational Costs

Wetlands for the treatment of acidic runoff are used as a cost-effective low maintenance option to conventional chemical treatment systems. A limitation for the cost effectiveness could conservatively be considered a condition where the cost of electrical pump use required to meet the retention or recycle flow requirements, exceeds the cost of chemical addition. The Plant Gorgas ReRAPS pump use cost approximates one-third the
cost of base chemicals for acid neutralization $(50 \% \mathrm{NaOH}, \$ 0.1 / \mathrm{lb}$; and $\$ 0.07 \mathrm{kWh} .50 \mathrm{ft}$ head loss).

### 5.4 Summary of Conclusions

The Plant Gorgas ReRAPS wetland is an alternative RAPS-based wetland design that uses a pump and recirculates a portion of the treated water back to a detention pond which receives the acidic runoff. This study has proven that most of the acidic contaminants can be removed in the detention pond, minimizing the potential for Alhydroxide plugging in the RAPS. This study has also shown that nearly all of the toxicity as measured using the 7-day chronic toxicity tests can be removed in the ReRAPS.

Recommendations concerning the application of the ReRAPS design and further research are provided. A procedure that includes a series of simple design equations developed from this study have been scaled up to consider the treatment of acidic runoff with greater acidity concentrations and higher flow rates.

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## APPENDIX A

GARRETT, J., WILLIAM, E., BARTOLUCCI, A., A., \& VERMACE, M. E. (2001). CONSTRUCTED WETLAND RESEARCH FOR THE TREATMENT OF THE PLANT GORGAS COAL PILE RUNOFF.

# CONSTRUCTED WETLAND RESEARCH FOR THE TREATMENT OF THE PLANT GORGAS COAL PILE RUNOFF ${ }^{\prime}$ 


#### Abstract

by

William E. Garrett, Jr., Alfred A. Bartolucci, Michael E. Vermace?

Abstract. Research was conducted to study the transport and fate of inorganic pollutants through a constructed wetland using a Reducing and Alkalinity Producing System (RAPS). RAPS have been used to successfully treat acid mine drainage (AMD). This wetland is designed to treat coal pile runoff, similar to AMD. A primary goal of this research was to evaluate an alternative design that might result in improved pollutant removal. The design was based on the partial re-circulation of treated water into a detention basin, located immediately upstream from the RAPS, containing untreated water. This modification created a semi-passive RAPS-based system we refer to as a Recirculating RAPS (ReRAPS).

To test the ReRAPS modification a full-scale RAPS-based wetland capable of recirculation was constructed, operated, and monitored. Factors that may promote improved pretreatment performance in the detention pond during the ReRAPS mode were evaluated using a series of batch tank studies. The wetland monitoring and tank studies have determined that the ReRAPS modification has the potential to enhance the basic RAPS wetland design by moderating the pH of contaminated water and reducing the contaminant loading prior to the RAPS component. The batch tank studies revealed that significant amounts of inorganic contaminants could be precipitated from mixtures of AMD and treated wetland water after 24 hours. Primary factors controlling the removal were pH , initial metal concentration and retention time.


Additional Key Words: reducing and alkalinity producing system, RAPS, successive alkalinity producing system, SAPS, recirculating RAPS, ReRAPS, sulfate reduction

## Introduction

A wetland containing a Reducing and Alkalinity Producing System (RAPS) was constructed to treat coal pile runoff at the Plant Gorgas coal-fired steam electric power station. RAPS have been successfully used to treat acid mine drainage (AMD). This wetland was designed to treat acidic runoff from a bituminous coal pile.

[^1]Research was conducted to determine the merits of recirculation and to develop design data for the removal of inorganic pollutants such as aluminum ( Al ), iron ( Fe ), and manganese ( Mn ) through the RAPS-based wetland.

RAPS are designed as passive, vertical-flow systems. Watzlaf et al. (2000) clarified the terminology that describes these types of systems. In this paper, a single vertical flow component that relies on reducing organic substrate and limestone dissolution will be referred to as RAPS. More than one RAPS, operated in series with each RAPS followed by aerobic settling basins, may be necessary to treat AMD to desired discharge levels. Utilizing the terminology proposed by Watzlaf et al. (2000). a treatment system where a series of RAPS components are used in conjunction with
oxidation/precipitation basins may be more appropriately termed Successive Alkalinity Producing Systems or SAPS (Kepler and McCleary 1994).

Although similar to AMD, coal pile runoff contaminant loading is intermittent. Rain events for example, often result in "shock" loading to the system. The effects of intermittent events on contaminant removal and limestone dissolution rates in RAPS-based wetlands are not well understood. Furthermore, the long-term performance of these systems may be negatively affected by the eventual accumulation of metal precipitates within the organic and limestone substrate of the RAPS component. Pretreatment of contaminants prior to the RAPS may be one way to dampen highly variable contaminant loading, reduce plugging, reduce limestone dissolution, and ultimately increase the life expectancy of the RAPS-based wetland.

An alternative design of the RAPS system would recirculate a portion of the alkaline water produced by the system back to the detention pond, which is located immediately upstream from the RAPS component. This modification might result in the pretreatment of highly contaminated coal pile runoff, lessening the effects of "shock" loads. Recirculation would also result in increased pH in the detention pond, which would allow for the precipitation of metal hydroxides. The formation of Fe and AI hydroxides can adsorb and co-precipitate other dissolved metals (Stumm and Morgan, 1981; Langmuir, 1997). Not only would this lessen the metal loading to the RAPS component. it would also lower maintenance of the RAPS component and possibly reduce wetland size requirements. This modification to the RAPS design can be referred to as a "Recirculating RAPS" or ReRAPS.

A goal of this study has been to determine the contaminant removal rates for this newly developed ReRAPS wetland. Other goals include determining the ability of the ReRAPS to reduce metal loading and limestone dissolution in the RAPS component. In this paper, we describe the morphological, hydrological, and retention characteristics of the wetland. The performance of the wetland during the treatment of coal pile runoff resulting from a rain event is also described. This ReRAPS treatment occurred
while the wetland was in its third year of operation. The results from a series of batch tank studies designed to determine the factors that may affect metal removal in the detention pond during the ReRAPS mode of operation are also presented.

## Wetland Desina Characteristics

The Plant Gorgas wetland employs most of the RAPS-based constructed wetland technologies to date. The 0.6ha ( 2.5 ac ) wetland has been designed and constructed to treat runoff from a 4.5 ha (1 lac) coal pile storage area and is capable of operating in a "once through" RAPS mode or in a "partial recirculation" ReRAPS mode. The system is designed to produce effluent meeting the regulatory limits set by the Alabama Department of Environmental Management (ADEM). The discharge limitations are as follows: pH is to be maintained between 6 and 9. total Fe and Mn are limited to levels of less than 6 and $4 \mathrm{mg} / \mathrm{L}$. respectively, and total suspended solids to less than $50 \mathrm{mg} / \mathrm{L}$.

Approximately 1.2 ha (3ac) adjacent to the main Plant Gorgas coal pile were available for the construction of the wetland. Design factors such as mean flow rates, space limitations, and topography determined the size and type of routing within the components. A schematic of the wetland, along with morphometeric and hydraulic measurements, are presented in Figure 1. The wetland has been constructed to include twelve components and thirteen discharge nodes ( N ):

N1 Coal Pile Runoff
N2 Detention Pond
N3 Stilling Basin
N4 RAPS Component Surface Water
N5 RAPS Component Discharge Water
N6 Settling Basin
N7 Cattail Drain
N8 Aeration Drain
N9 Algae Basin
N10 Rock Drain
NII Cattail Wetland
N12 Storage (recycled water)
N13 Storage (discharged water)
Wetland Component Descriptions
The detention pond ( $\mathrm{N} \mid-\mathrm{N} 2$ ) is designed to contain a 10 year-24hr rain event (Birmingham.


Figure I. Schematic of the Plant Gorgas Wetland configuration.

AL-152mm (6in)). Coal pile runoff accumulates at the lower end of the coal pile and is routed into the detention pond through a culvert. Runoff storage is allowed to back up into the base of the coal pile during high volume events. Low and high volume events can be treated using a one or two pump combination to route water through N2 to the stilling basin (N2-N3). The recirculated water from N12 is stored in the detention pond to pretreat the next runoff event. An automatic switch activates the pumps at various presel stage elevations.

The RAPS component (N2-N5) was constructed usmg lugh-grade 3 - 15 cm ( 3 -om. $\mathbf{9 0 \%} \mathrm{CaCO}_{3}$ ) limestonc. A PVC pipe drain ficld was placed on 10 of a 15 cm (6in) limestone layer. The drain field was covered by a 1.2 m ( 4 f ) layer of limestonc. A 30 cm (1fi) layer of organic material was then spread over the limestone. The organic mixture contained horse manure. chicken manure. pine bark and limestone sand. A Im (3f) pool of water. which includes the stilling basin. is maintained above the organic substrate ( $\mathrm{N} 2-\mathrm{N} 4$ ). The 0.06 ha ( $6161 \mathrm{ft}^{2}$ ) interface between the pooled water and the organic mixture is considered as $\mathrm{N} \downarrow$. The

RAPS component is constructed so that accumulated solids can be flushed directly from the drain field. This maintenance option will not be used unless plugging of the RAPS substrate occurs.

The sctuling basin (N5-N6) is designed to (re)aerate the anoxic RAPS effluent by routing the water under and over a series of five concrete baflles. Oxidized metals are allowed to precipitate in this basin. The cattail filter (N6-N7) contains a dense stand of vegetation to encourage filtration and further setuling of oxidized metals. Additional shallow rock drains and algac basins (N7-N10) exist further downstream. These structures are designed to provide substrate wath large aralabic surface area to promote the oxidation of Mn by bacteria. cyanobacteria. diatoms. green-alga and fungi in circumneutral water (Brant and Ziemkiewicz. 1997). Robbins et al. (1999) have determined that these microbes biologically oxidize reduced Mn . The final treated water collects in the wetland storage pool (N10-N13). Treated water is discharged through N12 (recycle) and N13 (river discharge). which are in close proximity to each other. The qualities of water from these two nodes are similar and can therefore be indicated as N12/13.

## Wetland Morphology

Hydrographic. land. and photagrammetric (aerial photography analyses) survey data sets were combined into a digital terrain model. The areas and volumes of the wetland were calculated using a digital CAD package. Included in Figure 2 are the typical operating surface areas. volumes, and nominal retention times for each of the main wetland components.

## Wetland Hydrology

The water losses between the primary nodes (N2. N5. N6. N7. N10. N12 and N13) were measured manually on a daily basis using a bucket during steady-state flow conditions. Water losses in the detention pond were estimated by measuring stage elevations using continuous recording level indicators during periods of no flow and rain. Evaporation rates were measured daily using an onsite pan cvaporator. Kadlec and Knight (1996) have suggested that wetland evapotranspiration is well represented by 0.7 to 0.8 times the Class A pan evaporation. Pan evaporation at the wetland was estimated at $3.3 \mathrm{~mm} / \mathrm{d}(0.13 \mathrm{in} / \mathrm{d})$. Using a
multiplier of 0.75 . the predicted evapotranspiration rate was estimated to be $2.5 \mathrm{~mm} / \mathrm{d}$ ( $0.1 \mathrm{in} / \mathrm{d}$ ). Differences between the overall losses and evapotranspiration were used to estimate seepage. Overall evapotranspiration and seepage from the wetland system accounts for 9.5 Lpm ( 2.5 gpm ) and $34.8 \mathrm{Lpm}(9.2 \mathrm{gpm})$. respectively. An unexpected leak in the cattail filter component (N6-N7) accounted for $71 \%$ of the overall seepage. All of the wetland components were clay lined; however. the clay may have been disrupted within the cattail filter component during construction. The seepage rate ranged from $2.2-14.7 \mathrm{~L} / \mathrm{d} / \mathrm{m}^{2}\left(0.8-2.5 \mathrm{gal} / \mathrm{wk}^{2} \mathrm{ff}^{2}\right)$ in all other components

## Wetland Retention

Two bromide tracer studies were performed to accurately assess retention within the major wetland components. Potassium bromide salt solutions were injected into the detention pond at NI during the first tracer study and into the stilling basin at N 2 during the second study. Automatic sequential sampling and manual sampling were performed every $1-24$ hours until the tracer concentrations returned to non-detectable levels at the monitored nodes. The $50 \%$ recovery period is considered the


|  | Detention | RAPS | Setuling | Cattalts | Crains | Storape | Total |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Area, ha | 0.13 | 0.09 | 0.07 | 0.02 | 0.09 | 0.28 | 0.68 |
| Vol., cu-m | 841 | 885 | 583 | 49 | 414 | 876 | 3,648 |
| 114Lpm Ta (Tn), d | 3.4 (5.1) | 5.4 (5.4) | 5.0 (3.6) | 0.5 (0.3) | 1.5 (2.5) | 2.6 (5.4) | 18.5 (19.4) |
| 170Lpm Ta (Tn), d | 2.3 (3.4) | 3.6 (3.6) | 3.3 (2.4) | 0.3 (0.2) | 1.0 (1.7) | 1.8 (3.6) | 12.3 (13.0) |
| 284Lpm Ta (Tn), d | 1.4 (2.1) | 2.2 (2.2) | 2.0 (1.4) | 0.2 (0.1) | 06 (1.0) | 1.1 (2.1) | 7.5 (7.7) |

Figure 2. Topographic schematic of the Plant Gorgas Wetland in ReRAPS mode along with area. volume. actual (Ta), and nominal (Tn) retention values. The RAPS surface water area and total water volume including limestone voids are presented. Retention values in bold font represent components and flows that were tracer tested.
actual (Ta) or tracer retention. Retention times for the untested flow rates are based on flowweighted calculations (Figure 2). The nominal ( $\mathrm{T} n$ ) retention values are based on void volume calculations.

During the first tracer study, the detention pond pumps operated at 284 Lpm ( 75 gpm ) while recycling approximately 50 percent of the pumped water. Acid mine drainage from a nearby pit was used as a runoff substitute during the first study. Daily inflows (N12-recycle and Nl-piped AMD) were equivalent to outflows (N2-pump). Excellent recovery of the ion was achieved to accurately determine the actual retention of the detention pond (NI-N2). Results from this study indicate that the open water design of the detention pond makes this component susceptible to short-circuiting. Shortcircuiting is apparent because the 1.4-day tracer retention (Ta) time was significantly lower than the 2.1-day nominal retention ( Tn ) time.

The second tracer study was performed using a 170 Lpm ( 45 gpm )-flow rate at N 2 . Comparisons between the nominal and tracer retention times for the remaining components down stream from the detention pond reveal that they are similar. Figure 3 presents the concentration and cumulative flow fraction or residence time distribution (RTD) for the bromide ion from the second study. Again, excellent recovery of the ion was achieved to accurately determine the actual retention of the RAPS surface waters (N2-N4) and the RAPS substrate (N4-N5). A rain event reduced the recovery of the tracer for the remaining downstream nodes. However, flows were stable during the period of time required to achieve a $50 \%$ salt recovery at the later nodes (N7, N10, N12/13).

The tracer tested retention at 170 Lpm ( 45 gpm ) within the RAPS surface waters and the organic/limestone substrate were 2.2 and 1.4 days, respectively. Retention time within the RAPS limestone is greater than the 12-23 hour residence time considered adequate for achieving optimal limestone dissolution (Hedin and Watzlaf. 1994; Kepler and McCleary. 1994: Skovran and Clouser. 1998).


Figure 3. Bromide concentrations and cumulative RTD for all components downstream from N2. Wetland pumps operated at continuous 170Lpm (45gpm) flow rate.

## Methods

Monitoring of the wetland during the runoff treatment event occurred during January 2000. The batch tank studies were performed during June 2000. Chemical analyses and field measurements performed during both studies were conducted according to U.S. EPA (1983. 1994) methods or Standard Methods (APHA 1998). Total anions (Br. $\mathrm{SO}_{4}$ ) were analyzed using ion chromatography (EPA Method 300.0 \& 340.2). Total cations (AI, Fe. Mn. Ca) were analyzed using the Atomic Emission Inductively Coupled Plasma Method (ICAP. EPA Method 200.7). Alkalinity (EPA Method 310.1) and acidity (Std. Methods 2310. hot peroxide) measurements were performed within 24 hours of sampling. Field measurements included pH . water temperature. conductivity, dissolved oxygen. and oxidation-reduction potential (ORP).

## Wetland Monitoring

Monitoring was performed to evaluate the treatment of coal pile runoff resulting from a $2.0 \mathrm{~cm}(0.8 \mathrm{in}) 24 \mathrm{hr}$ rain event which occurred on January 11. 2000. The RAPS component operated for 2 years prior to this event in the ReRAPS mode. Water quality monitoring was performed daily from January 12 till flows at N2 ceased on January 25 due to low detention pond levels. Detention pond levels were continuously monitored just prior to the rain event and throughout the treatment period. Manually measured flows were also performed throughout the 14 -day treatment period.

The wetland was operated in a ReRAPS mode to treat the runoff from the coal pile using the following conditions:

1. The intermittent pumping rate from the detention pond through N2 was 114 Lpm ( $\mathbf{3 0} \mathrm{gpm}$ ).
2. Treated water was allowed to recirculate back through NI2 to the detention pond at a rate of approximately 57 Lpm ( 15 gpm ).
3. Excess water was discharged to the river via a storage basin standpipe (NI3) or was lost due to the previously described seepage.

## Batch Tank Studies

Dissolved Fe and Al in AMD react to form flocculent particles, which co-precipitate with other dissolved metals when the pH of the water increases (Stumm and Morgan. 1981; Langmuir, 1997). A series of tank or drum experiments were performed to determine the beneficial effects of recycling treated water back into acidic water for pretreatment of metals in the wetland detention pond, thus confirming the pretreatment effects which were believed to have occurred during the ReRAPS mode.

The tank studies were designed to determine the effect of factors such as pH , initial metal concentration. retention, and depth on metal removal. The 200L tanks were filled with mixtures of treated (N12) and AMD water. The AMD water was obtained from an abandoned mine pit. Mixtures of AMD and treated water that were tested contained ratios ranging from $100 \%$-AMD: $0 \%$-N 12 water to $2.5 \%$ -AMD:97.5\%-NI2 water. AMD water used
during these series of tank studies was characterized as clear in color where $100 \%$ of the metals were dissolved into solution.

Samples were collected using a syringe and tubing at the $21,42,63$ and $84-\mathrm{cm}$ depths. Samples for total metal analyses were collected and pH measurements were performed every 8 hours for up to 48 hours.

The tank results are compared with the theoretical chemical equilibrium values using the MINTEQA2 geochemical equilibrium model developed by the U.S. EPA (Allison et al. 1991).

## Resalos

## Wetland Monitoring

Monitoring of the wetland effluent indicated that the wetland could easily produce compliance grade water in the ReRAPS mode. The total Fe and total Mn levels at the wetland discharge (N12/13) were reduced to below 6 and $4 \mathrm{mg} / \mathrm{L}$. respectively. Field measurements for pH are presented as box plots in Figure 4. The box plots summarize data based on the median, quartile. outliers and extreme values (SPSS 1999). Measurements for pH were maintained above 6 at $\mathrm{N} 12 / 13$. Some of the pH measurements at $\mathrm{N} 12 / 13$ exceeded 9 . These high pH levels were due to elevated levels of photosynthetic activity by filamentous algae, which limited dissolved $\mathrm{CO}_{2}$ levels in the last two components. During the treatment period. the detention pond (N2) pH was significantly greater than the runoff (NI), with values of 5.3 and 3.2 , respectively.


Figure 4. Box plot of pH values from the wetland nodes N1-N12 ( $\mathrm{n}=14$ ).

The concentrations, loadings, percent removals, and removal rates for the components prior to N 7 are presented in Figure 5. Over 92\% of the primary contaminants ( $\mathrm{Al}, \mathrm{Fe}, \mathrm{Mn}$ and acidity) were removed prior to the discharge of the cattail filter (N7).

Resuits from this treatment reveal that the majority of contaminant removal occurred in the detention pond or within the RAPS component. The resulting pH from the mixture of CPR (N1) and recirculated water (NI2) in the detention pond promoted the development of metal precipitates. Nearly all of the $\mathrm{Fe}(\mathbf{9 8 \%}$ ) was removed in the detention pond. Excellent removal of $\mathrm{Al}(81 \%)$ and acidity ( $75 \%$ ) were achieved. Significant amounts of $\mathbf{M n}$ (40\%) were also removed in the detention pond.

Figure 6 presents the cumulative percent removal for contaminants within the RAPS component. The majority of contaminant removal in the RAPS component occurred within the organic/limestone substrate. Aluminum removal in the RAPS surface water (N2-N4) and substrate (N4-N5) accounted for 4 and 14 percent of the overall weland removal. respectively. There was no significant removal of Mn in the surface waters (N2-N4). However another $28 \%$ of the Mn was removed in the RAPS substrate (N4-N5).

A small amount of acidity removal (3\%) occurred in the RAPS surface water, but the remaining $20 \%$ was removed inside the substrate layer. Within the RAPS component. the net alkalinity measured by titration balanced favorably with values indirectly obtained by accounting for any calcium ion increases and sulfate ion decreases. Even though hydrogen sulfide gas production was observed and average ORP values were -256 mv at N , there was no significant sulfate removal within the RAPS substrate (N4-N5). Alkalinity is produced due to sulfate reduction based on the following assumed stoichiometric relationship:

$$
\begin{equation*}
2 \mathrm{CH}_{2} \mathrm{O}+\mathrm{SO}_{4}{ }^{2-} \rightarrow \mathrm{H}_{2} \mathrm{~S}+2 \mathrm{HCO}_{3}^{-} \tag{I}
\end{equation*}
$$

> Where: $1 \mathrm{mg} / \mathrm{L}$ decrease in sulfate yields $1.04 \mathrm{mg} / \mathrm{L}$ alkalinity as $\mathrm{CaCO}_{3}$

There were no significant reductions in total sulfate concentrations prior to ( N 4 ) or after the RAPS substrate (N5). Average sulfate levels were $1632 \mathrm{mg} / \mathrm{L}$. Therefore nearly all of the
alkalinity generated was due to limestone dissolution based on the following stoichiometric relationship:

$$
\begin{array}{r}
2 \mathrm{H}^{+}+\mathrm{CaCO}_{3} \rightarrow \mathrm{Ca}^{2+}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \\
\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CaCO}_{3} \rightarrow 2 \mathrm{HCO}_{3}+\mathrm{Ca}^{2+} \tag{3}
\end{array}
$$

## Where: $\mathrm{Img} / \mathrm{L}$ increase in calcium yields $2.50 \mathrm{mg} / \mathrm{L}$ alkalinity as $\mathrm{CaCO}_{3}$

Based on the dissolved calcium values. approximately $23 \mathrm{gd}^{-1} \mathrm{~m}^{-2}$ as $\mathrm{CaCO}_{3}$ were generated within the RAPS component ( $572 \mathrm{~m}^{2}$ RAPS surface. 114 Lpm, 7-day flow).

This indirectly measured alkalinity estimate balances with the net alkalinity, based on the following equation:

> Acidity Consumed + Available Alkalinity $=$ Net Alkalinity (as $\mathrm{CaCO}_{3}$ )

Acidity was consumed at a rate of $10 \mathrm{gd}^{-1} \mathrm{~m}^{-2}$ and the available alkalinity was measured at $13 \mathrm{gd}^{-1} \mathrm{~m}^{-2}$. Therefore, the overall net alkalinity generated is $23 \mathrm{gd}^{-1} \mathrm{~m}^{-2} \mathrm{CaCO}_{3}$ This alkalinity generation rate is less than those reported by Watzlaf et al. (2000). which range from $43-62 \mathrm{gd}^{-1} \mathrm{~m}^{-2}$ as $\mathrm{CaCO}_{3}$ for RAPS which receive direct inflows from AMD. However. Watzlaf et al. (2000) report that for a second RAPS. receiving pretreatment from a previous
RAPS/settling basin in series, the alkalinity generation rates reduce to $16-2 \mathrm{Igd}^{-1} \mathrm{~m}^{-2}$. As previously described, a series of RAPS may otherwise be known as a SAPS.

## Batch Tank Study

As previously discussed, the purpose of the batch tank study was to reveal factors that may influence the removal of total $\mathrm{AI}, \mathrm{Fe}$, and Mn in the detention pond where runoff water and recirculated treated waters are mixed. Batch tank study results using AMD show that significant reductions of total Fe and Al could occur within 48 hours and that these removals were highly pH dependent. Neither total Al nor total Fe concentrations measured during the tank study approached the minimum detectable levels (MDL) possible with the Inductively Coupled Plasma Method (ICAP, EPA Method 200.7). Figure 7 presents the concentrations of Al and Fe at various pHs after 24 hours in the batch tanks. Significant reductions in Fe and Al occurred at pH values greater than 4 and 5.5 , respectively. The results from the tank study support the observed rapid removal of Fe and Al inside the detention pond. which had an average pH of 5.3 . The $40 \%$ removal of Mn inside
the detention pond was not supported by the tank study. Significant removal of Mn did not occur in the batch tanks within a 48 -hour period.

SPSS (1999) statistical modeling software was used to evaluate factors that may influence metal removal in large open mixtures of treated and untreated water. A parametric stepwise regression analysis evaluated factors that improved the prediction of tank metal concentrations after 24 hours of retention. The $\log$ transformed Al concentrations were best explained by the pH main effect alone ( $\mathrm{r}^{2}=0.95$. $\mathrm{p}<0.05$ ). The log-transformed Fe concentration may be best explained by pH . the initial Fe concentration in the tank. and the retention time ( $r^{2}=0.95, p<0.05$ ).

The MINTEQA2 model (Allison et al. 1991) was used to compare the resulting batch tank metal concentrations to the theoretical equilibrium concentrations at various pHs. Aluminum concentrations in the tank study did not approach the minimum equilibrium values for the pH adjusted AMD water predicted by MINTEQA2. Further AI removal may be limited by the relatively low specific gravity of the A hydroxide floc particles.

Currents induced by thermal gradients within the tanks may also resuspend the floc. This was not the case with Fe. Iron concentrations in the tank study did approach the minimum equilibrium values for the pH adjusted AMD water predicted by MINTEQA2 for pH values ranging from 4.5 to 6.5.


|  | CPR | Removals, Percent of CPR Loading |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Loading (kg) | Detention | RAPS | Settling | Filter |
| Al | 30.4 | 80.8 | 99.5 | 98.5 | 99.4 |
| Fe | 36.6 | 97.5 | 99.8 | 98.9 | 99.9 |
| Mn | 4.8 | 40.2 | 68.1 | 86.7 | 92.0 |
| Acidity | 356.5 | 75.1 | 98.7 | 100.0 | 100.0 |


|  |  | Removal Rates, g/day/sq-m (g/day/cu-m) |  |  |  |
| ---: | ---: | ---: | ---: | ---: | ---: |
|  |  | Detention | RAPS | Setting | Filter |
| Al |  | $1.3(4.8)$ | $0.7(1.1)$ | $0.0(0.0)$ | $0.0(0.0)$ |
| Fe |  | $1.9(7.0)$ | $0.1(0.1)$ | $0.0(0.0)$ | $0.0(0.0)$ |
| Mn |  | $0.1(0.4)$ | $0.2(0.3)$ | $0.1(0.1)$ | $0.1(0.4)$ |
| Acidity |  | $14.4(52.4)$ | $0.9(16.3)$ | $0.5(0.5)$ | $0.0(0.0)$ |

Figure 5. Concentrations. loadings. removal percentages, and removal rates for total AI. total Fe. total Mn , and Acidity (as $\mathrm{CaCO}_{3}$ ).


|  | Cumulative Percent Rem oval |  |  |
| ---: | ---: | ---: | ---: |
|  | Detention | Surface | Substrate |
|  | 80.8 | 85.2 | 99.5 |
| Fe | 97.9 | 99.1 | 99.8 |
| Mn | 40.2 | 39.6 | 68.1 |
| Acidity | 75.1 | 78.8 | 98.7 |

Figure 6. Cumulative percent removal of total aluminum. total iron. total manganese and acidity prior to (N1-N2) and within the RAPS component (N2-N5).

MINTEQA2 also predicts that. at cquilibrium. any Fe in solution exists in the ferrous form Fe(II) form. The total Fe in the AMD used in this study contained $18 \mathrm{mg} / \mathrm{L}$ of the ferric form ( Fe (III)) and $2 \mathrm{mg} / \mathrm{L}$ of Fe (II). Therefore. the complete removal of Fe would be limited by the presence of Fe (II). Again. the regression analyses revealed that the initial total Fe concentration. which is positively correlated with Fe (II). was a factor which significantly affected Fe removal in the tanks.

## Conclusion

The monitoring of a coal pile munof treatment and a series of tank studies have determined that the ReRAPS modification has the potential to enhance the basic RAPS wetland design. The Plant Gorgas Wetland easily produced compliance grade effluent water when treating the coal pile runoff in a ReRAPS mode. Locating the wetland discharge near an open water area should be discouraged duc to photosynthetic consumption of CO, by algac. Water should be routed through a rock drain or dense stand of emergent vegetation prior to bcing discharged.

The detention pond pretreated the acidity. Fe. Al, and Mn in the ReRAPS mode of operation. The retention and the pH of the detention pond were sufficiently high to promote the precipitation of Fe and Al based on the results of the batch tank study and MINTEQA2 equilibrium modeling. The MINTEQA2 equilibrium results do predict that the pretreatment of Fc in the detention pond may be hindered by the presence of Fe(II). Ferrous iron levels were not measured at N2. However. subsequent sampling of CPR treatments has shown that Fe (II) is routed to the RAPS. MINTEQA2 was not used to predict any effects in the detention pond due to co-precipitation. However. the pretreatment of Mn is possibly duc to adsorption. co-precipitation. or bio-oxidative processes. which could not be duplicated in the tank study.

Pretreatment of these contaminants prior to the RAPS component reduces limestone dissolution and the buildup of solids within the substrate of the RAPS component. A $75 \%$ pretreatment of acidity could conceivably increase the operational life of the RAPS limestonc by $\&$ fold. Approximately $50 \%$ of the ( $12.323 \mathrm{cu}-\mathrm{ft}$ total) limestone can be consumed to maintain the recommended $12-15 \mathrm{hr}$ retention within the substrate at 170 Lpm ( 45 gpm ).


Figure 7. Concentrations of total AI and total Fe in tank mixtures of AMD and wetland storage water.

Therefore, it is estimated that the normal once-through RAPS mode of treatment would consume the available limestone in approximately 14 years (assuming: $96.6 \mathrm{lbs} / \mathrm{cu}-\mathrm{ft}$ loose bulk density, $90 \% \mathrm{CaCO}_{3}$, 60 in rain/yr, $50 \%$ initial abstraction of rain, 11 ac runoff basin, $509 \mathrm{mg} / \mathrm{L}$ runoff acidity as $\mathrm{CaCO}_{3}$ ).

The use of the ReRAPS mode could increase the operational life of the Plant Gorgas wetland to more than 50 years.

Assuming that the plugging of the limestone voids is a controlling factor, the life expectancy of the system could be increased by 10 -fold when operating in a ReRAPS mode. This estimate also assumes that the buildups of Al and Fe oxides are similar in their effects and that there is a near complete pretreatment of Fe and $80 \%$ pretreatment of AI. A detention pond
designed for better mixing could eliminate any AI and Fe fouling of the RAPS component and any build up of precipitates could be easily removed from an open detention basin.

Prior to January 2000, the Plant Gorgas wetland had been operating in the ReRAPS mode for over 2 years. Evidence of the past pretreatment capabilities of the ReRAPS wetland was demonstrated when the treatment mode was changed to a "once-through" RAPS mode after the January 2000 treatment. After another series of rains, the pH in the detention pond dropped. Fe was solubilized and portions of the previously pretreated contaminants were pumped directly into the RAPS component. This event clearly demonstrated that the detention pond had been accumulating metal precipitates while operating in the ReRAPS mode. However, it also demonstrates that excessive runoff would overwhelm the detention pond and threaten to re-suspend the previously pretreated metals. Further research and careful design of the detention pond storage is required. Design criteria such as detention pond storage. retention, runoff flow, recirculation flow, and pumping schemes should be carefully developed if a stable pretreatment of the detention pond is required. Other design options could consider multiple detention pools and the use of flow control weirs to reduce the shock loading effects of the detention pond.

Results from the tracer studies have shown that the Plant Gorgas wetland behaves like a series of mixed reactors. However, the detention pond component does exhibit short-circuiting. A reconfiguration of the open water scheme into an initial mixing basin followed by a series of settling chambers would improve pretreatment in the detention pond. This configuration would need to account for changes in water level. The initial mixing chamber which would receive inflows from treated recycled wetland water and untreated runoff or AMD would need a dead storage of sufficient volume to moderate the initial flush of runoff resulting from a rain event.

The overall size of the RAPS-based wetland is dependent on the final removal of Mn . It has been shown that Mn removal is dependent on the initial removal of Fe . The pretreatment of Fe would likely move the primary Mn removal front into the settling basin and may reduce the size or eliminate the need for other downstream components (i.e. rock drains or cattail filters).

Most RAPS-based wetlands are configured to operate passively (without pumps). A disadvantage of the ReRAPS mode of operation (recirculation) is that a pump is required. However, pumps have been required to lift contaminated water to an available wetland site. as is the case with the Plant Gorgas wetland. A ReRAPS design should be considered in these cases.

This wetland uses a 2.2 KW (3hp) and a 2.6 KW (3.5hp) pump. If continuously used and assuming an electrical cost of $\$ 0.07 / \mathrm{KWH}$, the operational costs for the two-pump operation would range from $\$ 1,200$ to $\$ 3,600 /$ year. Alabama typically receives $152 \mathrm{~cm}(60 \mathrm{in})$ of rain per year. The treatment of coal pile runoff in Alabama during a ReRAPS mode could approach a third of the continuous duty electrical cost assuming a $50 \%$ initial abstraction of rain and a $50 \%$ recirculation of pumped water. However, the cost of pumping in the normal RAPS mode could be reduced to onefifth of the continuous duty cost.

A passive variant of the ReRAPS mode is possible if an alternate dependable source of alkaline water were available to moderate the pH of contaminated water in a detention pond prior to the RAPS component.

In a ReRAPS wetland the detention pond removes most of the contaminants by recycling a portion of the generated alkalinity. In a RAPS wetland the RAPS component collects nearly all of the AI precipitant, a significant portion of the Fe , and wastes all of the alkalinity to the wetland discharge. The ReRAPS design may eliminate potential plugging and short-circuiting due to precipitant buildup in the substrate of the RAPS component. The reuse of alkalinity greatly increases the operational life of the system. The ReRAPS wetland may accomplish these things at the cost of pumping and the use of a well-designed detention pond.

## Acknowledrements

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## APPENDIX B

## AVERAGE MONTHLY FIELD MEASURED VALUES AND CHEMICAL COMPOSITION OF WETLAND WATER SAMPLES

## Sulfates, Total (mg/L)




## Bromide, Total (mg/L)



a. Permater $=$ Eromice (mq/)

## Chloride, Total (mg/L)




[^2]Fluoride, Total ( $\mathrm{mg} / \mathrm{L}$ )

a Paremeter $=$ Ftuonde $(m, f)$

## lodide, Total (mg/L)


a. Parameter $=$ lodide $(m g /)$

## Sulfide, Total (mg/L)

iverage montily monmoring values for nodes M1 (CPR), M2, MM, M6, MT, M1O, and N12 in the Plant Gorges RaRAPS Wetiond.

a. Parameter $=$ Sulfide (mg/)

## Silver, Total (mg/L)




[^3]Aluminum, Dissolved (mg/L)


[^4]Aluminum, Total (mg/L)



[^5]Arsenic, Dissolved (mg/L)


- Permeter = Arsenic. Dissolved (mp/)


## Arsenic, Total (mg/L)



[^6]
## Barium, Dissolved (mg/L)



a. Paremeter $=$ Bertum, Dissoned (mal)

## Barium, Total (mg/L)



a. Parminter a Bertum. Total (mol)

## Beryllium, Dissolved (mg/L)


a. Parmenter $=$ Beryluinh Diacolved (mal)

Beryllium, Total (mg/L)


## Calcium, Dissolved (mg/L)



a. Peremetor $=$ Celchm. Dissotved (myl)

## Calcium, Total (mg/L)




[^7]
## Cadmium, Dissolved (mg/L)




[^8]
## Cadmium, Total (mg/L)


a. Perarneter = Cedrium, Total (mgl)

## Cobalt, Dissolved (mg/L)



[^9]
## Cobalt, Total (mg/L)


C. Perrmeter $=$ Cobent. Totel (mpl)

## Chromium, Dissolved (mg/L)



a. Parameter $=$ Chromium. Diasonved ( mol )

## Chromium, Total (mg/L)



a. Parameter $=$ Chromimin. Totel (mol)

## Copper, Dissolved (mg/L)




[^10]
## Copper, Total (mg/L)



- Parameter $=$ Copper, Total (mg/l)


## Iron, Dissolved (mg/L)




Iron, Total (mg/L)



## Potassium, Dissolved (mg/L)




## Potassium, Total (mg/L)



a. Perrmeter $=$ Potassium, Total (mg/)

Magnesium, Dissolved (mg/L)




Magnesium, Total (mg/L)


a. Perombier a Megneatum. Tote (mpl)

## Manganese, Dissolved (mg/L)




[^11]Manganese, Total (mg/L)



Molybdenum, Dissolved (mg/L)


a. Perameter = Molyedenum, Diseotved (mgl)

## Molybenum, Total (mg/L)




## Sodium, Dissolved (mg/L)



a. Perameter $=$ Soolum, Dissohed (mg/t)

Sodium, Total (mg/L)


a. Perameter = Soaim, Totel (mg/)

Nickel, Dissolved (mg/L)



Nickel, Total (mg/L)



[^12]
## Lead, Dissolved (mg/L)



a. Perameter = Leed. Dissolved (mg/I)

Lead, Total (mg/L)


a. Parmeter $=$ Leed. Totel $(\mathrm{mg} / \mathrm{I})$

## Antimony, Dissolved (mg/L)



|  |  |  | N1 | N2 | N | NS | NB | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1803 | Feorumy | 0000 | 0000 | . 0000 | 0000 | 0000 |  | 0000 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) |  | (1) |  |
|  |  | june | . 0000 | . 0030 | . 0000 | . 0000 | 0000 | 0000 | . 0000 |  |
|  |  |  | (1) 0000 | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | July | 0000 | 0000 | 0000 | 0000 | 0000 | 0000 | 0000 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | August | $0000$ | $0000$ | $.0000$ | $.0000$ | $0000$ | $0000$ | (1) 0000 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | September |  | 0000 | 0000 | . 0000 | . 0000 |  | 0000 |  |
|  |  |  |  | (1) | (1) | (1) | (1) |  | (1) |  |
|  |  | October | . | 0000 | . 0000 | 0090 | . 0080 |  |  |  |
|  |  |  |  | (1) | (1) | (1) | (1) |  |  |  |
|  |  | Annual | 0000 | 0018 | . 0000 | . 0015 | 0010 | 0000 | 0000 |  |
|  | 1999 |  | (4) | (6) | (6) | (6) | (6) | (3) | (5) |  |
|  |  | Januery | (1) 0000 | (1) 0000 | $0630$ | . 0000 | 0210 | 0000 | 0000 |  |
|  |  |  | (1) 0000 | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | February | $0000$ | $0015$ | $0015$ | 0000 | $0000$ | 0000 | $0015$ |  |
|  |  |  | (2) | (2) | (2) | (2) | (2) | (2) | (2) |  |
|  |  | March | (3) 0000 | (3) 0000 | 0033 | 0000 | 0033 | (3) 0000 | (3) 0000 |  |
|  |  |  | (3) | (3) | (3) | (3) | (3) | (3) | (3) |  |
|  |  | April | 0130 | (3) 0137 | 0007 | . | 0013 |  | 0043 |  |
|  |  |  |  | (3) | (3) |  | (3) |  | (3) |  |
|  |  | May | 0148 | 0040 | 0050 | 0020 | 0028 | 0043 | 0020 |  |
|  |  |  |  | (4) | (4) | (3) | (4) | (3) | (4) |  |
|  |  | Anruas | $.0065$ | $0046$ | .0075 | . 0007 | 0035 | 0014 | 0018 |  |
|  |  |  | (11) | (13) | (13) | (9) | (13) | (9) | (13) |  |
|  | 2000 | Janury | $0210$ | $0403$ | $0224$ | 0448 | 0482 | 1408 | $0360$ | 0205 |
|  |  |  | (5) | (3) | (5) | (6) | (5) | (4) | (2) | (4) |
|  |  | Annual | 0210 | . 0403 | . 0224 | 0448 | 0482 | . 1408 | 0360 | 0205 |
|  |  |  | (5) | (3) | (5) | (6) | (5) | (4) | (2) | (4) |
|  | 2001 | March | 0128 | (2) 0000 | . 0095 | 0067 | 0060 | 0130 | 0120 | 0150 |
|  |  |  | (4) | (2) | (2) | (3) | (2) | (1) | (4) | (1) |
|  |  | April |  |  |  |  |  |  | 0120 | . 0090 |
|  |  |  |  |  |  |  | (0) | (0) | (1) | (1) |
|  |  | May |  | . | - | . | . 0040 | . 0030 |  | 0030 |
|  |  |  |  |  | (0) |  | (1) | (1) |  | (1) |
|  |  | Annual | 0128 | 0080 | . 0095 | 0067 | 0053 | 0080 | 0120 | 0090 |
|  |  |  | (4) | (2) | (2) | (3) | (3) | (2) | (5) | (3) |
| Total | Overal |  | . 0095 | 0087 | . 0088 | 0127 | 0114 | 0329 | 0062 | 0156 |
|  |  |  | (2a) | (24) | (26) | (24) | (27) | (18) | (25) | (7) |

a. Permeneter = Antimony. Dissolved (mp/)

Antimony, Total (mg/L)


a. Peremeter = Antimony. Totid (mgl)

Selenium, Dissolved (mg/L)


a. Parameter $=$ Setenium. Dissolved ( $\mathrm{mg} / \mathrm{l}$ )

## Selenium, Total (mg/L)




[^13]
## Silica, Dissolved (mg/L)



a. Parmeter = Sifice. Dissolved (mg/l)

## Silicon, Total (mg/L)


a. Percrinter $=$ Sivicon, Totall (mol)

## Tin, Dissolved (mg/L)



a. Parameter $=\mathrm{Tn}$. Dissotved (mg/)

Tin, Total (mg/L)

a. Parammer $=\operatorname{Tin}$, Total $(\mathrm{mol})$

## Strontium, Dissolved (mg/L)



Strontium, Total (mg/L)



Titanium, Dissolved (mg/L)


a. Peremeter = Titanium. Dissokved ( $\mathrm{mog} / \mathrm{m}$

## Titanium, Total (mg/L)




Thallium, Dissolved (mg/L)



[^14]Thallium, Total (mg/L)



[^15]Vanadium, Dissolve (mg/L)d


a. Peraneter $=$ Varadium. Dissolve (mgh)d

Vanadium, Total (mg/L)


a. Permener $=$ Venadium. Totion (mp/)

## Zinc, Dissolved (mg/L)


a. Parameter $=$ Zinc. Dissotved $(\mathrm{mg} / \mathrm{I})$

## Conductivity (umhos)



a. Parimater $=$ Conductivity (untios)

## Dissolved Oxygen (mg/L)



a. Parameter a Dissonved Oxygen (mal)

Hardness, Total, (mg/L as CaCO3)


a. Permmeter $=$ Hardiness. Toten. (man as CeCO 3$)$

## Oxidation Reduction Potential (mv)



a. Pertmeter $=$ Ondation Recuction Potertial (ITM)

Field pH (SU)


a Permeter = Field pH (SU)

## Solids, Suspended (mg/L)




[^16]
## Solids, Total (mg/L)



a. Perameter $=$ Solids. Totel $(\mathrm{mg} / \mathrm{l})$

Temperature (C)



- Partrneter = Tempernture (C)


## Turbidity (NTU)



a. Perameter $=$ Turbidity (NTU)

## Total Organic Carbon (mg/L)



a Parameter $=$ Total Organic Carbon (ma/l)

## Chlorophyll A, Corrected (ug/l)



|  |  |  | N 1 | N2 | N/ | $N 5$ | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 180 | Fetruay | 5300 | 0000 | 3.7400 | 13.8000 | 16.0200 |  | 42700 | N12 |
|  |  |  | (1) | (1) | (1) | (1) | (1) |  | (1) |  |
|  |  | dre | 13.8000 | 25.6300 | 49.1300 | 12.8200 | 6.4100 | 7.4000 | 103.6000 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) |  |  |
|  |  | Juny | 78800 | 24.5000 | 10.1500 | 19.2200 | 93.8300 | 141.5100 | 69400 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | August | 5.3400 | 8.5400 | 18. 1600 | 188 7400 | 86.5100 | 445.3600 | 16.0200 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | Septernber |  | $16.8600$ | 55.5400 | $22.0600$ | 19.0700 |  | 0000 |  |
|  |  |  |  | (1) | (1) | (1) | (1) |  | (1) |  |
|  |  | October |  | 0000 | 6.4100 | 2.1400 | 42700 |  |  |  |
|  |  |  |  | (1) | (1) | (1) | (1) |  |  |  |
|  |  | Anruen | 68075 | 12.5893 | 23.8550 | 398100 | 370033 | 1901167 | 261660 |  |
|  |  |  | (4) | (6) | (6) | (6) | (6) | (3) | (5) |  |
|  | 1999 | tanuery | $0000$ | $0000$ | $0000$ | (1) 0000 | 0000 | 0000 | (1) 0000 |  |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |  |
|  |  | Feoruery | 16050 | 5.8750 | 192200 | 8000 | 20.5600 | 144200 | 18700 |  |
|  |  |  | (2) | (2) | (2) | (2) | (2) |  |  |  |
|  |  | Manch | 94067 | 2.3400 | 191067 | 23567 | 150833 | 59000 | 40967 |  |
|  |  |  | (3) | (3) | (3) 366 | (3) | (3) | (3) |  |  |
|  |  | Apri | 2.6200 | (3) 6700 | 103567 |  | 13.2067 |  | 28967 |  |
|  |  |  | (1) | (3) | (3) |  | (3) |  |  |  |
|  |  | May | 9350 | 4.4050 | 2.4775 | 3100 | 28.6875 | 316500 | 40225 |  |
|  |  |  |  | (4) | (4) | (3) | (4) | (3) | (4) |  |
|  |  | Annusat | 3.4355 | 2.9785 | 105185 | 1.0667 | 185185 | 157211 | 3. 1392 |  |
|  |  |  | (11) | (13) | (13) | (9) | (13) | (9) | (13) |  |
|  | 2000 | Lamury | 12925 | 48193 | 9.8507 | 10671 | 6.6906 | 81508 | 9.3475 | 14521 |
|  |  |  | (12) | (14) | (14) | (14) | (14) | (12) | (12) | (14) |
|  |  | Armual | 12925 | 4.8193 | 9.8507 | 10671 | 66986 | 8.1908 | 93475 | 14521 |
| Totat |  |  | (12) | (14) | (14) | (14) | (14) | (12) | (12) | (14) |
|  | Overall |  | ${ }_{(27}^{2.5826}$ | $\begin{aligned} & 5.5085 \\ & \text { (33) } \end{aligned}$ | $\begin{array}{r} 12.6600 \\ \text { (33) } \\ \hline \end{array}$ | $\begin{aligned} & 9.0828 \\ & (29) \end{aligned}$ | $\begin{aligned} & 169903 \\ & (33) \end{aligned}$ | $\begin{aligned} & 347554 \\ & (24) \end{aligned}$ | $\begin{aligned} & 94603 \\ & (30) \end{aligned}$ | $14521$ |

a. Parmeter $=$ Chlorophyi A. Spectro. Comectd (ugh)

## Biochemical Oxygen Demand, 5 Day (mg/L)



|  |  |  | N1 | N2 | NH | N5 | N8 | N7 | N10 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 18\%8 | February | 2.0000 | 3.0000 | 4.0000 | 61.0000 | 82.0000 |  | 3.0000 |
|  |  |  | (1) | (1) | (1) | (1) | (1) |  | (1) |
|  |  | June | 3.0000 | 7.0000 | 70000 | 7.0000 | 8.0000 | 6.0000 | 22.0000 |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
|  |  | July | 3.0000 | 6.0000 | 70000 | 10000 | 1.0000 | 30000 | 60000 |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
|  |  | August | 40000 | 6.0000 | 8.0000 | 22.0000 | 170000 | 12.0000 | 60000 |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
|  |  | Septernber |  | 21.0000 | 240000 | 22.0000 | 270000 |  | 20000 |
|  |  |  |  | (1) | (1) | (1) | (1) |  | (1) |
|  |  | Octaber |  | 70000 | 25.0000 | 70000 | 14.0000 |  |  |
|  |  |  |  | (1) | (1) | (1) | (1) |  |  |
|  |  | Annual | 3.0000 | 8.3333 | 12.5000 | 20.0000 | 215000 | 70000 | 78000 |
|  |  |  | (4) | (6) | (6) | (6) | (6) | (3) | (5) |
|  | 1999 | January | 30000 | 5.0000 | 5.0000 | 90000 | 40000 | 60000 | 30000 |
|  |  |  | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
|  |  | February | 5000 | 15000 | 2.0000 | 15000 | 2.5000 | 15000 | 10000 |
|  |  |  | (2) | (2) | (2) | (2) | (2) | (2) | (2) |
|  |  | March | 40000 | 43333 | 43333 | 30000 | 50000 | 26867 | 23333 |
|  |  |  | (3) | (3) | (3) | (3) | (3) | (3) | (3) |
|  |  | April | 10000 | 1.3333 | 60000 |  | 70000 |  | 46667 |
|  |  |  | (1) | (3) | (3) |  | (3) |  | (3) |
|  |  | May | 1.2500 | 15000 | 32500 | 153333 | 45000 | 33333 | 2.7500 |
|  |  |  | (4) | (4) | (4) | (3) | (4) | (3) | (4) |
|  |  | Annual | 20000 | 2.3846 | 4.0769 | 74444 | 48462 | 30000 | 28462 |
|  |  |  | (11) | (13) | (13) | (9) | (13) | (9) | (13) |
| Totar | Overall |  | 2.2667 | 42632 | 67368 | 124887 | 101053 | 40000 | 42222 |
|  |  |  | (15) | (19) | (19) |  | (19) | (12) | (18) |

[^17]Nitrogen, Nitrite (mg/L)



[^18]Nitrogen, Nitrate (mg/L)


a. Parameter $=$ Nitrogen. Nitrate $(\mathrm{mq} / \mathrm{I})$

## Nitrogen, Ammonia (mg/L)




[^19]Nitrogen, Total Kjeldahl (mg/L)



[^20]
## Dissolved Phosphate, Ortho (mg/L)




[^21]
## Total Phosphate, Ortho (mg/L)




[^22]Phosphorus, Total (mg/L)



- Parameter = Phosphorus. Totel (ma/)


## Alkalinity, Total, (mg/L as $\mathrm{CaCO}_{3}$ )




[^23]
## Bicarbonate Alkalinity (mg/L as $\mathrm{CaCO}_{3}$ )



a. Parmeter $=$ Bicarboncte Alcanty $(\mathrm{mpl} / \mathrm{as} \mathrm{CaCO} 3)$

## Carbonate Alkalinity (mg/L as $\mathrm{CaCO}_{3}$ )



[^24]Hydroxide Alkalinity (mg/L as $\mathrm{CaCO}_{3}$ )



[^25]
## Acidity, Hot Peroxide (mg/L as $\mathrm{CaCO}_{3}$ )


a. Parameter $=509$

## APPENDIX C <br> THE DAILY FLOWS AND DAILY FLOW-WEIGHTED AVERAGE MEASUREMENTS FOR THE PRIMARY CONTAMINANTS

Oally flowe (Cu-mid) at nodes N1, M2, M4, MS, M7, N10 and M12 during the 41 day treatment of CPR.
CPR Runofil Event 1

|  |  | N1 | N2 | N | N5 161.14 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| JenuaryFebruary | 29 | 457.40 | 148.61 | 148.61 |  | 16114 | 161.14 | 121.50 |
|  | 30 | 84.20 | 398.29 | 396.29 | 38741 | 387.41 | 38741 | 32400 |
|  | 31 | 19.00 | 398.29 | 398.29 | 381.82 | 36182 | 36182 | 26970 |
|  | 1 | 2.60 | 377.42 | 377.42 | 3479 | 347.94 | 34794 | 22300 |
|  | 2 | 00 | 388.29 | 398.29 | 345.29 | 345.29 | 34529 | 22460 |
|  | 3 | 00 | 186.99 | 188.98 | 341.52 | 341.52 | 34152 | 21005 |
|  | 4 | 00 | 190.79 | 190.79 | 215.44 | 21544 | 215.44 | 182.18 |
|  | 5 | 00 | 125.46 | 125.46 | 99.53 | 9953 | 9953 | 12897 |
|  | 6 | 00 | 130.10 | 130.10 | 124.04 | 12404 | 12404 | 10276 |
|  | 7 | 00 | 00 | 00 | 7517 | 75.17 | 75.17 | 1967 |
|  | 8 | 00 | 56.39 | 56.39 | 28.67 | 28.67 | 2867 | 677 |
|  | 9 | 2.50 | 58.39 | 5639 | 28.67 | 2867 | 2867 | 9768 |
|  | 10 | 00 | 17149 | 171.49 | 116.21 | 116.21 | 116.21 | 13407 |
|  | 11 | 00 | 93.98 | 93.98 | 190.28 | 19028 | 190.28 | 13075 |
|  | 12 | $\infty$ | 3759 | 3759 | 9504 | 9504 | 9504 | 7222 |
| Total |  | 565.70 | 2764.09 | 2764.09 | 2918.17 | 2918.17 | 291817 | 2232.36 |

a. EVENT = CPR Runofi Event ${ }^{1} 1$

Dally flows (cu-m/d) at nodes N1, MR, NA, NE, N7, N10 and N12 during the 41 dery treatment of CPR.
CPR Runon Event ${ }^{2}$

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February |  | 3150 | 112.78 | 112.78 | 93.88 | 9388 | 9388 | 15689 |
|  | 13 | 93190 | 225.56 | 225.56 | 27446 | 27446 | 27446 | 18018 |
|  | 14 | 00 | 287.34 | 287.34 | 259.64 | 25964 | 25964 | 8344 |
|  | 15 | $\infty$ | 390.29 | 390.29 | 326.43 | 326.43 | 32643 | 5141 |
|  | 16 | $\infty$ | 162.62 | 162.62 | 15623 | 15623 | 15623 | 981 |
| Total |  | 963.40 | 1178.60 | 1178.60 | 1110.64 | 1110.64 | 111064 | 48173 |

a. EVENT = CPR Runoff Event 2

Dally flows (Cu-m/d) et nodes N1, N2, MA, M5, N7, N10 and N12 during the 41 day treatment of CPR.
CPR Runof Event ${ }^{3} 3$

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 563.60 | 149.83 | 14988 | 22524 | 22524 | 22524 | 16621 |
|  | 17 | 9.60 | 234.61 | 23461 | 22157 | 22157 | 22157 | 13413 |
|  | 18 | 370 | 234.89 | 23489 | 18148 | 18149 | 18149 | 11543 |
|  | 19 | 2.00 | 232.40 | 232.40 | 21816 | 21816 | 21816 | 22826 |
|  | 20 | 2.40 | 23161 | 23161 | 21890 | 21890 | 21890 | 12049 |
|  | 21 | 00 | 228.50 | 228.50 | 21687 | 21687 | 21687 | 3232 |
|  | 22 | 00 | 10378 | 103.78 | 21466 | 214.66 | 21466 | 13493 |
|  | 23 | 00 | 00 | 00 | 21416 | 21416 | 21416 | 7321 |
|  | 24 | 00 | 7059 | 7059 | 7462 | 7462 | 7462 | 1888 |
|  | 25 | 5320 | 20757 | 20757 | 485 | 4.85 | 485 | 13572 |
|  | 26 | 7100 | 15823 | 15823 | 7494 | 7494 | 7494 | 15865 |
|  | 27 | 5050 | 23003 | 23003 | 172.94 | 17294 | 17294 | 19418 |
|  | 28 | 00 | 23003 | 23003 | 21331 | 21331 | 21331 | 15034 |
| March | 1 | 00 | 14831 | 14831 | 14046 | 14046 | 14046 | 17369 |
|  | 2 | 00 | 136 | 136 | 3352 | 3352 | 3352 | 742 |
| Total |  | 75600 | 246175 | 246175 | 242569 | 242569 | 242569 | 184385 |

a EVENT = CPR Runoff Event 13

Daly fome (cu-mid) et nodes N1, M2, MA, MS, N7, N1O and M12 during the 41 day treatment of CPR.
CPR Runcif Event 制

|  | N1 | N2 | Na | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Warch 2 | 502.30 | 12703 | 12703 | 38.26 | 38.26 | 3826 | 18407 |
|  | 238.30 | 229.49 | 22949 | 168.79 | 16879 | 168.79 | 302.46 |
| 4 | 00 | 229.49 | 229.49 | 231.33 | 231.33 | 23133 | 14886 |
| 5 | 00 | 229.49 | 229.49 | 22365 | 22365 | 223.65 | 15140 |
| 6 | 7.50 | 229.49 | 229.49 | 22024 | 220.24 | 220.24 | 152.74 |
| 7 | 1.80 | 229.49 | 229.49 | 21564 | 215.64 | 21564 | 152.84 |
| 8 | $\infty$ | 229.49 | 229.49 | 213.49 | 21349 | 21349 | 12727 |
| 9 | 00 | 229.49 | 22949 | 218.17 | 218.17 | 21817 | 13611 |
| 10 | 8.50 | 22949 | 22949 | 222.05 | 222.05 | 22205 | 17371 |
| 11 | 00 | 10518 | 10518 | 100.40 | 10040 | 10040 | 10418 |
| Total | 758.40 | 2068.12 | 2068.12 | 1852.01 | 185201 | 1852.01 | 163364 |

a. EVENT = CPR Runof Event in

Totan flows (cu-m/ovent) at nodes N1, N2, MA, M5, N7, N10 and N12 during each of the four CPR events.

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CP'R Runofit Event ${ }^{1 / 7}$ | 565.70 | 2764.09 | 2764.09 | 2918.17 | 2918.17 | 291817 | 2232.36 |
| CPR Runoff Event ${ }^{\text {P2}}$ | 963.40 | 1178.60 | 1178.60 | 1110.64 | 111064 | 111064 | 48173 |
| CPR Runoff Event 3 | 75600 | 2461.75 | 2461.75 | 242569 | 242569 | 242569 | 184385 |
| CPR Runofi Event 34 | 75840 | 206812 | 206812 | 1852.01 | 1852.01 | 185201 | 163364 |
| Total | 304350 | 8472.56 | 8472.56 | 830651 | 830651 | 830651 | 619157 |


CPR Runof Event 1

|  |  | N1 | N2 | N4 | N5 | N7 | $N 10$ | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| JanueryFebruary | 29 | 50.82 | 16.51 | 16.51 | 17.90 | 17.90 | 1790 | 13.50 |
|  | 30 | 3.51 | 16.51 | 1651 | 18.14 | 16.14 | 16.14 | 1350 |
|  | 31 | 79 | 16.51 | 16.51 | 15.08 | 15.08 | 15.08 | 11.24 |
|  | 1 | 11 | 15.73 | 15.73 | 14.50 | 1450 | 14.50 | 929 |
|  | 2 | 00 | 16.51 | 16.51 | 14.39 | 14.39 | 1439 | 9.38 |
|  | 3 | 00 | 779 | 7.79 | 14.23 | 1423 | 1423 | 8.75 |
|  | 4 | 00 | 795 | 795 | 8.98 | 898 | 898 | 759 |
|  | 5 | 00 | 523 | 5.23 | 4.15 | 4.15 | 415 | 5.29 |
|  | 6 | $\infty$ | 5.42 | 542 | 517 | 517 | 517 | 428 |
|  | 7 | 00 | 00 | 00 | 313 | 3.13 | 313 | 82 |
|  | 8 | 00 | 2.35 | 2.35 | 119 | 119 | 119 | - 28 |
|  | 9 | 10 | 2.35 | 2.35 | 1.19 | 119 | 119 | 407 |
|  | 10 | 00 | 715 | 715 | 484 | 484 | 484 | 559 |
|  | 11 | 00 | 392 | 3.92 | 793 | 793 | 793 | 545 |
|  | 12 | 00 | 3.13 | 3.13 | 7.92 | 792 | 792 | 6.02 |
| Total |  | 1.70 | 830 | 8.30 | 8.76 | 876 | 876 | 6.70 |

a. EVENT = CPR Runoff Event 1

Hourty flows (cu-minr) at nodes N1, M2, MA, ME, NT, N1O and M12 during the 41 dey trentmem of CPR.
CPR Runof Event ${ }^{[2}$

|  |  | N1 | N2 | N/ | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 2.63 | 9.40 | 9.40 | 7.82 | 782 | 782 | 1307 |
|  | 13 | 38.83 | 9.40 | 9.40 | 1144 | 11.44 | 1144 | 751 |
|  | 14 | 00 | 11.97 | 11.97 | 10.82 | 1082 | 1082 | 348 |
|  | 15 | 00 | 1626 | 16.26 | 13.60 | 1360 | 1360 | 2.14 |
|  | 16 | 00 | 16.26 | 16.26 | 15.62 | 1562 | 1562 | 98 |
| Total |  | 10.25 | 12.54 | 12.54 | 1182 | 1182 | 1182 | 512 |

a. EVENT = CPR Runoff Event \%2

Hourly fiows (cu-m/hr) at nodes N1, N2, M4, NS, N7, N10 and N12 during the 41 dey treatment of CPR. a
CPR Runoff Event 3

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 40.26 | 10.70 | 10.70 | 16.09 | 1609 | 1609 | 1187 |
|  | 17 | 40 | 978 | 978 | 923 | 923 | 923 | 559 |
|  | 18 | 15 | 979 | 979 | 756 | 756 | 756 | 481 |
|  | 19 | 08 | 9.68 | 968 | 909 | 909 | 909 | 951 |
|  | 20 | 10 | 965 | 965 | 912 | 912 | 912 | 502 |
|  | 21 | 00 | 952 | 952 | 904 | 904 | 904 | 135 |
|  | 22 | 00 | 4.32 | 432 | 894 | 894 | 894 | 562 |
|  | 23 | 00 | 00 | 00 | 892 | 892 | 892 | 305 |
|  | 24 | 00 | 2.94 | 2.94 | 311 | 311 | 311 | 79 |
|  | 25 | 2.22 | 865 | 865 | 20 | 20 | 20 | 566 |
|  | 26 | 2.96 | 659 | 659 | 312 | 312 | 312 | 661 |
|  | 27 | 210 | 958 | 958 | 721 | 721 | 729 | 809 |
|  | 28 | 00 | 958 | 958 | 889 | 889 | 889 | 626 |
| March | 1 | 00 | 618 | 618 | 585 | 585 | 585 | 724 |
|  | 2 | 00 | 15 | 15 | 372 | 372 | 372 | 82 |
| Total |  | 226 | 735 | 735 | 724 | 724 | 724 | 550 |

a EVENT = CPR Runof Event \#3

CPR Runof Evemt

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 33.49 | 8.47 | 847 | 2.55 | 2.55 | 2.55 | 1227 |
| 3 | 9.93 | 9.56 | 956 | 703 | 703 | 703 | 1260 |
| 4 | 00 | 9.56 | 9.56 | 964 | 9.64 | 964 | 620 |
| 5 | 00 | 9.56 | 956 | 932 | 932 | 932 | 631 |
| 6 | 31 | 9.56 | 956 | 918 | 918 | 918 | 6.36 |
| 7 | 08 | 956 | 9.56 | 898 | 898 | 898 | 637 |
| 8 | 00 | 9.56 | 956 | 890 | 890 | 890 | 530 |
| 9 | 00 | 9.56 | 956 | 909 | 9.09 | 909 | 567 |
| 10 | 35 | 9.56 | 956 | 925 | 925 | 925 | 724 |
| 11 | 00 | 956 | 956 | 913 | 913 | 913 | 947 |
| Total | 3.48 | 949 | 949 | 8.50 | 850 | 850 | 749 |

a. EVENT $=$ CPR Runoff Event ${ }^{\prime 4}$

Hourty flows (Cu-m/hr) at noted M1, M2, MA, MK, M7, W10 and M12 durine aech of the four CPE overns.

|  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runow Event 1 | 1.70 | 8.30 | 8.30 | 876 | 876 | 8.76 | 670 |
| CPR Runof Event ${ }^{\text {en }}$ | 1025 | 12.54 | 12.54 | 1182 | 1182 | 1182 | 512 |
| CPR Runcof Event 3 | 2.26 | 735 | 735 | 724 | 724 | 724 | 550 |
| CPR Runoff Event 94 | 348 | 949 | 949 | 8.50 | 850 | 850 | 749 |
| Total | 311 | 8.65 | 865 | 8.48 | 848 | 848 | 632 |

 enemenent of CPI.
CPR Runof Event 11

| danuary |  | N4 | N2 12.00 | NM 11.50 | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 29 | 13.80 |  |  | 920 | 10.80 | 1160 | 12.20 |
|  | 30 | 13.40 | 12.17 | 1188 | 882 | 10.91 | 12.01 | 12.37 |
|  | 31 | 15.55 | 12.43 | 12.91 | 10.65 | 11.46 | 13.05 | 1308 |
| February | 1 | 17.30 | 12.03 | 12.40 | 11.24 | 11.26 | 12.53 | 12.80 |
|  | 2 |  | 10.24 | 10.11 | 11.38 | 9.51 | 9.40 | 9.30 |
|  | 3 |  | 7.47 | 6.92 | 10.55 | 7.62 | 653 | 6.39 |
|  | 4 |  | 8.73 | 889 | 10.29 | 762 | 719 | 730 |
|  | 5 |  | 8.97 | 9.32 | 10.59 | 9.54 | 1098 | 962 |
|  | 6 |  | 9.03 | 8.87 | 10.10 | 8.34 | 845 | 889 |
|  | 7 |  |  |  | 10.20 | 849 | 847 | 848 |
|  | 8 |  | 1150 | 1100 | 1090 | 1020 | 11.50 | 1130 |
|  | 9 | 12.10 | 11.50 | 1100 | 10.90 | 10.20 | 1150 | 1130 |
|  | 10 |  | 12.27 | 12.03 | 1108 | 1162 | 12.48 | 1164 |
|  | 11 |  | 13.50 | 1360 | 11.10 | 11.80 | 12.60 | 1230 |
|  | 12 |  | 12.75 | 12.90 | 11.17 | 1180 | 12.60 | 1230 |
| Total |  | 13.82 | 11.09 | 11.07 | 10.61 | 10.10 | 1066 | 1073 |

a. EVENT = CPR Runoff Event *!

Dathy flow weighted water ternpersture (C) at nodes N1, M2, M, M5, N7, N10 and N12 during the 41 doy trectiment of CPR.
CPR Runof Event *2

|  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February 12 | 10.60 | 10.50 | 1080 | 12.00 | 1080 | 10.30 | 1030 |
| 13 | 1060 | 10.23 | 1040 | 1192 | 1067 | 10.30 | 10.17 |
| 14 |  | 10.47 | 1153 | 1178 | 1148 | 1174 | 1189 |
| 15 |  | 1120 | 1353 | 1162 | 1310 | 1433 | 1268 |
| 16 |  | 1167 | 1453 | 1167 | 1365 | 1490 | 1520 |
| Total | 1060 | 1084 | 1232 | 1177 | 1199 | 1247 | 1089 |

a. EVENT = CPR Runof Event ${ }^{62}$

Daily flow weighted whter temperature (C) at nodes N1, M2, M4, MS, NT, N10 and N12 during the 41 day treetment of CPR.

CPR Runof Event *3

| February |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 16 | 2130 | 1500 | 16.60 | 1300 | 1500 | 1730 | 1980 |
|  | 17 | 2130 | 1363 | 1429 | 1303 | 1371 | 1526 | 1706 |
|  | 18 | 12.40 | 1111 | 1127 | 1332 | 951 | 913 | 1069 |
|  | 19 | 84 | 1030 | 1010 | 1327 | 944 | 932 | 894 |
|  | 20 | 8.70 | 1147 | 1127 | 13.01 | 1095 | 1086 | 941 |
|  | 21 |  | 12.86 | 1302 | 12.90 | 12.94 | 1336 | 1359 |
|  | 22 |  | 1363 | 1395 | 1310 | 1403 | 1450 | 1461 |
|  | 23 |  |  |  | 1320 | 1420 | 1450 | 1500 |
|  | 24 |  | 1370 | 1420 | 1321 | 1416 | 1445 | 1408 |
|  | 25 | 1450 | 1370 | 1420 | 1350 | 1330 | 1330 | 1360 |
|  | 28 | 1290 | 1454 | 1443 | 1399 | 1310 | 1348 | 1393 |
|  | 27 | 12.90 | 1487 | 1503 | 1439 | 1347 | 1335 | 1428 |
|  | 28 |  | 1415 | 1454 | 1462 | 1348 | 1360 | 1419 |
| March | 1 |  | 1322 | 1376 | 1474 | 1307 | 1323 | 1302 |
|  | 2 |  | 1310 | 1370 | 1479 | 1280 | 1260 | 1250 |
| Total |  | 1935 | 1309 | 1339 | 1348 | 1279 | 1324 | 1357 |

a EVENT = CPR Runof Event 3 trectment of CPr.


## 

 crums.|  | N1 | N2 | N | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcil Event ${ }^{\text {a }}$ | 13.82 | 11.09 | 11.07 | 10.61 | 10.10 | 10.66 | 10.73 |
| CPR Runof Event ${ }^{4}$ | 10.60 | 10.84 | 12.32 | 11.77 | 11.99 | 12.47 | 10.89 |
| CPR Runof Event ${ }^{\text {B }}$ | 19.35 | 13.09 | 13.39 | 13.48 | 12.79 | 13.24 | 13.57 |
| CPR Runofl Evem ${ }^{\text {P4 }}$ | 15.94 | 12.97 | 12.51 | 14.15 | 12.16 | 12.06 | 13.10 |
| Total | 14.70 | 12.09 | 12.27 | 12.39 | 11.60 | 11.97 | 1221 |

 CPR Runof Evem :1

|  |  | $N 1$ | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| January | 29 | 3.00 | 6.67 | 6.49 | 7.21 | 7.50 | 7.61 | 7.87 |
|  | 30 | 3.14 | 5.51 | 6.20 | 7.04 | 7.37 | 7.59 | 7.81 |
|  | 31 | 3.20 | 4.92 | 5.38 | 6.79 | 7.09 | 7.43 | 7.81 |
|  | 1 | 3.05 | 4.88 | 5.01 | 6.67 | 7.01 | 7.37 | 7.79 |
|  | 2 |  | 4.95 | 5.03 | 6.76 | 7.17 | 7.37 | 7.83 |
|  | 3 |  | 5.04 | 5.19 | 6.86 | 716 | 7.34 | 7.73 |
|  | 4 |  | 5.14 | 5.08 | 6.90 | 7.20 | 7.37 | 7.87 |
|  | 5 |  | 5.48 | 5.08 | 6.97 | 7.25 | 7.36 | 7.96 |
|  | 6 |  | 5.99 | 5.07 | 6.85 | 7.10 | 7.40 | 7.71 |
|  | 7 |  |  |  | 6.85 | 7.16 | 7.44 | 7.49 |
|  | 8 |  | 6.21 | 5.38 | 7.02 | 7.57 | 7.57 | 7.25 |
|  | 9 | 3.09 | 6.21 | 5.38 | 7.02 | 7.57 | 7.57 | 7.25 |
|  | 10 |  | 6.59 | 5.45 | 7.06 | 769 | 7.68 | 7.37 |
|  | 11 |  | 7.21 | 5.55 | 7.07 | 7.70 | 7.69 | 7.62 |
|  | 12 |  | 7.03 | 5.66 | 7.07 | 7.70 | 7.69 | 7.62 |
| Total |  | 3.03 | 5.46 | 5.41 | 6.90 | 7.27 | 7.47 | 7.74 |

a. EVENT = CPR Runoff Event *1

CPR Runof Event ${ }^{2}$

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Februery 12 | 5.05 | 6.50 | 598 | 711 | 765 | 767 | 8.04 |
| 13 | 506 | 6.35 | 637 | 706 | 772 | 770 | 783 |
| 14 |  | 6.17 | 6.44 | 692 | 760 | 773 | 753 |
| 15 |  | 548 | 6.20 | 6.81 | 729 | 751 | 754 |
| 16 |  | 512 | 605 | 679 | 720 | 741 | 744 |
| Toter | 5.06 | 586 | 625 | 6.92 | 749 | 761 | 781 |

a. EVENT $=$ CPR Runof Evont 2


|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February 16 | 306 | 452 | 5.57 | 6.64 | 712 | 728 | 820 |
| 17 | 308 | 390 | 511 | 667 | 710 | 732 | 804 |
| 18 | 368 | 378 | 4.69 | 6.78 | 725 | 745 | 773 |
| 19 | 351 | 400 | 452 | 6.71 | 740 | 750 | 758 |
| 20 | 337 | 424 | 448 | 670 | 760 | 754 | 761 |
| 21 |  | 450 | 454 | 662 | 752 | 745 | 808 |
| 22 |  | 458 | 458 | 666 | 724 | 733 | 790 |
| 23 |  |  |  | 671 | 715 | 729 | 783 |
| 24 |  | 472 | 458 | 670 | 714 | 729 | 766 |
| 25 | 309 | 472 | 458 | 639 | 702 | 717 | 757 |
| 26 | 337 | 468 | 463 | 662 | 656 | 650 | 686 |
| 27 | 337 | 440 | 459 | 644 | 677 | 691 | 697 |
| 28 |  | 448 | 459 | 640 | 677 | 699 | 742 |
| March 1 |  | 474 | 475 | 660 | 671 | 660 | 675 |
| 2 |  | 477 | 478 | 685 | 670 | 625 | 631 |
| Total | 312 | 435 | 470 | 664 | 714 | 723 | 750 |

a EVENT = CPR Runof Event $\boldsymbol{w}^{3}$

Dally flow maighood pH (SU) at nodes N1, N2, MA, M5, M7, N10 and N12 during the 41 doy treatment of CPR.

CPR Runof Evant wa

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Wrach 2 | 3.69 | 509 | 4.63 | 645 | 680 | 700 | 753 |
| 3 | 582 | 4.91 | 4.66 | 659 | 6.87 | 703 | 734 |
| 4 |  | 4.96 | 476 | 645 | 674 | 708 | 721 |
| 5 |  | 533 | 495 | 645 | 6.71 | 707 | 721 |
| 6 | 4.18 | 5.44 | 501 | 655 | 6.79 | 703 | 718 |
| 7 | 4.18 | 5.81 | 5.23 | 662 | 699 | 723 | 740 |
| 8 |  | 5.91 | 569 | 6.78 | 721 | 741 | 774 |
| 9 |  | 5.79 | 572 | 673 | 698 | 725 | 732 |
| 10 | 333 | 575 | 560 | 662 | 674 | 711 | 713 |
| 11 |  | 571 | 5.68 | 665 | 682 | 715 | 721 |
| Total | 4.36 | 547 | 5.19 | 659 | 687 | 715 | 733 |

a. EVENT = CPR Runof Event Hat $_{4}$


|  | N1 | N2 | N4 | N5 | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Rundil Event ${ }^{\text {al }}$ | 303 | 546 | 541 | 6.90 | 727 | 747 | N12 77 |
| CPR Runofl Evem ${ }^{2}$ | 506 | 586 | 6.25 | 6.92 | 749 | 761 | 781 |
| CPR Runofl Event 43 | 312 | 435 | 470 | 664 | 714 | 723 | 750 |
| CPR Runcif Event ${ }^{\text {a }}$ | 436 | 547 | 519 | 659 | 687 | 715 | 733 |
| Total | 403 | 520 | 527 | 676 | 717 | 735 | 757 |

##  trenment of CPR

CPR Runofin Event \#1

|  |  | N1 | N2 | N4 | N5 | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Jaminy | 29 | 10.31 | 10.51 | 10.47 | 5.63 | 10.08 | 10.20 | 10.14 |
|  | 30 | 10.24 | 10.41 | 10.45 | 5.69 | 9.87 | 10.15 | 10.09 |
|  | 31 | 8.89 | 10.15 | 10.11 | 5.07 | 9.58 | 9.89 | 9.98 |
| February | 1 | 9.00 | 10.07 | 9.85 | 4.85 | 9.63 | 9.98 | 9.99 |
|  | 2 |  | 10.30 | 10.13 | 3.98 | 9.96 | 10.40 | 10.48 |
|  | 3 |  | 11.15 | 11.04 | 4.04 | 10.67 | 11.01 | 10.91 |
|  | 4 |  | 11.19 | 11.03 | 4.97 | 10.96 | 11.14 | 11.08 |
|  | 5 |  | 10.96 | 10.76 | 5.91 | 10.63 | 10.61 | 10.95 |
|  | 6 |  | 10.80 | 10.87 | 5.86 | 10.84 | 10.78 | 10.76 |
|  | 7 |  |  |  | 5.34 | 10.81 | 10.72 | 10.76 |
|  | 8 |  | 10.28 | 10.24 | 3.21 | 10.40 | 10.12 | 10.17 |
|  | 9 | 10.65 | 10.28 | 10.24 | 3.21 | 10.40 | 10.12 | 10.17 |
|  | 10 |  | 9.91 | 10.04 | 2.17 | 10.03 | 9.89 | 9.86 |
|  | 11 |  | 9.31 | 9.74 | 2.04 | 9.98 | 9.86 | 9.25 |
|  | 12 |  | 9.51 | 9.86 | 2.05 | 9.98 | 9.86 | 9.25 |
| Total |  | 10.25 | 10.38 | 10.32 | 4.52 | 10.12 | 10.32 | 10.27 |

a. EVENT = CPR Runof Event : 1

Delly flow weighed dissolved oxygen (mg/l) at nodes N1, M2, MA, M5, NT, N10 and N12 during the 41 day treatineot of CPR.
CPR Runoff Event *2

|  |  | ${ }^{1} 1$ | N2 | N | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 10.20 | 10.11 | 10.22 | 2.26 | 9.95 | 10.11 | 10.30 |
|  | 13 | 10.20 | 10.41 | 10.40 | 2.80 | 10.08 | 10.14 | 10.31 |
|  | 14 |  | 10.51 | 10.26 | 2.91 | 9.84 | 9.94 | 9.82 |
|  | 15 |  | 10.41 | 9.94 | 3.21 | 9.28 | 9.57 | 9.65 |
|  | 16 |  | 10.33 | 9.78 | 3.30 | 9.09 | 9.49 | 9.18 |
| Total |  | 10.20 | 10.39 | 10.11 | 2.97 | 9.64 | 9.83 | 10.12 |

a. EVENT = CPR Runoff Event *2
 trennemt of CPR.

CPR Runof Event 3

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Feinary 16 | 8.98 | 9.67 | 9.49 | 3.07 | 8.56 | 9.21 | 9.54 |
| 17 | 8.98 | 9.93 | 9.70 | 2.83 | 8.91 | 9.55 | 9.65 |
| 18 | 10.21 | 10.43 | 10.25 | 2.22 | 10.23 | 10.70 | 10.08 |
| 19 | 11.27 | 10.92 | 10.67 | 2.31 | 10.58 | 10.90 | 10.84 |
| 20 | 11.27 | 10.52 | 10.28 | 2.23 | 10.28 | 10.38 | 10.85 |
| 21 |  | 10.24 | 10.09 | 2.23 | 9.94 | 9.96 | 10.22 |
| 22 |  | 10.14 | 10.03 | 2.00 | 9.47 | 9.40 | 9.99 |
| 23 |  |  | . | 1.86 | 9.26 | 9.10 | 9.86 |
| 24 |  | 10.02 | 9.67 | 1.88 | 9.29 | 9.12 | 9.68 |
| 25 | 10.44 | 10.02 | 9.67 | 2.30 | 9.97 | 9.61 | 9.59 |
| 26 | 10.70 | 9.98 | 10.13 | 1.79 | 10.87 | 9.86 | 9.78 |
| 27 | 10.70 | 9.68 | 9.66 | 1.69 | 10.01 | 9.14 | 9.51 |
| 28 |  | 9.67 | 9.53 | 1.64 | 9.98 | 9.60 | 9.31 |
| March 1 |  | 10.04 | 10.06 | 1.67 | 10.07 | 10.02 | 9.79 |
| 2 |  | 10.11 | 10.17 | 1.75 | 9.93 | 9.95 | 10.03 |
| Total | 9.38 | 10.12 | 9.96 | 2.16 | 9.75 | 9.79 | 9.92 |

a. EVENT = CPR Runof Event 3

Dalty flow welghted dissolved oxygen (mgl) at nodes N1, N2, M4, N5, N7, N10 and N12 during the 41 day treatment of CPR.

|  | N1 | N2 | N4 | N5 | N7 | NiO | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 9.18 | 1039 | 993 | 1.84 | 977 | 914 | 10.66 |
| 3 | 917 | 10.04 | 970 | 160 | 909 | 916 | 982 |
| 4 |  | 963 | 9.80 | 163 | 951 | 957 | 943 |
| 5 |  | 1004 | 10.30 | 179 | 1031 | 1044 | 982 |
| 6 | 1025 | 1034 | 1046 | 184 | 1044 | 1073 | 986 |
| 7 | 1025 | 10.71 | 10.42 | 189 | 1014 | 1072 | 1025 |
| 8 |  | 10.29 | 1015 | 175 | 1000 | 1056 | 1036 |
| 9 |  | 962 | 978 | 164 | 964 | 998 | 965 |
| 10 | 938 | 940 | 956 | 163 | 9.33 | 964 | 964 |
| 11 |  | 972 | 972 | 169 | 948 | 981 | 979 |
| Total | 919 | 1002 | 1000 | 172 | 980 | 1008 | 993 |

a EVENT = CPR Runof Event :4

Average flow weighted dienolved orygen (mgh) et nodes N1, M2, MA, MS. N7. N10 and N12 during each of the four CPR evente.

|  | N 1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runoif Event \% 1 | 1025 | 1038 | 1032 | 452 | 1012 | 1032 | 1027 |
| CPR Runof Event ${ }^{\text {B }}$ | 1020 | 1039 | 1011 | 297 | 964 | 983 | 1012 |
| CPR Runoft Event 13 | 938 | 1012 | 996 | 216 | 975 | 979 | 992 |
| CPR Runcof Event 04 | 919 | 1002 | 1000 | 172 | 980 | 1008 | 993 |
| Total | 976 | 1022 | 1011 | 300 | 988 | 1005 | 1007 |

 at dey treetment of CPR.
CPR Runoff Event ${ }^{1} 1$

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| January | 20 | 450.00 | 228.00 | 218.00 | -35.00 | 182.00 | 188.00 | 221.00 |
|  | 30 | 454.01 | 285.42 | 255.04 | 69.15 | 194.15 | 200.17 | 21888 |
|  | 31 | $\begin{array}{r} 481.10 \\ 489.00 \end{array}$ | 30700 | 291.58 | 97.22 | 195.91 | 205.35 | 20197 |
| February | 1 |  | 305.93 | 30590 | 3568 | 182.47 | 189.66 | 19104 |
|  | 2 | $409.00$ | 295.00 | 301.50 | -70.00 | 130.37 | 149.83 | 15322 |
|  | 3 |  | 303.36 | 205.63 | -9.36 | 203.47 | 20436 | 18881 |
|  | 4 |  | 293.20 | 268.37 | 36.39 | 230.98 | 21719 | 176.44 |
|  | 5 |  | $\begin{aligned} & 250.45 \\ & 183.43 \end{aligned}$ | 27673 | -1.33 | 199.85 | 190.51 | 14745 |
|  | 8 |  |  | 288.28 | -3700 | 163.32 | 16590 | 13512 |
|  | 7 |  |  |  | -4.34 | 145.99 | 148.33 | 104.18 |
|  | 8 |  | $\begin{aligned} & 196.00 \\ & 198.00 \end{aligned}$ | 150.00 | -70.00 | 125.00 | 132.00 | 10700 |
|  | 9 | 52400 |  | 15000 | -70.00 | 12500 | 132.00 | 10700 |
|  | 10 |  | 18104 | 130.94 | -13208 | 14008 | 15240 | 12310 |
|  | 11 |  | 15700 | 102.00 | -14000 | 142.00 | 15500 | 155.00 |
|  | 12 | 452.15 | $\begin{array}{r} 162.75 \\ 268.80 \\ \hline \end{array}$ | $\begin{array}{r} 100.25 \\ 252.67 \\ \hline \end{array}$ | $\begin{array}{r} -140.33 \\ -6.23 \\ \hline \end{array}$ | $\begin{array}{r} 142.00 \\ 177.60 \\ \hline \end{array}$ | $\begin{array}{r} 155.00 \\ 183.79 \\ \hline \end{array}$ | $\begin{aligned} & 15500 \\ & 17454 \end{aligned}$ |
| Total |  |  |  |  |  |  |  |  |

a. EVENT = CPR Runof Evemt ह1

Daily flow welghted oxidation reduction potentid (mv) et nodes M1, M2, M4, MS, M7, M10 and N12 during the 41 day treetment of CPR.
CPR Runof Event $\boldsymbol{u}^{2}$

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| February | 12 | 262.00 | 180.00 | 95.00 | -14400 | 114.00 | 118.00 | 106.00 |
|  | 13 | 261.71 | 195.33 | 195.00 | -14168 | 102.42 | 120.17 | 122.61 |
|  | 14 |  | 219.24 | 219.16 | -14810 | 111.32 | 12877 | 15617 |
|  | 15 |  | 239.00 | 224.00 | -13389 | 143.50 | 152.92 | 158.51 |
|  | 16 |  | 24785 | 228.50 | -12536 | 152.71 | 16000 | 17500 |
| Total |  | 261.72 | 221.40 | 205.55 | -13879 | 124.63 | 13723 | 128.02 |

a. EVENT = CPR Runof Event *2

Dally flow weighted oxidation reduction potential (my) at nodes N1, N2. M4, MS, N7, N10 and M12 during the 41 day treatment of CPR.

CPR Runof Event ${ }^{*} 3$

|  |  | N1 | N2 | N4 | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 485.00 | 283.00 | 20600 | -7600 | 159.00 | 17200 | 160.00 |
|  | 17 | 485.00 | 41488 | 289.75 | -94 36 | 159.00 | 17071 | 16812 |
|  | 18 | 422.00 | 48389 | 376.28 | -13124 | 17094 | 17472 | 176.90 |
|  | 19 | 44655 | 45944 | 384.08 | -13735 | 17625 | 17512 | 17589 |
|  | 20 | 45500 | 41529 | 39702 | -14188 | 14950 | 15650 | 17959 |
|  | 21 |  | 40329 | 398.40 | -12871 | 16967 | 17521 | 18857 |
|  | 22 |  | 39809 | 38809 | -12133 | 162.73 | 16931 | 172.39 |
|  | 23 |  |  |  | . 122.00 | 14800 | 15500 | 16000 |
|  | 24 |  | 35200 | 358.00 | -117 76 | 14902 | 15610 | 18178 |
|  | 25 | 55400 | 352.00 | 358.00 | -2400 | 17300 | 182.00 | 19300 |
|  | 26 | 53500 | 31773 | 383.13 | -12967 | 18572 | 19943 | 16296 |
|  | 27 | 53500 | 33700 | 34100 | -146 18 | 18384 | 18696 | 16239 |
|  | 28 |  | 35950 | 33583 | -14940 | 13558 | 16338 | 16531 |
| March | 1 |  | 30423 | 28393 | -14652 | 14474 | 17398 | 18965 |
|  | 2 |  | 28900 | 24200 | . 14422 | 17312 | 19900 | 20600 |
| Total |  | 49739 | 38337 | 34741 | . 12538 | 15910 | 17069 | 17297 |

[^26]Dally flow melgined ouidetion recuction potentid (mw) at nodes N1, M2, M4, M5, N7, N10 and N12 during the 41 coy trectiment of CPR.

CPR Runofl Event ina

a. EVENT = CPR Runof Event wa
 each of the four CPR events.

|  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Rundi Event 11 | 452.15 | 268.80 | 252.67 | 623 | 17760 | 183.79 | 17454 |
| CPR Runofl Event 62 | 261.72 | 22140 | 20555 | -138.79 | 124.63 | 13723 | 128.02 |
| CPR Runofl Event 33 | 49739 | 383.37 | 34741 | -125 38 | 15910 | 17069 | 172.97 |
| CPR Runofl Event it | 373.28 | 25617 | 25780 | -199 10 | 14463 | 17446 | 15025 |
| Total | 383.45 | 292.41 | 27489 | -10175 | 15776 | 17166 | 16413 |

CPR Runof Evem 1

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| January | 29 | $\begin{aligned} & 1045.00 \\ & 1830.16 \\ & 2286.95 \\ & 2930.00 \end{aligned}$ | 1079.00 | 1034.00 | 1129.00 | 994.00 | 857.00 | 102900 |
|  | 30 |  | 1101.33 | 108125 | 1114.72 | 1044.97 | 1029.15 | 97038 |
|  | 31 |  | 1115.08 | 1003.83 | 1124.58 | 1098.57 | 1102.45 | 1004.68 |
| February | 1 |  | 1150.05 | 1129.21 | 115196 | 1120.54 | 1121.76 | 1088.38 |
|  | 2 | $2930.00$ | 1170.75 | 1141.75 | 1164.37 | 1132.75 | 1132.42 | 1120.10 |
|  | 3 |  | 1186.60 | 1148.88 | 1178.31 | 1143.07 | 1145.07 | 1133.54 |
|  | 4 |  | 1171.64 | 116180 | 1184.50 | 1149.60 | 1155.14 | 1142.19 |
|  | 5 |  | 1174.83 | 1172.78 | 120120 | 1162.51 | 117483 | 1158.22 |
|  | 6 |  | 117388 | 1172.14 | 1206.23 | 1168.25 | 118183 | 117132 |
|  | 7 |  |  |  | 1211.23 | 1171.34 | 1187.23 | 117472 |
|  | 8 |  | 1186.00 | 1182.00 | 1233.00 | 1183.00 | 1202.00 | 118600 |
|  | 9 | 3520.00 | 1186.00 | 1182.00 | 123300 | 118300 | 1202.00 | 118600 |
|  | 10 |  | 1168.35 | 1162.54 | 123832 | 1159.94 | 111153 | 115951 |
|  | 11 |  | 1140.00 | 1133.00 | 1239.00 | 115700 | 1100.00 | 110700 |
|  | 12 |  | 1132.75 | 1130.00 | 123793 | 115700 | 110000 | 110700 |
| Total |  | 1889.35 | 114543 | 1124.63 | 1168.10 | 1118.17 | 1109.52 | 108983 |

a. EVENT = CPR Runof Event 1

Dally flow weighted conductivity (umhoa/cm) at nodes N1, M2, MA, M5, NT, N10 and N12 during the 41 day trectiment of CPR.

|  |  | N1 | N2 | NA | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 1100.00 | 1111.00 | 112100 | 1228.00 | 1080.00 | 106600 | 1093.00 |
|  | 13 | 109671 | 99100 | 99633 | 1164.24 | 1139.34 | 853.95 | 996.60 |
|  | 14 |  | 953.89 | 910.37 | 112883 | 1145.91 | 96447 | 82942 |
|  | 15 |  | 963.33 | 928.00 | 107571 | 112727 | 112732 | 85277 |
|  | 16 |  | 962.20 | 942.90 | 1061.07 | 1121.86 | 113100 | 96300 |
| Total |  | 1098.82 | 980.30 | 95730 | 1120.65 | 112985 | 101703 | 98256 |

a. EVENT = CPR Runof Event 2

Dally flow waighted conductivity (umhos/cm) at nodes N1, N2. M4, N5, NT, N10 and N12 during the 41 day trectiment of CPR.
CPR Runoff Event ${ }^{(1)}$

|  |  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 2140.00 | 928.00 | 960.00 | 102500 | 109400 | 1108.00 | 105400 |
|  | 17 | 214000 | 1105.50 | 94188 | 102743 | 1076.21 | 107760 | 102355 |
|  | 18 | 1236.00 | 120012 | 97791 | 102752 | 1026.31 | 104012 | 96785 |
|  | 19 | 139915 | 117577 | 104179 | 104339 | 102388 | 104712 | 100243 |
|  | 20 | 150900 | 114784 | 107936 | 107450 | 1026.25 | 104350 | 1012.09 |
|  | 21 |  | 112014 | 109628 | 110416 | 1030.73 | 103827 | 103864 |
|  | 22 |  | 110964 | 1100.27 | 112398 | 104697 | 104598 | 103723 |
|  | 23 |  |  |  | 112900 | 1054.00 | 105200 | 103800 |
|  | 24 |  | 110300 | 111400 | 113047 | 1055.38 | 105578 | 105188 |
|  | 25 | 2460.00 | 110300 | 111400 | 116300 | 108800 | 114500 | 105900 |
|  | 26 | 201000 | 113270 | 106983 | 116887 | 107332 | 107987 | 104333 |
|  | 27 | 201000 | 122933 | 109933 | 116742 | 109073 | 109098 | 104300 |
|  | 28 |  | 120800 | 111692 | 116099 | 110481 | 108138 | 104234 |
| March | 1 |  | 116661 | 113392 | 116196 | 111827 | 109541 | 103570 |
|  | 2 |  | 116800 | 113900 | 116861 | 113030 | 112200 | 103500 |
| Total |  | 213324 | 114219 | 1080.22 | 109656 | 106233 | 106569 | 103052 |

a EVENT = CPR Runoff Event \#3
 treamert of CPR.
CPR Runcfi Event at

|  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 1698.00 | 1160.00 | 1128.00 | 1177.00 | 113400 | 1129.00 | 1052.00 |
| 3 | 725.79 | 1088.75 | 109488 | 1178.14 | 112190 | 1058.04 | 103148 |
| 4 |  | 1013.50 | 1045.50 | 114775 | 1115.03 | 105827 | 960.46 |
| 5 |  | 881.00 | 1009.12 | 1101.15 | 1114.08 | 109566 | 800.24 |
| 6 | 923.00 | 95100 | 100500 | 1090.00 | 1116.00 | 1108.00 | 92100 |
| 7 | 923.00 | 957.67 | 988.33 | 1085.60 | 1108.58 | 111789 | 97514 |
| 8 |  | 97167 | 98067 | 1046.75 | 109775 | 111775 | 1054.00 |
| 9 |  | 977.00 | 982.62 | 1041.35 | 1082.97 | 1110.45 | 1083.33 |
| 10 | 1480.00 | 977.00 | 98400 | 104000 | 1074.00 | 1108.00 | 1086.00 |
| 11 |  | 988.73 | 988.45 | 1038.16 | 1069.27 | 110064 | 108975 |
| Total | 1379.25 | 997.89 | 101717 | 108584 | 1102.13 | 109834 | 101514 |

a. EVENT = CPR Runof Event tad
 tour Cem evente.

|  | N1 | N2 | Na | N5 | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcur Event 11 | 1869.35 | 1145.43 | 112463 | 1168.10 | 1118.17 | 1109.52 | 108983 |
| CPR Runofit Event 02 | 1096.82 | 980.30 | 95730 | 1120.65 | 1129.85 | 101703 | 98256 |
| CPR Runcill Event 3 | 2133.24 | 1142.19 | 106022 | 109656 | 1062.33 | 106569 | 103052 |
| CPR Runcil Event 4 | 137925 | 99789 | 101717 | 108584 | 110213 | 109834 | 101514 |
| Total | 1568.23 | 1085.50 | 1056.41 | 1122.52 | 1099.85 | 108186 | 104434 |


| JanueryFebruary |  | N1 | $\mathrm{N2}$ | M4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 29 | $\begin{aligned} & 4.46 \\ & 3.85 \\ & 4.52 \\ & 6.80 \end{aligned}$ | 04 | 04 | 15 | 09 | 00 | 00 |
|  | 30 |  | 43 | 08 | 16 | 05 | 00 | 00 |
|  | 31 |  | 59 | 22 | 23 | 01 | 00 | 00 |
|  | 1 |  | 64 | 36 | 29 | 00 | 00 | 00 |
|  | 2 |  | 65 | 37 | 33 | 01 | 01 | 00 |
|  | 3 |  | 54 | 32 | 27 | 01 | 00 | 00 |
|  | 4 | . | 44 | 29 | 29 | 00 | 00 | 00 |
|  | 5 |  | 42 | 25 | 49 | $\infty$ | 00 | 00 |
|  | 6 |  | 32 | 21 | 62 | 00 | 01 | 00 |
|  | 7 |  |  |  | 66 | 00 | 01 | 00 |
|  | 0 |  | 10 | 13 | 71 | 00 | $\infty$ | 00 |
|  | 9 | 2.44 | 10 | 13 | 71 | 00 | $\infty$ | $\infty$ |
|  | 10 |  | 07 | 10 | 1.02 | 00 | 00 | 00 |
|  | 11 |  | 01 | 08 | 108 | 00 | $\infty$ | 00 |
|  | 12 |  | 01 | 05 | 107 | $\infty$ | 00 | 00 |
| Total |  | 437 | 44 | 22 | 40 | 02 | 00 | 00 |

a. EVENT = CPR Runoff Event 1

Dally flow welighted ferrous iron (mg/l) at nodes $\mathrm{N} 1, \mathrm{M2}, \mathrm{M}, \mathrm{NH}, \mathrm{N7}, \mathrm{~N} 10$ and N12 during the 41 day treatment of CPR.
CPR Runof Event ${ }^{6} 2$

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 64 | 01 | 00 | 116 | 00 | 00 | 00 |
|  | 13 | 84 | 07 | 00 | 95 | 04 | 01 | 01 |
|  | 14 |  | 05 | 00 | 81 | 02 | 01 | 00 |
|  | 15 |  | 06 | 00 | 62 | 02 | 00 | 00 |
|  | 16 |  | 10 | 01 | 56 | 03 | 00 | 00 |
| Total |  | 64 | 06 | 00 | 78 | 02 | 00 | 00 |

a. EVENT = CPR Runoff Event *2

Daily flow welghted ferrous iron (mgRL) ak nodes N1, M2, M4, M5, NT, N10 and N12 during the 41 day treetment of CPR.

CPR Runofit Event ${ }^{*} 3$

|  |  | N1 | N2 | N4 | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 5.84 | 49 | 08 | 11 | 00 | 00 | 00 |
|  | 17 | 5.84 | 35 | 11 | 23 | 00 | 00 | 00 |
|  | 18 | 161 | 26 | 10 | 59 | 00 | 00 | 01 |
|  | 19 | 319 | 23 | 14 | 86 | 00 | 00 | 00 |
|  | 20 | 336 | 16 | 15 | 69 | 01 | 00 | 00 |
|  | 21 |  | 10 | 13 | 71 | 00 | 01 | 00 |
|  | 22 |  | 10 | 13 | 74 | 00 | 00 | 01 |
|  | 23 |  |  |  | 75 | $\infty$ | 00 | 01 |
|  | 24 |  | 12 | 16 | 76 | 00 | 00 | 00 |
|  | 25 | 263 | 12 | 16 | 108 | 09 | 01 | 00 |
|  | 26 | 00 | 23 | 14 | 108 | 04 | 02 | 00 |
|  | 27 | 00 | 49 | 12 | 111 | 03 | 01 | 02 |
|  | 28 |  | 27 | 12 | 105 | 01 | 00 | 02 |
| March | 1 |  | 09 | 11 | 97 | 00 | 00 | 00 |
|  | 2 |  | 09 | 11 | 94 | 00 | 01 | 00 |
| Total |  | 464 | 24 | 13 | 69 | 00 | 00 | 01 |

[^27] trememert of CPR.

|  | N1 | N2 | M | N5 | $N 7$ | $N 10$ | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 3.52 | . 09 | 10 | 102 | 01 | 01 | 00 |
| 3 | 20 | 11 | 09 | 84 | 01 | 01 | 03 |
| 4 |  | . 08 | 08 | 88 | 01 | 01 | 03 |
| 5 |  | . 02 | 03 | 79 | 00 | 00 | 00 |
| 6 | 43 | 02 | 04 | 78 | $\infty$ | 00 | 00 |
| 7 | 43 | 03 | 02 | 68 | 00 | 00 | 00 |
| 8 |  | 03 | 01 | 58 | 01 | $\infty$ | 00 |
| 9 |  | 04 | 01 | 56 | 00 | 00 | 00 |
| 10 | 428 | 05 | 01 | 55 | 00 | 00 | 00 |
| 11 |  | 08 | 02 | 53 | 00 | 00 | 00 |
| Totar | 2.45 | 05 | 04 | 71 | 00 | 00 | 01 |

a. EVENT = CPR Runof Event ${ }_{4} 4$
 CER overne.

|  | N1 | N2 | Na | N5 | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runow Evemt ${ }^{1}$ | 437 | 44 | 22 | 40 | 02 | 00 | 00 |
| CPR Runofl Event ${ }^{\text {\% }}$ | 64 | 06 | 00 | 78 | 02 | 00 | 00 |
| CPR Rundil Event ${ }^{\text {e3 }}$ | 4.64 | 24 | 13 | 69 | 00 | 00 | 01 |
| CPR Runof Event it | 2.45 | 05 | 04 | 71 | 00 | 00 | 01 |
| Toter | 2.78 | 23 | 12 | 61 | 01 | 00 | 00 |


the if dey treatiment of CPI.

|  |  | N1 | H2 | N4 | N5 | N7 | ${ }^{\text {N10 }}$ | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Jenuary | 20 | $\begin{aligned} & 36.86 \\ & 15.43 \\ & 28.21 \\ & 79.80 \end{aligned}$ | 1.23 | 55 | 23 | 2.61 |  | 80 |
|  | 30 |  | 4.79 | 74 | 14 | 114 | 52 | 52 |
|  | 31 |  | 5.06 | 1.58 | 20 | 12 | 04 | 17 |
|  | 1 |  | 4.83 | 2.45 | 22 | 08 | 03 | 04 |
|  | 2 |  | 413 | 3.20 | 28 | 08 | 05 | 04 |
|  | 3 |  | 3.10 | 3.61 | 18 | 08 | 05 | 05 |
|  | 4 |  | 1.90 | 3.50 | 50 | 07 | 03 | 05 |
|  | 5 |  | 99 | 2.95 | 13 | 08 | 02 | 04 |
|  | 6 |  | 40 | 2.45 | 08 | 03 | 01 | 04 |
|  | 7 |  |  |  | 15 | 04 | 02 | 07 |
|  | 8 |  | 27 | 184 | 18 | 07 | 03 | 19 |
|  | 9 | 15900 | 27 | 184 | 18 | 07 | 03 | 19 |
|  | 10 |  | 23 | 1.55 | 08 | 14 | 08 | 20 |
|  | 11 |  | 16 | 110 | 07 | 15 | 09 | 21 |
|  | 12 |  | 60 | 99 | 10 | 15 | 09 | 21 |
| Total |  | 34.20 | 317 | 2.11 | 20 | 37 | 17 | 20 |

a. EVENT = CPR Runof Evemt ${ }^{1} 1$

Dally flow weighted total eluminum (mg/L) concentrations at nodes Ng, N2, M4, M5, M7, N10 and M12 during the 41 doy treetment of CPR.

a. EVENT = CPR Runof Event

Deily flow weighted total shuminum (mg/L) concentritions at nodes Mg, M2, M4, N5, N7, N10 and N12 during the 41 dry trectment of CPR.

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 54.18 | 906 | 80 | 01 | 02 | 02 | 05 |
|  | 17 | 20.27 | 1537 | 127 | 07 | 07 | 08 | 18 |
|  | 18 | 1720 | 1389 | 407 | 22 | 19 | 11 | 36 |
|  | 19 | 3017 | 1280 | 7.60 | 33 | 12 | 05 | 10 |
|  | 20 | 32.50 | 1125 | 9.21 | 44 | 09 | 04 | 09 |
|  | 21 |  | 991 | 968 | 54 | 16 | 08 | 14 |
|  | 22 |  | 964 | 997 | 58 | 20 | 11 | 16 |
|  | 23 |  |  |  | 59 | 20 | 12 | 16 |
|  | 24 |  | 594 | 1020 | 35 | 20 | 12 | 12 |
|  | 25 | 7452 | 673 | 1020 | 32 | 17 | 05 | 09 |
|  | 26 | 5424 | 780 | 848 | 34 | 10 | 04 | 12 |
|  | 27 | 3930 | 939 | 773 | 44 | 14 | 01 | 13 |
|  | 28 |  | 728 | 729 | 26 | 06 | $\infty$ | 06 |
| March | 1 |  | 581 | 688 | 26 | 05 | 02 | 05 |
|  | 2 |  | 218 | 684 | 28 | 11 | 03 | 08 |
| Totar |  | 5388 | 1008 | 698 | 34 | 12 | 06 | 12 |

a EVENT = CPR Runof Event *3

curing the 41 coy tracturnt of CPR.
CPR Runof Event in

|  | N1 | N2 | NH | N5 | N7 | N10 | N 12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 10.35 | 3.50 | 6.98 | 25 | 00 | 00 | 01 |
| 3 | 2.61 | 1.82 | 6.17 | 31 | 17 | 00 | 16 |
|  |  | 1.27 | 4.50 | 21 | 16 | 01 | 27 |
| 5 |  | 49 | 2.79 | 17 | 11 | 04 | 25 |
| 6 | 8.17 | 28 | 2.49 | 09 | 11 | 04 | 23 |
| 7 | 1370 | 38 | 1.63 | 12 | 04 | 02 | 13 |
| 8 |  | 37 | 83 | 03 | 04 | 00 | 03 |
| 9 |  | 52 | 61 | 03 | 17 | 10 | 18 |
| 10 | 18.88 | 67 | 59 | 00 | 25 | 17 | 23 |
| 11 |  | 60 | 56 | 03 | 22 | 15 | 19 |
| Total | 8.00 | 89 | 2.63 | 11 | 13 | 05 | 16 |

a. EVENT $=$ CPR Runof Event ita
 each of the four CPR events.

|  | $N 1$ | N2 | N/ | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Rund Event 11 | 3420 | 3.17 | 2.11 | 20 | 37 | 17 | 20 |
| CPR Runowl Evert ${ }^{\text {H2}}$ | 985 | 2.14 | 42 | 11 | 54 | 38 | 33 |
| CPR Runcofl Event 43 | 53.88 | 1008 | 698 | 34 | 12 | 06 | 12 |
| CPR Runofl Event ${ }^{\text {en }}$ | 800 | 89 | 2.63 | 11 | 13 | 05 | 16 |
| Fotal | 2485 | 4.48 | 3.42 | 21 | 27 | 14 | 18 |

CPR Runof Evert ${ }^{11}$

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Januery | 20 | 11.64 | 1.57 | 27 | 50 | 170 | 84 | 60 |
|  | 30 | 4.98 | 1.01 | 35 | 36 | 81 | 38 | 45 |
|  | 31 | 10.88 | . 97 | 40 | 41 | 18 | 03 | 18 |
|  | 1 | 34.00 | 82 | 49 | 44 | 20 | 04 | 06 |
|  | 2 |  | 69 | 49 | 29 | 29 | 06 | 06 |
|  | 3 |  | 60 | 41 | 38 | 21 | 07 | 06 |
|  | 4 |  | 53 | 42 | 64 | 20 | 06 | 05 |
|  | 5 |  | 56 | 32 | 49 | 15 | 02 | 03 |
|  | 6 |  | 39 | 25 | 63 | 12 | 02 | 04 |
|  | 7 |  |  |  | 80 | 12 | 02 | 07 |
|  | 8 |  | 43 | 22 | 93 | 13 | 04 | 41 |
|  | 9 | 42.50 | 43 | 22 | 93 | 13 | 04 | 41 |
|  | 10 |  | 37 | 20 | 118 | 17 | 05 | 33 |
|  | 11 |  | 27 | 19 | 121 | 17 | 05 | 17 |
|  | 12 |  | 53 | 16 | 116 | 17 | 05 | 17 |
| Total |  | 10.85 | 76 | 37 | 55 | 35 | 13 | 20 |

a. EVENT = CPR Runof Event 1

Dally flow waighted total iron (mall) concentrations whodes N1, M2, M4, MK, N7, N10 and N12 during the 41 dey treatment of CPR.

a. EVENT = CPR Runoff Event \% 2

Delly flow weighted total iron (mghl) concentrations at nodes N1, M2, M, NS, N7, N10 and N12 during the 41 dry treatment of CPR.

a EVENT = CPR Runoli Event

##  41 doy treationt of CPR.

CPR Runof Event *a

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Manch | 2 | 730 | 16 | 15 | 119 | -17 | 01 | 05 |
|  | 3 | 1.90 | 23 | 20 | 1.41 | 32 | 02 | 12 |
|  | 4 |  | 28 | 20 | 1.02 | 29 | 03 | 25 |
|  | 5 |  | 15 | 30 | 87 | 21 | 03 | 30 |
|  | 6 | 149 | 11 | 37 | 52 | 21 | 02 | 23 |
|  | 7 | 3.64 | 16 | 19 | 60 | 23 | 03 | 19 |
|  | 8 |  | 15 | 09 | 67 | 23 | 02 | 13 |
|  | 9 |  | 25 | 16 | 45 | 29 | 03 | 08 |
|  | 10 | 10.63 | 44 | 23 | 74 | 34 | 04 | 07 |
|  | 11 |  | 49 | 21 | 69 | 33 | 04 | 07 |
| Total |  | 5.57 | 23 | 21 | 77 | 27 | 03 | 15 |

a. EVENT $=$ CPR Runof Event tal
 to four Con everna.

|  | N1 | N2 | N4 | NS | N7 | N10 | N 12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcin Event 11 | 10.85 | 76 | 37 | 55 | 35 | 13 | 20 |
| CPR Runofl Event 12 | 10.95 | 100 | 20 | 78 | 66 | 29 | 21 |
| CPR Runow Event 3 | 23.90 | 113 | 35 | 82 | 25 | 06 | 10 |
| CPR Runctif Evont ${ }^{\text {a }}$ | 557 | 23 | 21 | 77 | 27 | 03 | 15 |
| Total | 12.81 | 77 | 30 | 71 | 34 | 19 | 16 |

 cundrey the 41 day fremenent of CPR.
CPR Runof Evem: 11

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| JenueryFebruary | 20 | 3.82 | 46 | 63 | 98 | 46 | 06 | 04 |
|  | 30 | 2.00 | 104 | 67 | 97 | 47 | 03 | 03 |
|  | 31 | 2.95 | 102 | 75 | 1.00 | 43 | 01 | 02 |
|  |  | 7.42 | 1.01 | 87 | 102 | 39 | 01 | 01 |
|  | 2 |  | 94 | 95 | 105 | 39 | 00 | 01 |
|  | 3 |  | 88 | 99 | 1.10 | 37 | 00 | 00 |
|  | 4 |  | 74 | 93 | 111 | 33 | 00 | 01 |
|  | 5 |  | 68 | 87 | 114 | 22 | 00 | 01 |
|  | 6 |  | 55 | 03 | 112 | 15 | 00 | 01 |
|  | 7 |  |  |  | 1.12 | 13 | $\infty$ | 04 |
|  | 8 |  | 49 | 78 | 1.14 | 08 | 00 | 51 |
|  | 9 | 1150 | 49 | 78 | 114 | 08 | 00 | 51 |
|  | 10 |  | 49 | 75 | 119 | 11 | 02 | 36 |
|  | 11 |  | 49 | 70 | 120 | 12 | 02 | 06 |
|  | 12 |  | 37 | 68 | 114 | 12 | 02 | 07 |
| Total |  | 3.57 | 83 | 81 | 106 | 34 | 01 | 07 |

a. EVENT = CPR Runof Event 1

Dally flow waighted total mangenese (ma/l) concentrations at nodes M1, N2, M4, N5, N7, N10 and M12 during the 41 dey treatment of CPR.
CPR Runoff Evem *2

|  |  | N1 | $N 2$ | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February |  | 2.31 | 35 | 60 | 113 | 09 | 01 | 02 |
|  | 13 | 154 | 72 | 47 | 100 | 20 | 02 | 08 |
|  | 14 |  | 77 | 44 | 97 | 27 | 01 | 25 |
|  | 15 |  | 88 | 54 | 86 | 37 | 01 | 23 |
|  | 16 |  | 1.24 | 60 | 80 | 40 | 01 | 05 |
| Total |  | 157 | 82 | 51 | 93 | 29 | 01 | 11 |

a. EVENT = CPR Runof Event ${ }^{\text {W }} 2$

Daily flow welghted total manganese (mgh) concentrations at nodes M1, M2, M4, NS, N7, N10 and N12 during the 41 dey treatiment of CPR.

| February |  | N1 | N2 | N4 | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 16 | 483 | 1.34 | 76 | 80 | 37 | 01 | 08 |
|  | 17 | 2.44 | 185 | 81 | 83 | 32 | 01 | 07 |
|  | 18 | 208 | 176 | 103 | 87 | 20 | 01 | 05 |
|  | 19 | 266 | 164 | 130 | 91 | 16 | 00 | 02 |
|  | 20 | 327 | 146 | 139 | 97 | 14 | 00 | 02 |
|  | 21 |  | 133 | 142 | 97 | 15 | 00 | 03 |
|  | 22 |  | 131 | 147 | 100 | 20 | 00 | 03 |
|  | 23 |  |  |  | 99 | 22 | 01 | 02 |
|  | 24 |  | 111 | 149 | 110 | 21 | 01 | 02 |
|  | 25 | 630 | 119 | 1.49 | 109 | 07 | 00 | 02 |
|  | 26 | 430 | 132 | 123 | 113 | 23 | 09 | 09 |
|  | 27 | 481 | 151 | 128 | 110 | 23 | 00 | 08 |
| March | 28 |  | 135 | 131 | 114 | 27 | 03 | 02 |
|  | 1 |  | 128 | 128 | 115 | 28 | 02 | 04 |
|  | 2 |  | 122 | 128 | 118 | 26 | 00 | 05 |
| Total |  | 483 | 146 | 124 | 98 | 23 | 01 | 05 |

a EVENT = CPR Runof Event ${ }^{3}$
 curing the 44 coy trentment of CPR.

CPR Runof Event A4

|  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Werch 2 | 2.71 | 1.26 | 1.35 | 1.21 | 16 | 00 | N12 02 |
| 3 | 87 | 1.13 | 1.24 | 125 | 29 | 00 | 05 |
| 4 |  | 1.09 | 1.08 | 1.18 | 34 | 00 | 10 |
| 5 |  | 1.08 | 102 | 1.04 | 39 | 00 | 12 |
| 6 | 134 | 98 | 107 | 100 | 41 | 00 | 08 |
| 7 | 1.83 | 95 | 106 | 94 | 26 | 00 | 07 |
| 8 |  | 81 | 94 | 98 | 13 | 00 | 04 |
| 9 |  | 82 | 84 | 91 | 13 | 00 | 03 |
| 10 | 2.53 | 89 | 79 | 94 | 14 | 00 | 03 |
| 11 |  | 85 | 78 | 88 | 14 | 00 | 03 |
| Tota | 2.11 | 98 | 101 | 102 | 25 | 00 | 06 |

a. EVENT = CPR Runof Event :"as
 each of tie four CPR evertie.

|  | $N 1$ | N2 | N4 | NS | N7 | $N 10$ | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcin Event ${ }^{1} 1$ | 357 | 83 | 81 | 106 | 34 | 01 | N12 07 |
| CPR Runchil Event ${ }^{\text {en }}$ | 1.57 | 82 | 51 | 93 | 29 | 01 | 11 |
| CPR Runchl Event ${ }^{\text {a }}$ | 483 | 146 | 124 | 98 | 23 | 01 | 05 |
| CPR Runoflil Event ${ }^{4}$ | 2.11 | 98 | 107 | 102 | 25 | 00 | 06 |
| Toter | 2.88 | 105 | 94 | 1.01 | 28 | 01 | 06 |

Dolly flow meigined total hot peroxide setiny (mgh an CaCO3) concentrations at nodes M1, M2, MA, MS, M7, W10 and W12 during the 41 dey trenement of CPR.

a. EVENT = CPR Runon Evem

Dally flow welghed total hot perozide scidily (mgh as CaCO3) concentrations at nodes N1, N2, N4, NS, N7, N10 and N12 during the 41 day tratiment of CPR.

a. EVENT = CPR Runof Event \#2

Dally flow weighted total hot peroxide acidity (mghl as CaCO3) concentrations af nodes NT, N2, NM, MS, NT. N10 and N12 during the 41 diry trectment of CPR.

|  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February 16 | 368.60 | 20.00 | 6100 | 10 | 10 | 10 | 10 |
| 17 | 368.60 | 65.25 | 36.62 | 10 | 10 | 10 | 10 |
| 18 | 10030 | 55.12 | 8.30 | 10 | 10 | 10 | 10 |
| 19 | 12875 | 82.65 | 53.73 | 472 | 10 | 10 | 02 |
| 20 | 15800 | 100.68 | 8434 | 2.63 | 10 | 10 | 01 |
| 21 |  | 9171 | 8137 | 00 | 04 | 04 | 02 |
| 22 |  | 8164 | 82.33 | 00 | 00 | 00 | 00 |
| 23 |  |  |  | 00 | $\infty$ | $\infty$ | 00 |
| 24 |  | 7500 | 83.00 | 00 | 00 | 00 | $\infty$ |
| 25 | 478.00 | 7500 | 83.00 | 00 | 00 | 00 | 00 |
| 26 | 26700 | 7576 | 7584 | 00 | 00 | 00 | $\infty$ |
| 27 | 28700 | 8293 | 72.53 | 00 | 00 | 00 | 00 |
| 28 |  | 8302 | 7340 | 00 | 00 | 00 | 00 |
| March 1 |  | 4689 | 4858 | 00 | 00 | 00 | 00 |
| 2 |  | 3820 | 4200 | 00 | $\infty$ | 00 | 00 |
| Total | 35735 | 7362 | 6286 | 69 | 05 | 05 | 03 |

a EVENT = CPR Runofl Event \%3

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 MT, M1O and M12 during the 41 dry trenmert of CPR.
CPR Runofi Event ${ }^{2} 4$

|  | N1 | N2 | N4 | NS | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Wrerch 2 | 87.70 | 50.00 | 63.00 | 00 | 00 | 00 | 00 |
| 3 | 29.06 | 45.00 | 56.13 | 00 | 00 | 00 | 00 |
| 4 |  | 39.80 | 4700 | 00 | 00 | 00 | 00 |
| 5 |  | 2787 | 36.00 | 00 | 00 | 00 | 00 |
| 6 | 6700 | 23.00 | 32.40 | 00 | 00 | 00 | 00 |
| 7 | 6700 | 25.67 | 34.13 | 00 | 00 | 00 | 00 |
| 8 |  | 20.87 | 21.67 | 00 | 00 | 00 | 00 |
| 9 |  | 24.30 | 21.83 | 00 | 00 | 00 | 00 |
| 10 | 14600 | 28.20 | 27.60 | 00 | 00 | 00 | 00 |
| 11 |  | 28.09 | 27.71 | 00 | 00 | 00 | 00 |
| Total | 69.67 | 30.54 | 35.99 | 00 | 00 | 00 | 00 |

a. EVENT = CPR Runon Event :4
 N10 and N12 during each of the four CPR evente.

|  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcil Event 1 | 26936 | 20.93 | 14.91 | 4.95 | 362 | 135 | 176 |
| CPR Runcif Event ${ }^{\text {en }}$ | 68.86 | 19.58 | 20.94 | 139 | 64 | 10 | 171 |
| CPR Runof Event ${ }^{\text {e3 }}$ | 35735 | 73.62 | 62.86 | 69 | 05 | 05 | 03 |
| CPR Runoff Event 4 | 6967 | 30.54 | 3599 | 00 | 00 | 00 | 00 |
| Total | 17799 | 38.40 | 3483 | 2.12 | 137 | 50 | 78 |

CPR Runof Event ©

|  |  | N1 | N2 | M | N5 | N7 | N10 | $N 12$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Samiary | 2 | 10 | 19.40 | 4060 |  |  | 33.50 | 3740 |
|  | 30 | 10 | 8.50 | 7.57 | 29.21 | 27.88 | 33.14 | 3740 |
|  | 31 | 10 | 3.17 | 3.82 | 32.13 | 30.07 | 32.32 | 3728 |
| February | 1 | 00 | 2.67 | 2.76 | 33.83 | 30.73 | 31.91 | 38.46 |
|  | 2 |  | 20.02 | 2.11 | 1431 | 31.70 | 34.30 | 35.28 |
|  | 3 |  | 736 | 349 | 20.08 | 33.73 | 3768 | 3521 |
|  | 4 |  | 4.00 | 3.70 | 31.70 | 34.39 | 38.27 | 36.81 |
|  | 5 |  | 3.86 | 2.76 | 34.63 | 32.78 | 38.15 | 3762 |
|  | 6 |  | 6.14 | 2.34 | 35.45 | 31.82 | 39.34 | 36.89 |
|  | 7 |  |  |  | 36.00 | 3158 | 3997 | 3549 |
|  | 8 |  | 8.80 | 220 | 38.10 | 30.80 | 3950 | 1020 |
|  | 9 | 10 | 8.80 | 2.20 | 38.10 | 3080 | 3950 | 1020 |
|  | 10 |  | 9.80 | 2.36 | 49.38 | 2823 | 4189 | 2009 |
|  | 11 |  | 1140 | 2.60 | 50.80 | 2790 | 42.20 | 3970 |
|  | 12 |  | 13.40 | 3.05 | 5166 | 2790 | 42.20 | 3970 |
| Total |  | 10 | 8.74 | 3.98 | 3116 | 30.62 | 36.00 | 3462 |

a. EVENT = CPR Runor Event w1
 N12 during the 41 dey trederient of CPR.
CPR Runoff Event ${ }^{1} 2$

|  |  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | $\begin{aligned} & 3.60 \\ & 3.60 \end{aligned}$ | 19.40 | 440 | 6130 | 32.10 | 46.10 | 4330 |
|  | 13 |  | 11.33 | 607 | 53.89 | 33.40 | 36.91 | 3773 |
|  | 14 |  | 575 | 528 | 4921 | 4184 | 4073 | 2703 |
|  | 15 |  | 273 | 483 | 42.38 | 48.42 | 4975 | 2948 |
|  | 16 |  | 143 | 500 | 40.58 | 48.28 | 5100 | 4450 |
| Total |  | 3.60 | 6.53 | 5.16 | 48.17 | 4177 | 4434 | 3693 |

a. EVENT = CPR Runofl Event ${ }^{1} 2$

Daily flow whighted total ankelinity (mgh as CaCO3) concentrations at nodga N1, N2, M4, N5, NT, N10 and N12 during the 41 dey tremement of CPR.
CPR Runoff Event 3

|  |  | N1 | N2 | N 4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 10 | 10 | 590 | 3650 | 4610 | 4760 | 5180 |
|  | 17 | 10 | 10 | 396 | 38.61 | 44.52 | 4821 | 3591 |
|  | 18 | 10 | 10 | 130 | 45.44 | 3986 | 4711 | 1874 |
|  | 19 | 10 | 10 | 20 | 45.13 | 4040 | 45.48 | 4950 |
|  | 20 | 10 | 10 | 2.57 | 4381 | 4069 | 4656 | 4863 |
|  | 21 |  | 2.15 | 2.08 | 42.59 | 4317 | 4564 | 4528 |
|  | 22 |  | 2.82 | 147 | 4370 | 42.61 | 4718 | 42.79 |
|  | 23 |  |  |  | 4450 | 4150 | 4880 | 4140 |
|  | 24 |  | 70 | $\infty$ | 4471 | 4178 | 5031 | 4483 |
|  | 25 | 00 | 70 | 00 | 4940 | 4830 | 8590 | 4660 |
|  | 26 | 00 | 146 | 122 | 5938 | 4311 | 5848 | 4758 |
|  | 27 | 00 | 57 | 53 | 6149 | 4263 | 5592 | 4872 |
|  | 28 |  | 87 | 47 | 5629 | 4436 | 5256 | 5033 |
| March | 1 |  | 84 | 16 | 5155 | 4709 | 5251 | 5111 |
|  | 2 |  | 70 | 00 | 50.30 | 4955 | 5460 | 5090 |
| Total |  | 08 | 72 | 156 | 4626 | 4299 | 4917 | 4558 |

a EVENT = CPR Runof Evemt 3
 M12 dring the 41 dry treetment of CPR.
CPR Runcif Event eat

|  |  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March | 2 | 00 | 1.70 | 1.50 | 51.50 | 53.80 | 59.50 | 51.90 |
|  | 3 | 4.60 | 2.76 | 2.00 | 52.36 | 52.75 | 58.61 | 51.56 |
|  | 4 |  | 3.95 | 3.10 | 51.36 | 51.01 | 57.81 | 52.47 |
|  | 5 |  | 4.77 | 2.65 | 48.54 | 50.12 | 55.49 | 54.28 |
|  | 6 | 00 | 4.90 | 1.90 | 4750 | 50.50 | 54.30 | 5450 |
|  | 7 | 00 | 11.83 | 1.90 | 43.61 | 4834 | 52.57 | 54.68 |
|  | 8 |  | 17.97 | 3.63 | 4166 | 45.12 | 47.81 | 5419 |
|  | 9 |  | 17.30 | 4.39 | 40.49 | 42.84 | 47.38 | 5158 |
|  | 10 | 00 | 16.10 | 4.30 | 3950 | 41.90 | 48.60 | 5110 |
|  | 11 |  | 18.24 | 446 | 3955 | 41.55 | 4736 | 5138 |
| Total |  | 1.45 | 976 | 2.97 | 4529 | 4750 | 52.56 | 5265 |

a. EVENT = CPR Runof Event 14
 during oech of the four CPR owerte.

|  | N 1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Rundir Event ${ }^{1 / 1}$ | 10 | 8.74 | 398 | 31.16 | 3062 | 36.00 | 34.62 |
| CPR Runofitert 12 | 3.60 | 6.53 | 5.16 | 48.17 | 41.77 | 44.34 | 36.93 |
| CPR Runof Evert 3 | 08 | 72 | 156 | 46.26 | 4299 | 4917 | 4558 |
| CPR Runofl Event 4 | 1.45 | 976 | 297 | 45.29 | 4750 | 5256 | 5265 |
| Tobal | 1.54 | 6.35 | 3.19 | 40.99 | 3949 | 4465 | 4278 |

 tive 41 dey inctiment of CPR.
CPR Runof Event :1

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 29 | $\begin{aligned} & 172.72 \\ & 170.47 \\ & 190.95 \\ & 232.00 \end{aligned}$ | 163.00 | 152.00 | 169.00 | 14600 | 144.00 | 16900 |
|  | 30 |  | 161.71 | 159.87 | 173.68 | 162.78 | 159.25 | 14888 |
|  | 31 |  | 162.87 | 154.00 | 179.49 | 169.43 | 168.19 | 15346 |
|  | 1 |  | 168.98 | 157.90 | 183.29 | 175.09 | 177.04 | 170.67 |
|  | 2 |  | 17633 | 16725 | 186.96 | 182.13 | 182.98 | 18277 |
|  | 3 |  | 186.73 | 170.13 | 194.31 | 18588 | 182.46 | 18446 |
|  | 4 |  | 182.21 | 173.47 | 192.75 | 188.80 | 180.51 | 18100 |
|  | 5 |  | 184.67 | 172.83173.14 | 20315 | 187.58 | 184.68 | 182.38 |
|  | 6 |  | 183.71 |  | 20184 | 192.55 | 18912 | 186.32 |
|  | 7 |  |  |  | 193.62 | 197.11 | 192.67 | 189.30 |
|  | 8 |  | 186.00 | 185.00 | 195.00 | 201.00 | 202.00 | 19400 |
|  | 9 | 363.00 | 186.00 | 18500 | 195.00 | 20100 | 202.00 | 19400 |
|  | 10 |  | 181.40 | 183.81 | 206.53 | 19479 | 18692 | 19266 |
|  | 11 |  | 174.00 | 182.00 | 208.00 | 19400 | 18500 | $19000$ |
|  | 12 |  | 172.25 | 180.75 | $\begin{array}{r} 20167 \\ 188.27 \\ \hline \end{array}$ | $\begin{array}{r} 194.00 \\ 179.24 \\ \hline \end{array}$ | $\begin{aligned} & 18500 \\ & 176.19 \end{aligned}$ |  |
| Total |  | 174.11 | 172.99 | 165.79 |  |  |  | $\begin{array}{r} 19000 \\ 17415 \\ \hline \end{array}$ |

a. EVENT = CPR Runof Event *1

Daiky flow wrighted total catcium (ma/l) concentrations at nodes N1, M2, M4, MS, M7, N10 and N12 during the 41 day treetment of CPR.

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February 12 | 154.36 | 168.75 | 17700 | 196.25 | 169.00 | 17100 | 172.00 |
| 13 | 149.95 | 148.96 | 151.00 | 172.68 | 168.28 | 13481 | 15637 |
| 14 |  | 147.78 | 13579 | 17935 | 178.54 | 15430 | 13730 |
| 15 |  | 142.04 | 141.00 | 170.36 | 180.55 | 18172 | 14185 |
| 16 |  | 133.15 | 144.50 | 160.95 | 178.10 | 182.00 | 15400 |
| Total | 150.09 | 146.09 | 14557 | 173.90 | 175.73 | 162.85 | 156.51 |

a. EVENT = CPR Runof Event ${ }^{1} 2$

Dally frow welghted total calcium (mghl) concentrations at nocese N1, N2, MA, M5, N7, N10 and N12 during the 19 day treatment of CPR.

|  |  | N1 | N2 | N/ | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 180.23 | 136.54 | 149.00 | 161.86 | 179.00 | 178.00 | 17500 |
|  | 17 | 148.33 | 14681 | 142.13 | 166.22 | 17544 | 17380 | 16823 |
|  | 18 | 12600 | 14794 | 13988 | 180.92 | 170.98 | 16500 | 15559 |
|  | 19 | 149.50 | 14596 | 148.29 | 15785 | 16197 | 16312 | 15462 |
|  | 20 | 154.00 | 15046 | 145.33 | 174.63 | 15663 | 16138 | 15441 |
|  | 21 |  | 14858 | 143.98 | 17345 | 158.24 | 16597 | 16507 |
|  | 22 |  | 148.27 | 149.09 | 170.71 | 16565 | 182.09 | 17742 |
|  | 23 |  |  |  | 17000 | 16900 | 190.00 | 18400 |
|  | 24 |  | 15145 | 15800 | 18798 | 16904 | 189.35 | 172.12 |
|  | 25 | 24976 | 15764 | 15800 | 18575 | 17000 | 17400 | 16600 |
|  | 28 | 25924 | 163.39 | 14353 | 192.77 | 170.00 | 16574 | 16469 |
|  | 27 | 29100 | 16958 | 15433 | 18169 | 17591 | 18199 | 97200 |
|  | 28 |  | 16600 | 15675 | 18405 | 17560 | 17058 | 17031 |
| March | 1 |  | 16668 | 152.20 | 18788 | 17648 | 16570 | 16009 |
|  | 2 |  | 16500 | 15200 | 19085 | 17985 | 17300 | 15800 |
| Total |  | 19911 | 15402 | 14868 | 17409 | 16935 | 17296 | 16595 |

a EVENT = CPR Runofi Evem
 the 41 day trectiment of CPR.
CPR Runcif Event ian

|  |  | N1 | N2 | M | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Werch | 2 | 180.47 | 168.00 | 165.00 | 198.60 | 178.00 | 18700 | 168.00 |
|  | 3 | 108.04 | 15756 | 155.00 | 193.05 | 16832 | 16765 | 14292 |
|  | 4 |  | 155.31 | 123.10 | 192.93 | 169.47 | 167.54 | 131.10 |
|  | 5 |  | 156.08 | 125.82 | 175.28 | 180.39 | 17645 | 14327 |
|  | 6 | 140.92 | 16713 | 143.00 | 16975 | 185.00 | 179.00 | 146.00 |
|  | 7 | 169.00 | 147.00 | 15767 | 17093 | 174.49 | 179.62 | 151.82 |
|  | 8 |  | 140.54 | 146.33 | 176.94 | 168.63 | 17825 | 162.88 |
|  | 9 |  | 150.25 | 134.83 | 167.73 | 162.38 | 16157 | 168.33 |
|  | 10 | 177.58 | 16738 | 133.00 | 179.37 | 15700 | 153.00 | 16500 |
|  | 11 |  | 187.36 | 13409 | 175.79 | 15945 | 15650 | 17132 |
| Total |  | 15728 | 156.57 | 14110 | 178.20 | 17032 | 189.76 | 153.49 |

a EVENT = CPR Runof Event int
 cueh of the four CPR events.

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcin Event ${ }^{\text {at }}$ | 174.11 | 172.99 | 165.79 | 188.27 | 179.24 | 176.19 | 174.15 |
| CPR Runoff Event ${ }^{2}$ | 150.09 | 146.09 | 145.57 | 173.90 | 175.73 | 162.85 | 156.51 |
| CPR Runoff Event ${ }^{\text {ch}}$ | 199.11 | 154.02 | 148.68 | 174.09 | 169.35 | 172.96 | 165.95 |
| CPR Runofitent ${ }^{\text {ch }}$ | 157.26 | 156.57 | 141.10 | 178.20 | 170.32 | 169.76 | 153.49 |
| Total | 168.52 | 159.73 | 151.98 | 179.96 | 173.89 | 172.03 | 164.94 |

 41 doy treetinent of CPR .

CPR Runof Event 1

|  |  | N1 | N2 | M4 | NS | $N 7$ | N10 | N 12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Janusy | 26 | $\begin{aligned} & 1551.81 \\ & 1284.00 \\ & 1681.68 \\ & 2809.00 \end{aligned}$ | 570.00 | 500.00 | 488.00 | 422.00 | 405.00 | 439.00 |
|  | 30 |  | 1016.21 | 486.29 | 500.72 | 461.39 | 44939 | 42063 |
|  | 31 |  | 1011.12 | 629.92 | 551.84 | 508.87 | 504.93 | 44770 |
| February | 1 |  | 1005.99 | 068.56 | 541.67 | 518.00 | 521.12 | 494.16 |
|  | 2 | 2889.00 | 94431 | 958.62 | 558.87 | 539.00 | 535.33 | 52088 |
|  | 3 |  | 874.98 | 81561 | 568.69 | 553.59 | 550.60 | 531.43 |
|  | 4 |  | 768.82 | 93194 | 558.71 | 561.11 | 559.34 | 544.83 |
|  | 5 |  | 733.64 | 829.01 | 585.39 | 587.63 | 58000 | 56116 |
|  | 6 |  | 745.83 | 849.72 | 573.19 | 575.08 | 57183 | 57012 |
|  | 7 |  |  |  | 587.35 | 578.11 | 580.12 | 588.87 |
|  | 8 |  | 1038.00 | 958.00 | 571.00 | 575.00 | 60500 | 68100 |
|  | 9 | 3658.00 | 1038.00 | 958.00 | 57100 | 57500 | 60500 | 68100 |
|  | 10 |  | 92559 | 889.29 | 61002 | 57145 | 533.16 | 63002 |
|  | 11 |  | 74500 | 785.00 | 615.00 | 57100 | 52400 | 529.00 |
|  | 12 |  | 56050 | 749.50 | 57123 | 571.00 | 52400 | 52900 |
| Total |  | 1527.19 | 90745 | 776.92 | 55304 | 52773 | 518.86 | 51449 |

a. EVENT = CPR Runof Event 1

Delly flow wrighted total sulfate (mel) concentrations at nodes M1, N2, MA, M5, N7, N10 and N12 during the 41 dey trectiment of CPR.

CPR Runof Event ${ }^{1} 2$

|  |  | N1 | N2 | NA | N5 | N7 | N10 | N12 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| February | 12 | 935.65 | 659.25 | 643.00 | 577.00 | 514.00 | 496.00 | 51800 |
|  | 13 | 792.53 | 500.08 | 528.33 | 541.96 | 504.59 | 38165 | 46850 |
|  | 14 |  | 531.12 | 462.83 | 521.36 | 523.20 | 438.45 | 384.29 |
|  | 15 |  | 721.46 | 485.67 | 443.52 | 53742 | 52402 | 39487 |
|  | 16 |  | 978.70 | 508.10 | 389.67 | 534.48 | 526.00 | 44000 |
| Total |  | 797.21 | 682.23 | 506.03 | 489.75 | 523.59 | 46675 | 461.36 |

a. EVENT $=$ CPR Runof Event *2

Dally flow wolghted total sulfate (mgll) concentrations at nodes N1, M2, M4, M5, N7, N10 and N12 during the 41 dey trextment of CPR.

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 197435 | 989.07 | 589.00 | 398.21 | 521.00 | 51400 | 52000 |
|  | 17 | 1201.40 | 1143.13 | 575.25 | 37833 | 476.05 | 47034 | 46012 |
|  | 18 | 1248.00 | 1067.74 | 76927 | 39160 | 45587 | 45437 | 37170 |
|  | 19 | 1162.45 | 86751 | 83501 | 603.75 | 418.92 | 42795 | 382.78 |
|  | 20 | 137300 | 88712 | 79632 | 45881 | 38325 | 38950 | 36986 |
|  | 21 |  | 94356 | 838.32 | 433.82 | 38649 | 38873 | 38757 |
|  | 22 |  | 91709 | 887.64 | 42454 | 410.61 | 40409 | 41496 |
|  | 23 |  |  |  | 422.00 | 422.00 | 41200 | 43200 |
|  | 24 |  | 77333 | 97400 | 453.01 | 422.85 | 41289 | 41946 |
|  | 25 | 199876 | 85841 | 97400 | 45600 | 44300 | 43400 | 41300 |
|  | 28 | 163525 | 93401 | 916.13 | 47424 | 42930 | 41474 | 40451 |
|  | 27 | 165400 | 97037 | 908.67 | 47383 | 428.28 | 42334 | 40123 |
|  | 28 |  | 91619 | 89533 | 46182 | 43581 | 42520 | 39943 |
| March | 1 |  | 88508 | 87889 | 46643 | 44183 | 42974 | 39439 |
|  | 2 |  | 69200 | 87800 | 46013 | 44277 | 43600 | 39300 |
| Total |  | 190540 | 94720 | 82460 | 44741 | 43410 | 43008 | 41216 |

a EVENT = CPR Runof Event :3

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 the 41 dey treatiment of CPR.
CPR Runch Event in

|  |  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March | 2 | 845.67 | 780.22 | 891.00 | 457.60 | 440.00 | 430.00 | 407.00 |
|  | 3 | 302.10 | 585.44 | 824.13 | 458.24 | 42468 | 392.10 | 382.49 |
|  | 4 |  | 497.75 | 679.50 | 433.75 | 421.50 | 390.72 | 33769 |
|  | 5 |  | 454.58 | 595.00 | 422.91 | 430.62 | 41264 | 322.32 |
|  | 6 | 81503 | 39988 | 60700 | 413.63 | 438.00 | 422.00 | 34800 |
|  | 7 | 95400 | 800.79 | 526.33 | 406.54 | 432.29 | 438.08 | 371.28 |
|  | 8 |  | 442.13 | 474.00 | 405.56 | 42750 | 44112 | 40353 |
|  | 9 |  | 429.50 | 433.33 | 405.30 | 422.14 | 432.26 | 41513 |
|  | 10 | 1101.85 | 436.25 | 404.00 | 40287 | 419.00 | 42900 | 41700 |
|  | 11 |  | 440.91 | 410.82 | 395.33 | 41672 | 42707 | 42095 |
| Totam |  | 67770 | 518.12 | 579.77 | 41704 | 428.46 | 42080 | 38180 |

a. EVENT = CPR Runoff Event tha
 of the four CPR ovens.

|  | N1 | N2 | NH | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPRR Runcir Event 1 | 1527.19 | 90745 | 77692 | 553.04 | 527.73 | 518.86 | 51449 |
| CPR Runof Evert ${ }^{\text {\# }}$ | 79721 | 662.23 | 506.03 | 489.75 | 523.59 | 46675 | 46136 |
| CPR Runof Event \#3 | 190540 | 94720 | 824.60 | 44741 | 434.10 | 43008 | 41216 |
| CPR Runori Event ${ }^{\text {a }}$ | 67770 | 518.12 | 57977 | 41704 | 426.46 | 42080 | 38180 |
| Total | 1178.38 | 789.85 | 704.97 | 483.41 | 47726 | $46 \times 10$ | 44520 |

## APPENDIX D

## THE DAILY CONTAMINANT LOADINGS

 of four Cind overis
CPR Runoif Evert ici

|  | N1 | N2 | NH | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 16.905 | 182 | 82 | 37 | 421 | 195 | 97 |
|  | 1.299 | 1.800 | 293 | 53 | 440 | 200 | 167 |
|  | 536 | 2.005 | 619 | 72 | 42 | 15 | 45 |
|  | 207 | 1.024 | 923 | 75 | 21 | 9 | 9 |
|  | 0 | 1.637 | 1.269 | 89 | 27 | 17 | 10 |
|  | 0 | 580 | 675 | 61 | 27 | 18 | 11 |
|  | 0 | 362 | 687 | 109 | 15 | 7 | 9 |
|  | 0 | 124 | 370 | 13 | 8 | 2 | 6 |
|  | 0 | 53 | 319 | 10 | 4 | 2 | 4 |
|  | 0 | 0 | 0 | 11 | 3 | 1 | -1 |
|  | 0 | 15 | 104 | 5 | 2 | 1 | -1 |
|  | 396 | 15 | 104 | 5 | 2 | 1 | 19 |
|  | 0 | 40 | 265 | 10 | 17 | 10 | 26 |
|  | 0 | 15 | 103 | 13 | 29 | 17 | 27 |
|  | 0 | 23 | 37 | 9 | 15 | 8 | 15 |
| Tate Total | 19.345 | 8.775 | 5.830 | 573 | 1.071 | 503 | 444 |

e. EVENT = CPR Runof Evert \%1

Total ahminum loeding (oid and ghevent es CecOS) at nodes N1, N2, M4, M6, W7, W10, and N12 during the treatment of four CPR enonti
CPR Runof Event ${ }^{1} 2$

| February |  | N1 | N2 | Na | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 12 | 221 | 49 | 74 | 12 | 80 | 10 | 20 |
|  | 13 | 9.273 | 366 | 145 | 52 | 335 | 245 | 51 |
|  | 14 | 0 | 122 | 134 | 23 | 169 | 144 | 53 |
|  | 15 | 0 | 755 | 104 | 25 | 15 | 15 | 31 |
|  | 16 | 0 | 1.229 | 42 | 12 | 5 | 7 | 2 |
| Table Total |  | 9.494 | 2.522 | 500 | 123 | 603 | 422 | 157 |

a. EVENT = CPR Runof Event *2

Total aluminum loeding (g/d and ghevent as CaCO3) at nodes M1, M2; MA, MS, N7, M10, and N12 during the treatinent of four CPT events

|  |  | N1 | N2 | NH | NS | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 16 | 30,536 | 1.357 | 120 | 3 | 5 | 4 | 8 |
|  | 17 | 195 | 3.606 | 297 | 15 | 15 | 13 | 24 |
|  | 18 | 64 | 3.262 | 956 | 40 | 34 | 19 | 42 |
|  | 19 | 60 | 2.976 | 1.765 | 72 | 25 | 11 | 24 |
|  | 20 | 78 | 2.607 | 2.133 | 97 | 19 | 8 | 11 |
|  | 21 | 0 | 2.263 | 2.207 | 117 | 34 | 16 | 4 |
|  | 22 | 0 | 1.000 | 1.035 | 124 | 43 | 24 | 21 |
|  | 23 | 0 | 0 | 0 | 125 | 43 | 26 | 12 |
|  | 24 | 0 | 419 | 720 | 26 | 15 | 9 | 2 |
|  | 25 | 3.565 | 1.396 | 2.117 | 2 | 1 | 0 | 13 |
|  | 26 | 3.851 | 1.235 | 1.342 | 25 | 8 | 3 | 19 |
|  | 27 | 1.985 | 2.159 | 1.779 | 77 | 24 | 2 | 24 |
|  | 28 | 0 | 1.671 | 1.676 | 55 | 13 | 0 | 9 |
| March | 1 | 0 | 861 | 1.020 | 37 | 7 | 2 | 9 |
|  | 2 | 0 | 3 | 9 | 9 | 4 | 1 | 1 |
| Table Total |  | 40.733 | 24.816 | 17.177 | 823 | 287 | 139 | 223 |

[^28] cfiont CPR Hurn

|  | N1 | N2 | N | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 5.180 | 445 |  | 9 | 0 | 0 | 1 |
| 3 | 622 | 417 | 1.415 | 52 | 29 | 0 | 48 |
| 4 | 0 | 290 | 1.032 | 49 | 37 | 3 | 40 |
| 5 | 0 | 113 | 641 | 37 | 24 | 8 | 37 |
| 6 | 61 | 63 | 571 | 21 | 25 | 9 | 35 |
| 7 | 25 | 89 | 374 | 25 | $g$ | 3 | 20 |
| 8 | 0 | 84 | 188 | 7 | 8 | 0 | 4 |
| 9 | 0 | 118 | 141 | 6 | 36 | 22 | 25 |
| 10 | 161 | 154 | 136 | 1 | 56 | 38 | 39 |
| 11 | 0 | 63 | 59 | 3 | 22 | 15 | 20 |
| Table Total | 6.065 | 1,836 | 5.442 | 212 | 246 | 98 | 269 |

a. EVENT = CPR Runcil Evert

Overall shummum loeding (slovent ese Ca3) whodes M1, M2, M, MS, MT, N1O, and M12 for aech of the four CPR events

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPRR Runct Evemtil | 19,345 | 8.775 | 5.830 | 573 | 1.071 | 503 | 44 |
| CPR Runof Event ${ }^{\text {\% }}$ | 9,494 | 2.522 | 500 | 123 | 603 | 422 | 157 |
| CPR Runofit Event \% | 40.733 | 24.816 | 17.177 | 823 | 287 | 139 | 223 |
| CPR Runoff Evert ${ }^{\text {cha }}$ | 6.066 | 1.836 | 5.442 | 212 | 246 | 98 | 269 |
| Table Total | 75,638 | 37.948 | 28.949 | 1.731 | 2.208 | 1,163 | 1.092 |

Total iron loeding (ald and gievert es CaCO3) at nodes N1, N2, M. M5, N7. N10. and N12 during the treetment of four CPR events

|  |  | N1 | N2 | Na | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Jomuary | 29 | 5.322 | 233 | 41 | ¢ิ | 274 | 136 | 73 |
|  | 30 | 418 | 401 | 141 | 140 | 315 | 146 | 146 |
|  | 31 | 202 | 385 | 158 | 148 | 64 | 13 | 49 |
| Februmy | 1 | 88 | 309 | 187 | 151 | 70 | 14 | 13 |
|  | 2 | 0 | 274 | 194 | 99 | 73 | 19 | 13 |
|  | 3 | 0 | 111 | 77 | 129 | 70 | 24 | 13 |
|  | 4 | 0 | 101 | 80 | 137 | 42 | 12 | 8 |
|  | 5 | 0 | 70 | 40 | 49 | 15 | 2 | 4 |
|  | 6 | 0 | 50 | 33 | 78 | 15 | 2 | 4 |
|  | 7 | 0 | 0 | 0 | 60 | 9 | 2 | 4 |
|  | 8 | 0 | 24 | 12 | 27 | 4 | 1 | - 3 |
|  | 9 | 106 | 24 | 12 | 27 | 4 | 1 | 40 |
|  | 10 | 0 | 64 | 35 | 137 | 19 | 6 | 4 |
|  | 11 | 0 | 26 | 17 | 230 | 33 | 10 | 22 |
|  | 12 | 0 | 20 | 6 | 111 | 16 | 5 | 12 |
| Table Total |  | 6.137 | 2.092 | 1.032 | 1,603 | 1.024 | 393 | 434 |

a EVENT = CPR Runof Event © 1

TCtal iron loeding (ald and grevent as CaCO3) ar noces M1, M2, MA, MS, MT, M1O, and M12 during the treetment of four CPR everte

|  |  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 51 | 47 | 11 | 134 | 65 | 4 | 7 |
|  | 13 | 10.497 | 284 | 54 | 296 | 271 | 170 | 30 |
|  | 14 | 0 | 108 | 66 | 237 | 193 | 107 | 39 |
|  | 15 | 0 | 336 | 72 | 152 | 137 | 25 | 24 |
|  | 16 | 0 | 397 | 32 | 49 | 62 | 12 | 3 |
| Table Total |  | 10.548 | 1.173 | 234 | 868 | 728 | 318 | 103 |

[^29] CPI evenes

CPR Runofl Evert 4

|  | N1 | N2 | NH | NS | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Februery 16 | 14.042 | 594 | 57 | 67 | 77 | 17 | 14 |
| 17 | 24 | 548 | 91 | 109 | 74 | 18 | 24 |
| 18 | 16 | 292 | 107 | 117 | 49 | 12 | 34 |
| 19 | 16 | 213 | 110 | 121 | 53 | 5 | 13 |
| 20 | 30 | 149 | 80 | 157 | 45 | 0 | 5 |
| 21 | 0 | 64 | 80 | 202 | 54 | 12 | 3 |
| 22 | 0 | 22 | 39 | 232 | 46 | 11 | 12 |
| 23 | 0 | 0 | 0 | 240 | 38 | 7 | 5 |
| 24 | 0 | 11 | 27 | 78 | 13 | 3 | 1 |
| 25 | 1.548 | 460 | 79 | 5 | 0 | 1 | 7 |
| 26 | 1.292 | 151 | 35 | 82 | 17 | 21 | 14 |
| 27 | 300 | 222 | 54 | 264 | 38 | 18 | 20 |
| 28 | 0 | 41 | 60 | 163 | 55 | 16 | 12 |
| March 1 | 0 | 20 | 38 | 115 | 39 | 10 | 15 |
| 2 | 0 | 0 | 0 | 35 | 9 | 2 | 1 |
| Trbie Toral | 18.068 | 2,787 | 873 | 1.906 | 607 | 153 | 180 |

a. EVENT = CPR Runof Event *3
 CPR eventis

|  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 3.665 | 21 | 19 | 45 | 6 | 0 | 9 |
| 3 | 454 | 54 | 47 | 239 | 54 | 4 | 36 |
| 4 | 0 | 60 | 47 | 237 | 68 | 7 | 37 |
| 5 | 0 | 34 | 68 | 194 | 48 | 6 | 45 |
| 6 | 11 | 25 | 85 | 115 | 46 | 4 | 35 |
| 7 | 7 | 36 | 44 | 130 | 50 | 6 | 29 |
| 8 | 0 | 33 | 20 | 143 | 50 | 4 | 17 |
| 9 | 0 | 58 | 36 | 97 | 63 | 6 | 11 |
| 10 | 90 | 100 | 52 | 163 | 75 | 8 | 12 |
| 11 | 0 | 52 | 23 | 69 | 33 | 4 | 7 |
| Table Totel | 4.227 | 474 | 439 | 1.432 | 493 | 49 | 238 |

a EVENT = CPR Runof Event 04

Overall iron loading (gevent as CaCO3) at nodes N1, N2, M4, N5, N7, N10, and N12 for each of the four CPR ovents

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runof Event ${ }^{\text {W }} 1$ | 6.137 | 2.092 | 1.032 | 1.603 | 1.024 | 393 | 434 |
| CPR Runoff Event ${ }^{\text {W } 2}$ | 10.548 | 1.173 | 234 | 868 | 728 | 318 | 103 |
| CPR Runoff Event ${ }^{\text {m }}$ | 18.088 | 2.787 | 873 | 1.986 | 607 | 153 | 180 |
| CPR Runof Event ${ }^{\text {m }}$ | 4.227 | 474 | 439 | 1.432 | 493 | 49 | 238 |
| Table Totar | 38,980 | 6.526 | 2,579 | 5,889 | 2.852 | 913 | 955 |


a. EVENT = CPR Runofl Evert 1
 tretinemt of four CPR everites

|  | N1 | N2 | Na | NS | $N 7$ | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Feorumy 12 | 73 | 40 | 67 | 106 | 8 | 1 | 3 |
| 13 | 1.436 | 162 | 106 | 274 | 55 | 5 | 15 |
| 14 | 0 | 222 | 126 | 251 | 71 | 3 | 21 |
| 15 | 0 | 342 | 209 | 280 | 121 | 2 | 12 |
| 16 | 0 | 201 | 97 | 125 | 62 | 1 | 1 |
| Table Total | 1,509 | 967 | 607 | 1.035 | 317 | 13 | 51 |

a. EVENT = CPR Runofl Evert wa
 treement of four CPN evertes

|  | N1 | N2 | NH | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 2.722 | 201 | 113 | 179 | 84 | 2 | N12 14 |
|  | 23 | 435 | 189 | 184 | 72 | 2 | 10 |
|  | 8 | 413 | 242 | 158 | 35 | 1 | 6 |
|  | 5 | 381 | 303 | 199 | 35 | 1 | 6 |
|  | 8 | 338 | 321 | 211 | 30 | 0 | 3 |
|  | 0 | 304 | 325 | 219 | 33 | 0 | 1 |
|  | 0 | 136 | 152 | 214 | 43 | 1 | 4 |
|  | 0 | 0 | 0 | 212 | 47 | 1 | 2 |
|  | 0 | 78 | 105 | 82 | 16 | 0 | 0 |
|  | 335 | 247 | 309 | 5 | 0 | 0 | 2 |
|  | 305 | 209 | 195 | 85 | 17 | 1 | 14 |
|  | 243 | 347 | 294 | 191 | 40 | 1 | 15 |
|  | 0 | 310 | 302 | 243 | 57 | 6 | 4 |
| March 1 | 0 | 190 | 190 | 162 | 39 | 3 | 6 |
| 2 | 0 | 2 | 2 | 39 | 9 | 0 | 0 |
| Table Total | 3.650 | 3.593 | 3.042 | 2.375 | 558 | 20 | 86 |

a EVENT = CPR Runofl Evert 3
 ranement of four CPI everter

CPR Runolin Event an

|  | N1 | NR | N | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 1.360 | 160 | 171 | 46 | 6 | 0 | 3 |
| 3 | 207 | 250 | 205 | 211 | 49 | 0 | 14 |
| 4 | 0 | 251 | 243 | 272 | 80 | 1 | 15 |
| 5 | 0 | 243 | 234 | 233 | 88 | 1 | 18 |
| 6 | 10 | 224 | 246 | 221 | 89 | 0 | 43 |
| 7 | 3 | 218 | 242 | 203 | 55 | 0 | 11 |
| 8 | 0 | 187 | 216 | 204 | 29 | 0 | 6 |
| 9 | 0 | 188 | 192 | 199 | 28 | 0 | 4 |
| 10 | 22 | 205 | 182 | 210 | 32 | 0 | 5 |
| 11 | 0 | 89 | 82 | 89 | 14 | 0 | 3 |
| Table Told | 1.602 | 2.024 | 2.095 | 1.887 | 470 | 2 | 92 |

a. EVENT = CPR Runof Evert of

Overall manganese loading (ghevent as CaCO3) at nodes M1. M2, MA, MS, M7, M1O, and N12 for aech of the four CPR events

|  | $N 1$ | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runch Evont ${ }^{\text {P1 }}$ | 2.018 | 2.301 | 2.251 | 3.101 | 978 | 36 | 131 |
| CPR Runoff Evont ${ }^{1}$ | 1.509 | 967 | 607 | 1.035 | 317 | 13 | 51 |
| CPR Runofr Event 3 | 3.650 | 3.593 | 3.042 | 2.375 | 558 | 20 | 86 |
| CPR Runorf Event 0 | 1.602 | 2.024 | 2.095 | 1.887 | 470 | 2 | 92 |
| Table Total | 8.778 | 8.884 | 7.995 | 8,388 | 2.324 | 71 | 359 |

 four CPR everts

|  | N1 | N2 | M | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Jencery 29 | 122.670 | 1.776 | 750 | 751 | 3,235 | 1.467 | 743 |
| 30 | 20.007 | 10.078 | 2.546 | 1,464 | 3.662 | 1.527 | 1.340 |
| 31 | 5.465 | 10.046 | 4.688 | 1.311 | 695 | 119 | 393 |
| Febriery 1 | 1.574 | 11.127 | 6,658 | 1.297 | 551 | 95 | 92 |
| 2 | 0 | 12.719 | 8.710 | 1.566 | 598 | 154 | 94 |
| 3 | 0 | 4.761 | 4.465 | 1.642 | 575 | 168 | 99 |
| 4 | 0 | 3.632 | 4.427 | 1.086 | 328 | 73 | 74 |
| 5 | 0 | 1.479 | 2.470 | 583 | 125 | 19 | 45 |
| 6 | 0 | 913 | 2.160 | 728 | 97 | 18 | 36 |
| 7 | 0 | 0 | 0 | 469 | 57 | 12 | -29 |
| 8 | 0 | 214 | 715 | 207 | 25 | 9 | -21 |
| 9 | 2.660 | 214 | 715 | 207 | 25 | 9 | 302 |
| 10 | 0 | 569 | 1.865 | 891 | 169 | 74 | 352 |
| 11 | 0 | 240 | 766 | 1.470 | 291 | 128 | 225 |
| 12 | 0 | 94 | 277 | 746 | 145 | 64 | 124 |
| Tate Total | 152.377 | 57. 862 | 41.212 | 14.438 | 10.578 | 3.935 | 3.870 |

a. EVENT = CPR Runcol Event \#1

Total ectilly loeding (ghd and grovent as CacOs) at noder M1, M2. M, MS, M7, M10, and M12 durime the trectment of four CPN event

CPR Runof Event 82

|  |  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 2.174 | 264 | 572 | 867 | 9 | 9 | 16 |
|  | 13 | 64.170 | 3.183 | 5.494 | 599 | 405 | 27 | 188 |
|  | 14 | 0 | 5.959 | 7.860 | 26 | 245 | 26 | 389 |
|  | 15 | 0 | 9.497 | 7.416 | 33 | 33 | 33 | 231 |
|  | 16 | 0 | 4.179 | 3.334 | 16 | 16 | 16 | 1 |
| Table Total |  | 66.343 | 23.083 | 24.675 | 1.540 | 708 | 111 | 825 |

a EVENT = CPR Runof Event ${ }^{2} 2$

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 sour CPR eveme

CPR Runctineme

|  | N1 | N2 | NH | NS | N7 | N10 | $N 12$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fabruer 16 | 207.743 | 2.907 | 9.140 | 23 | 23 | 23 | 17 |
| 17 | 3.539 | 15,308 | 8.593 | 22 | 22 | 22 | 13 |
| 18 | 371 | 12.948 | 1.950 | 18 | 18 | 18 | 12 |
| 19 | 258 | 19.207 | 12.408 | 1.029 | 22 | 22 | 5 |
| 20 | 379 | 23.374 | 19.534 | 575 | 22 | 22 | 0 |
| 21 | 0 | 20.955 | 18.593 | 0 | 8 | 8 | 1 |
| 22 | 0 | 8,472 | 8.544 | 0 | 0 | 0 | 0 |
| 23 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 24 | 0 | 5.294 | 5.059 | 0 | 0 | 0 | 0 |
| 25 | 25.430 | 15.567 | 17.228 | 0 | 0 | 0 | 0 |
| 26 | 18.957 | 11.900 | 12.000 | 0 | 0 | 0 | 0 |
| 27 | 13.484 | 19.077 | 18.685 | 0 | 0 | 0 | 0 |
| 28 | 0 | 19.099 | 16.884 | 0 | 0 | 0 | 0 |
| March 1 | 0 | 6.955 | 7.205 | 0 | 0 | 0 | 0 |
| 2 | 0 | 52 | 57 | 0 | 0 | 0 | 0 |
| Table Tota | 270.159 | 181,233 | 154.758 | 1,666 | 115 | 115 | 47 |

a. EVENT = CPR Runcil Event 103
 four CPR everte

|  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March 2 | 44.052 | 6.352 | 8.003 | 0 | 0 | 0 | 0 |
| 3 | 6.924 | 10.327 | 12.880 | 0 | 0 | 0 | 0 |
| 4 | 0 | 9.134 | 10.786 | 0 | 0 | 0 | 0 |
| 5 | 0 | 6.395 | 8.262 | 0 | 0 | 0 | 0 |
| 6 | 503 | 5.278 | 7.435 | 0 | 0 | 0 | 0 |
| 7 | 121 | 5.890 | 7.833 | 0 | 0 | 0 | 0 |
| 8 | 0 | 4.789 | 4.972 | 0 | 0 | 0 | 0 |
| 9 | 0 | 5.577 | 5.009 | 0 | 0 | 0 | 0 |
| 10 | 1.241 | 6.472 | 6.334 | 0 | 0 | 0 | 0 |
| 11 | 0 | 2.955 | 2.915 | 0 | 0 | 0 | 0 |
| Tabie Total | 52.840 | 63.167 | 74.428 | 0 | 0 | 0 | 0 |

a. EVENT = CPR Runof Event 94

Overall acidity loeding (ghevent as CaCO3) at nodes N1, N2, N4, NS, N7, N1O, and N12 for each of the four CPR events

|  | N1 | N2 | $\mathrm{N4}$ | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runoif Event 1 | 152.377 | 57.862 | 41.212 | 14.438 | 10.578 | 3.935 | 3.870 |
| CPR Runoff Event ${ }^{\text {\% }}$ | 66.343 | 23.083 | 24.675 | 1.540 | 708 | 111 | 825 |
| CPR Runoff Event ${ }^{\text {W }}$ | 270.159 | 181.233 | 154.758 | 1.666 | 115 | 115 | 47 |
| CPR Runow Event 4 | 52.840 | 63.167 | 74.428 | 0 | 0 | 0 | 0 |
| Table Totar | 541,720 | 325,345 | 295.074 | 17.644 | 11,401 | 4.161 | 4.741 |


|  | N1 | NR | M | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Jenuery 29 | 46 | 2.003 | 1.575 | 4.523 | 4.400 | 5.388 | 4.544 |
| 30 | 8 | 3.405 | 2.909 | 11.317 | 10.833 | 12.839 | 12.118 |
| 31 | 2 | 1.255 | 1.513 | 11.624 | 10.882 | 11.69 m | 10.049 |
| Februery 1 | 0 | 1.000 | 1.004 | 11.771 | 10.693 | 11.103 | 8.132 |
| 2 | 0 | 7.936 | 837 | 4.942 | 10.946 | 11.843 | 7.923 |
| 3 | 0 | 1.376 | 652 | 6.058 | 11.519 | 12.880 | 7.386 |
| 4 | 0 | 763 | 706 | 6.828 | 7.410 | 8.460 | 6.706 |
| 5 | 0 | 484 | 346 | 3.447 | 3.263 | 3.797 | 4.776 |
| 6 | 0 | 799 | 305 | 4.397 | 3.947 | 4.879 | 3.790 |
| 7 | 0 | 0 | 0 | 2.706 | 2.374 | 3.004 | 1.133 |
| 8 | 0 | 496 | 124 | 1.092 | 883 | 1.133 | -69 |
| 9 | 0 | 498 | 124 | 1.092 | 883 | 1.133 | 996 |
| 10 | 0 | 1,680 | 405 | 5.737 | 3.280 | 4.869 | 2.694 |
|  | 0 | 1.071 | 244 | 9.666 | 5.309 | 8.030 | 5.191 |
| 12 | 0 | 504 | 115 | 4.910 | 2.651 | 4.010 | 2.867 |
| Trobe Tater | 56 | 24,156 | 10,988 | 90.916 | 89.352 | 105.052 | 78.246 |

a. EVENT = CPR Runof Evert 1

Total alrabinity loading (gid and govent as CaCOS) at noses M1, M2, MA, M5, NT, N10, and M12 during the trectruent of four CPR ovente

CPR Runcfit Event 2

|  |  | N1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February | 12 | 113 | 2.188 | 496 | 5.755 | 3.013 | 4.328 | 6.793 |
|  | 13 | 3.353 | 2.556 | 1.368 | 14.790 | 9.168 | 10.130 | 6.798 |
|  | 14 | 0 | 1.652 | 1.516 | 12.778 | 10.862 | 10.574 | 2.255 |
|  | 15 | 0 | 1.067 | 1.886 | 13.833 | 15.804 | 16.241 | 1.491 |
|  | 16 | 0 | 233 | 813 | 6.340 | 7.539 | 7.968 | 436 |
| Table Totar |  | 3.467 | 7.696 | 6.080 | 53.496 | 46.387 | 49.241 | 17.775 |

a. EVENT = CPR Runof Event *2
 of four CPR everta
CPR Runoff Event ma

|  | N1 | N2 | N4 | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| February 16 | 56 | 15 | 884 | 8.221 | 10.384 | 10.722 | 8.610 |
| 17 | 1 | 23 | 930 | 8.556 | 9.863 | 10.683 | 4.817 |
| 18 | 0 | 23 | 305 | 8.246 | 7.234 | 8.550 | 2.154 |
| 19 | 0 | 23 | 47 | 9.845 | 8.814 | 9.923 | 11.298 |
| 20 | 0 | 23 | 595 | 9.591 | 8.907 | 10.193 | 5.893 |
| 21 | 0 | 492 | 475 | 9.237 | 9.363 | 9.897 | 1.463 |
| 22 | 0 | 292 | 153 | 9.380 | 9.145 | 10.128 | 5.774 |
| 23 | 0 | 0 | 0 | 9.530 | 8.888 | 10.451 | $3.03 ?$ |
| 24 | 0 | 49 | 0 | 3.336 | 3.117 | 3.754 | 854 |
| 25 | 0 | 145 | 0 | 239 | 234 | 416 | 6.325 |
| 26 | 0 | 231 | 193 | 4.450 | 3.231 | 4.458 | 7.548 |
| 27 | 0 | 130 | 123 | 10.634 | 7.372 | 9.670 | 9.460 |
| 28 | 0 | 201 | 107 | 12.008 | 9.463 | 11.211 | 7.567 |
| March 1 | 0 | 125 | 24 | 7.240 | 6.614 | 7.376 | 8.877 |
| 2 | 0 | 1 | 0 | 1.686 | 1.661 | 1.830 | 378 |
| Table Tota: | 58 | 1,776 | 3.836 | 112.200 | 104.290 | 119.262 | 84.048 |

a. EVENT = CPR Runof Event 43
 of four Citl overts
CPR Runctin Evert in

| March 2 | N1 | NR | M | NS | N7 | N 10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| March | 0 | 216 | 191 | 1.970 | 2.058 | 2.276 | 9.553 |
|  | 1.097 | 634 | 459 | 8.839 | 8,904 | 9.093 | 15.594 |
|  | 0 | 900 | 711 | 11.801 | 11.801 | 13.373 | 7.810 |
|  | 0 | 1.094 | 600 | 10,855 | 11.200 | 12.410 | 8.218 |
|  | 0 | 1.124 | 436 | 10.461 | 11.122 | 11,959 | 8.324 |
|  | 0 | 2.718 | 436 | 9.404 | 10.423 | 11.336 | 8.357 |
|  | 0 | 4.123 | 834 | 8.895 | 9.634 | 10.207 | 6.897 |
|  | 0 | 3.970 | 1.008 | 8.833 | 9.347 | 10.336 | 7.020 |
|  | 0 | 3.695 | 987 | 8.771 | 9.304 | 10.791 | 8.877 |
|  | 0 | 1.706 | 469 | 3.971 | 4.172 | 4.755 | 5.352 |
| are Tote | 1.097 | 20.106 | 6.139 | 83.880 | 87.972 | 97.337 | 86.004 |

a. EVENT = CPR Runofi Evert in

Overall alleminity loeding (9/ovent as CeCO3) at nodes M1, N2, MM, MS, NT, N10, and N12 for eweh of the four CPR cvente

|  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runot Evemt 1 | 56 | 24.156 | 10.988 | 90.916 | 89.352 | 105.052 | 78.248 |
| CPR Runoff Event 12 | 3.467 | 7.696 | 6.080 | 53.496 | 46.387 | 49.241 | 17.775 |
| CPR Runofl Event 13 | 58 | 1.776 | 3.836 | 112.200 | 104.290 | 119.262 | 84.048 |
| CPR Runoff Event ${ }^{\text {an }}$ | 1.097 | 20.186 | 6.139 | 83.880 | 87.972 | 97.337 | 86.004 |
| Table Total | 4.678 | 53,814 | 27.042 | 340,493 | 328.002 | 370,882 | 266.073 |

 evoris
CPR Runoff Event ${ }^{\text {M }}$

|  |  | N 1 | N2 | Na | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| tanuary | 29 | 79.002 | 24.223 | 22.589 | 27.233 | 23.849 | 23.204 | 19.562 |
|  | 30 | 14.353 | 64.083 | 63.357 | 67.278 | 63.083 | 61.695 | 48.236 |
|  | 31 | 3.628 | 64.546 | 61.029 | 64.944 | 61.303 | 60.856 | 41.388 |
| February | 1 | 603 | 63.767 | 59.594 | 63.775 | 60.921 | 61.600 | 38.060 |
|  | 2 | 0 | 69.879 | 66.280 | 64.555 | 62.886 | 63.174 | 41.049 |
|  | 3 | 0 | 34.817 | 31.812 | 66.362 | 63.476 | 62.315 | 38.745 |
|  | 4 | 0 | 34.763 | 33.096 | 41.526 | 40.674 | 38.889 | 32.974 |
|  | 5 | 0 | 23,169 | 21.685 | 20.221 | 18.668 | 18.382 | 23.157 |
|  | 6 | 0 | 23.901 | 22.526 | 25.036 | 23.884 | 23.458 | 19.145 |
|  | 7 | 0 | 0 | 0 | 14.554 | 14.816 | 14.482 | 3.642 |
|  | 8 | 0 | 10.489 | 10.432 | 5.591 | 5.763 | 5.792 | -1.312 |
|  | 9 | 908 | 10.489 | 10.432 | 5.591 | 5.763 | 5.792 | 18.949 |
|  | 10 | 0 | 31.108 | 31.521 | 24.001 | 22.637 | 21.722 | 25.829 |
|  | 11 | 0 | 16.353 | 17.105 | 39.579 | 36.915 | 35.202 | 24.843 |
|  | 12 | 0 | 6.476 | 6.795 | 19.166 | 18.437 | 17.582 | 13.721 |
| Tabe Tom |  | 98.494 | 478.162 | 458.252 | 549.410 | 523.054 | 514.145 | 387.987 |

a. EVENT = CPR Runcf Event :1
 events
CPR Runof Event ${ }^{4} 2$

| February |  | N1 | N2 | N/ | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 12 | 4.862 | 19.032 | 19.962 | 18.423 | 15.865 | 16.053 |  |
|  | 13 | 139.737 | 33.600 | 34.060 | 47.393 | 46.184 | 37.000 | 28.175 |
|  | 14 | 0 | 42.462 | 39.016 | 46.566 | 46.357 | 40.062 | 11.456 |
|  | 15 | 0 | 55.438 | 55.031 | 55.611 | 58.937 | 59.319 | 7.272 |
|  | 16 | 0 | 21.653 | 23.499 | 25.146 | 27.826 | 28.435 | 1.510 |
| Table Total |  | 144.599 | 172.185 | 171.569 | 193.139 | 195.170 | 180.869 | 75.398 |

a EVENT = CPR Runof Evert ${ }^{(22}$

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 cuate

CPR Runcill Evert *3

| Februery |  | N1 | N2 | NH | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 16 | 101.579 | 20.450 | 22.325 | 36,457 | 40.319 | 40.093 | 29.006 |
|  | 17 | 1,424 | 34.464 | 33.344 | 36.429 | 38,873 | 38.508 | 22.565 |
|  | 18 | 466 | 34.748 | 32.055 | 32.835 | 31.032 | 29.946 | 17.959 |
|  | 19 | 299 | 33.921 | 34.462 | 34.437 | 35.335 | 35.586 | 35.292 |
|  | 20 | 370 | 34.850 | 33.659 | 38.226 | 34.285 | 35.325 | 18.553 |
|  | 21 | 0 | 33.986 | 32.901 | 37.616 | 34.318 | 35,994 | 5.340 |
|  | 22 | 0 | 15.383 | 15,473 | 36.643 | 35.558 | 39.088 | 23.939 |
|  | 23 | 0 | 0 | 0 | 36.407 | 36.193 | 40.690 | 13.471 |
|  | 24 | 0 | 10.690 | 11.153 | 14.026 | 12.613 | 14.129 | 3.224 |
|  | 25 | 13.287 | 32.720 | 32.796 | 900 | 824 | 843 | 22.530 |
|  | 26 | 18.406 | 25.853 | 22.711 | 14.447 | 12.740 | 12.422 | 26.128 |
|  | 27 | 14.696 | 39.010 | 35.502 | 31.420 | 30.421 | 31.473 | 26.126 |
|  | 28 | 0 | 38.166 | 36.058 | 39.261 | 37.457 | 36.387 | 25.605 |
| Masch | 1 | 0 | 24.721 | 22.574 | 25.388 | 24.788 | 23.274 | 27.806 |
| Teble Toul |  | 0 | 225 | 207 | 6.398 | 6.029 | 5.800 | 1.173 |
|  |  | 150.527 | 379,161 | 366.019 | 422,290 | 410.786 | 419.558 | 306.070 |

a. EVENT = CPR Runof Evert *13
 evont

|  | N1 | N2 | N4 | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 90.648 | 21.341 | 20.960 | 7.529 | 6.810 | N10 | 30.924 |
|  | 25.747 | 36.159 | 35.571 | 32.586 | 28.411 | 28.297 | 43.227 |
|  | 0 | 35.642 | 28.250 | 44.630 | 39.203 | 38.758 | 19.515 |
|  | 0 | 35.819 | 28.875 | 39.200 | 40.342 | 39.461 | 21.690 |
|  | 1.057 | 38.353 | 32.817 | 37.386 | 40.745 | 39.423 | 22.299 |
|  | 304 | 33.735 | 36.183 | 36.859 | 37.626 | 38.732 | 23.203 |
|  | 0 | 32.253 | 33.582 | 37.775 | 36,000 | 37.628 | 20.730 |
|  | 0 | 34.489 | 30.943 | 36.593 | 35.428 | 35.249 | 22.639 |
|  | 1.509 | 38.411 | 30.522 | 39.830 | 34.861 | 33.973 | 28.663 |
|  | 0 | 17.604 | 14.104 | 17.650 | 16.010 | 15.714 | 17.847 |
| Table Toted | 119,266 | 323.798 | 291.807 | 330.037 | 315.436 | 314.389 | 250.739 |

a. EVENT = CPR Runof Event :

Overall calcium loeding (grevent) at nodes N1, N2, M4, M5, N7, N10, and N12 for eech of the four CPR events

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runof Event ${ }^{\text {\% }}$ | 98.494 | 478.162 | 458.252 | 549.410 | 523.054 | 514.145 | 387.987 |
| CPR Runofit Event ${ }^{\text {2 }}$ | 144.599 | 172.185 | 171.569 | 193.139 | 195,170 | 180.869 | 75.398 |
| CPR Rumoft Event \#3 | 150.527 | 379.161 | 366.019 | 422.290 | 410.786 | 419.558 | 306.070 |
| CPR Runofr Event ${ }^{\text {a }}$ | 119.286 | 323.798 | 291.807 | 330.037 | 315.436 | 314.389 | 250.739 |
| Table Total | 512.886 | 1.353.305 | 1.287.647 | 1.494 .876 | 1.444.446 | 1.428 .961 | 1.020.195 |

 enars

CPR Runol Evert 1

a. EVENT = CPR Runctif Event M
 ovents
CPR Runof Evout ${ }^{2}$

| February |  | N1 | N2 | N | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 12 | 29.473 | 74.351 | 72.519 | 54.167 | 48.253 | 46,563 | 81.270 |
|  | 13 | 738.561 | 112.801 | 118.722 | 148.744 | 138.488 | 104.747 | 84.415 |
|  | 14 | 0 | 152.611 | 132.989 | 135.366 | 135.843 | 113.839 | 32.064 |
|  | 15 | 0 | 281.581 | 189.553 | 144.780 | 175.431 | 171.058 | 20.226 |
|  | 16 | 0 | 159.159 | 82.629 | 60.880 | 83.504 | 82.179 | 4.314 |
| Table Tota |  | 768.034 | 780.503 | 596.411 | 543.936 | 581.519 | 518.386 | 222.289 |

a. EVENT = CPR Runof Event ${ }^{\text {W2 }}$

Toted sulkete loading (g/d and grevemi) at nodes N1, M2, MA, MS, M7, N10, and M12 during the tratrient of four CPR cuents

CPR Runofin Evern ${ }^{2}$

| Februery |  | N1 | N2 | N | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 16 | 1.112.744 | 148.193 | 89.749 | 89.695 | 177.352 | 115.775 | 86.428 |
|  | 17 | 11.533 | 268.191 | 134.961 | 83.827 | 105,478 | 104.214 | 61.715 |
|  | 18 | 4.618 | 250.796 | 180.690 | 71.071 | 82.736 | 82.463 | 42.887 |
|  | 19 | 2.325 | 201.606 | 194.052 | 131.715 | 91.391 | 93.362 | 87.373 |
|  | 20 | 3.295 | 205.471 | 184,440 | 100.435 | 83.894 | 85.262 | 44.330 |
|  | 21 | 0 | 215.604 | 191.556 | 94.083 | 83.817 | 84.304 | 12.527 |
|  | 22 | 0 | 95, 179 | 92.122 | 91.130 | 88.141 | 86.741 | 55.991 |
|  | 23 | 0 | 0 | 0 | 90.374 | 90.374 | 88.233 | 31.627 |
|  | 24 | 0 | 54.587 | 68.751 | 33.802 | 31.552 | 30.809 | 7.893 |
|  | 25 | 106.334 | 178.177 | 202.170 | 2.210 | 2.147 | 2.104 | 56.052 |
|  | 26 | 116.103 | 147.788 | 144.959 | 35.541 | 32.173 | 31.082 | 64.175 |
|  | 27 | 83.527 | 223.219 | 209.024 | 81.943 | 74.063 | 73.212 | 77.919 |
|  | 28 | 0 | 210.754 | 205.957 | 98.513 | 92.965 | 90.701 | 60.050 |
| March | 1 | 0 | 131.269 | 130.340 | 65.512 | 62.057 | 60.360 | 68.502 |
|  | 2 | 0 | 943 | 1.197 | 15.426 | 14.844 | 14.617 | 2.918 |
| Table Total |  | 1.440.479 | 2.331.776 | 2.029.965 | 1.085.277 | 1.052 .984 | 1.043.237 | 760.379 |

- EVENT = CPR Runoff Event *3
 -

CPR Runof Evert 4

| Masch |  | N1 | NR | Na | NS | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 424.779 | 96.573 | 113.185 | 17.506 | 16.033 | 16.450 | 74.918 |
|  | 3 | 71.991 | 134.351 | 189.127 | 77.009 | 71.682 | 66.183 | 115.609 |
|  | 4 | 0 | 114.228 | 155.937 | 100.339 | 97.504 | 90.386 | 50.268 |
|  | 5 | 0 | 104.322 | 138.546 | 94.581 | 96.305 | 92.285 | 48.758 |
|  | 6 | 6.113 | 91.767 | 139.300 | 91.098 | 96.025 | 92.942 | 53.152 |
|  | 7 | 1.717 | 183.773 | 120.787 | 87.664 | 93.217 | 94.465 | 56.743 |
|  | 6 | 0 | 101.463 | 100.778 | 88.585 | 91.288 | 94.176 | 51.358 |
|  | 9 | 0 | 96.565 | 99.445 | 88.424 | 92.099 | 94.307 | 56.502 |
|  | 10 | 9.366 | 100.114 | 92.713 | 89.457 | 93.038 | 95.258 | 72.439 |
|  | Teteretal |  | 0 | 46.376 | 43.211 | 39.693 | 41.841 | 42.880 | 43.853 |
|  |  |  | 513.866 | 1.071.531 | 1.199.030 | 772.355 | 789.811 | 779.331 | 623.720 |

a. EVENT $=$ CPR Runo Event ${ }^{\text {an }}$

Overall eulfete loeding (glovent) at nodes N1, M2, M4, ME, M7, N10. and N12 for each of the four CPR events

|  | N1 | N2 | N4 | N5 | N7 | N10 | N12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runcif Event 1 | 863.933 | 2.508.270 | 2.147.482 | 1.613.875 | 1.540.017 | 1.514.120 | 1.142.007 |
| CPR Runofl Evant 62 | 768.034 | 780.503 | 596.411 | 543.936 | 581.519 | 518.386 | 222.289 |
| CPR Runof Event ${ }^{\text {c }}$ | 1.440 .479 | 2.331.776 | 2.029.965 | 1.085.277 | 1,052,884 | 1,043.237 | 760.379 |
| CPR Runoff Event th | 513.966 | 1.071 .531 | 1.199.030 | 772.355 | 789.811 | 779.331 | 623.720 |
| ble Total | 3.586.412 | 6,682.087 | 5,972,888 | 4.015,443 | 3.964.332 | 3.855.075 | 2.748 .385 |

## APPENDIX E

## THE CONTAMINANT REMOVAL RATES

Porcent removal of aciniky relative to the CPR loeding

|  | Detention Pond | RAPS Surface | RAPS Substrate | Setting Basin | $\text { Drains } 8$ Basins | Storage |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Rundif Event ${ }^{\text {W }}$ | 62.0\% | 10.9\% | 17.6\% | 2.5\% | 4.4\% | 0\% |
| CPR Runoff Event ${ }^{\text {\% }}$ | 65.2\% | -2.4\% | 34.9\% | 1.3\% | 9\% | -1.1\% |
| CPR Runofi Event ${ }^{\text {\% }}$ | 32.9\% | 9.8\% | 56.7\% | .6\% | .0\% | 0\% |
| CPR Runoff Event ${ }^{\text {\% }}$ | -19.5\% | -21.3\% | 140.9\% | .0\% | 0\% | 0\% |
| Group Total | 35.2\% | -.7\% | 62.5\% | 1.1\% | 1.3\% | -.3\% |

Percent removal of aluminum relative to the CPR loading

|  | $\qquad$ | RAPS Surface | RAPS Substrate | Setting Basin | $\begin{gathered} \text { Drains \& } \\ \text { Basins } \\ \hline \end{gathered}$ | Storage |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runof Event ${ }^{1}$ | 54.6\% | 15.2\% | 27.2\% | -2.6\% | 2.9\% | 3\% |
| CPR Runoff Event *2 | 73.4\% | 21.3\% | 4.0\% | -5.1\% | 1.9\% | 2.8\% |
| CPR Runoff Event ${ }^{3}$ | 39.1\% | 18.8\% | 40.1\% | 1.3\% | 4\% | -.2\% |
| CPR Runoff Event ${ }^{\text {4 }}$ | 69.7\% | -59.5\% | 86.2\% | -6\% | 2.1\% | -2.8\% |
| Group Total | 59.2\% | -1.0\% | 39.4\% | -1.7\% | 1.9\% | 0\% |

Percent removal of iron relative to the CPR loeding

|  | Detention Pond | RAPS Surface | RAPS Substrate | Setting Basin | Drains \& Basins | Storage |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runof Event ${ }^{\text {\# }} 1$ | 65.9\% | 17.3\% | -9.3\% | 9.4\% | 10.3\% | -7\% |
| CPR Runoff Event *2 | 88.9\% | 8.9\% | -6.0\% | 1.3\% | 3.9\% | 2.0\% |
| CPR Runoff Event ${ }^{\text {\% }}$ | 84.6\% | 10.6\% | -6.2\% | 7.6\% | 2.5\% | -.2\% |
| CPR Runoff Event ${ }^{\text {a }}$ | 88.8\% | 8\% | -23.5\% | 22.2\% | 10.5\% | -4.5\% |
| Group Total | 82.0\% | 9.4\% | -11.2\% | 10.2\% | 6.8\% | -.8\% |

Percent removal of manganese relative to the CPR loading

|  | Detention <br> Pond | RAPS Surface | RAPS <br> Substrate | Setting Basin |  <br> Basins | Storage |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| CPR Runoff Event 14 | $-14.0 \%$ | $2.5 \%$ | $-42.1 \%$ | $105.2 \%$ | $46.7 \%$ | $-4.7 \%$ |
| CPR Runoff Event *2 | $35.9 \%$ | $23.9 \%$ | $-28.4 \%$ | $47.6 \%$ | $20.2 \%$ | $-2.5 \%$ |
| CPR Runoff Event 3 | $1.6 \%$ | $15.1 \%$ | $18.3 \%$ | $49.8 \%$ | $14.8 \%$ | $-1.8 \%$ |
| CPR Runoff Event *4 | $-26.3 \%$ | $-4.5 \%$ | $13.0 \%$ | $88.4 \%$ | $29.2 \%$ | $-5.6 \%$ |
| Group Total | $-.7 \%$ | $9.2 \%$ | $-9.8 \%$ | $72.7 \%$ | $27.7 \%$ | $-3.7 \%$ |

Removal rates (g/d-equere meter) of acidity within each component

|  | $\begin{gathered} \text { Detention } \\ \text { Pond } \\ \hline \end{gathered}$ | RAPS Surface | RAPS Substrate | Settling Basin | Drains 8 Basins | Storage |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runoff Event \$1 | 5.26 | 1.34 | 3.23 | 31 | 53 | 00 |
| CPR Runoff Event \% | 8.59 | - 46 | 9.95 | 24 | 17 | . 07 |
| CPR Runof Event *3 | 4.92 | 2.11 | 18.33 | 12 | 00 | 00 |
| CPR Runoff Event * 4 | - 88 | -1.38 | 13.72 | 00 | 00 | 00 |
| Group Total | 4.47 | 40 | 11.31 | 17 | 18 | - 02 |


|  | Detertion Pond | RAPS Suter | RAPS <br> Substint | Setuing Bman | Drans 8 Bences | Siorege |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPRRRUNOM Everth | 50 | 24 | 63 | -04 | 05 | 00 |
| CPR Runori Event ${ }^{\text {a }}$ | 1.38 | 58 | 16 | . 14 | 05 | 02 |
| CPR Runof Evert ${ }^{\text {ch}}$ | 88 | 61 | 1.98 | 04 | 09 | 00 |
| CPR Runoff Evert ${ }^{4}$ | 36 | -44 | 98 | 00 | 02 | - 01 |
| Group Total | 80 | 25 | . 93 | . 03 | 03 | 00 |

Aenowal ratee (gd-equere meted) of ivon within each componemt

|  | $\begin{aligned} & \text { Detention } \\ & \text { Pand } \end{aligned}$ | RAPS Surliee | RAPS Subatricte | Seotine Besin | $\begin{gathered} \text { Drans } 8 \\ \text { Basins } \end{gathered}$ | Storage |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPRR RUnCi Eveot ${ }^{\text {a }}$ | 22 | 09 | -07 | 05 | 05 | 00 |
| CPR Runofi Event ${ }^{\text {H2}}$ | 1.86 | 27 | - 27 | 04 | 12 | 02 |
| CPR Runofi Event ${ }^{\text {ch}}$ | 84 | 15 | - 13 | 11 | 04 | 00 |
| CPR Runofi Event ${ }^{4}$ | 32 | 00 | - 18 | 12 | 05 | - 01 |
| Group Total | . 81 | 13 | -16 | 08 | 06 | 00 |

Removal rates (gra-cquare meter) of mancancee within eech component

|  | Detention rond | RAPS Surfmine | RAPS Substrate | Setling Besin | Drains 8 Basins | Storage |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CPR Runoit Event ${ }^{\text {B7 }}$ | -02 | 00 | -10 | 17 | 08 | 00 |
| CPR Runof Event *2 | 11 | 10 | -18 | 21 | 09 | 00 |
| CPR Runof Event ${ }^{3}$ | 00 | 04 | 08 | 15 | 04 | 00 |
| CPR Runof Event ${ }^{\text {a }}$ | -04 | -01 | 04 | 17 | 06 | 00 |
| Group Total | 01 | 04 | -04 | 17 | 07 | 00 |

## APPENDIX F

## TOXICITY TESTING WATER QUALITY RESULTS

Toxicity testing chemistry for 17 samples collected during 2001 from the Plant Gorgas ReRAPS Wetland.

|  |  |  |  |  |  |  |  | RAPS Wot | na Noces 1 | Sampan ${ }^{\text {a }}$ |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | N1 | N2 | Na |  |  |  | N) |  | NB |  |  | N10 | N 11 |  |  |  |  |  |
| Solide Yotal (mot) | 031201 | $\frac{031201}{1715}$ | 05.1701 | 0425:1 | 051701 | 031201 | 042501 | 0541701 | 042501 | 0ar2sol | 05i1701 | 042501 | 042s.01 | 031201 | 040201 | O42501 | 031701 | Tron Totem |
| Soras Sumperdee (mgh) | 313 | 916 | \% | 2 | $\underline{0}$ | 76 | 603 | 624 | 66 | 86 | 700 | 659 | 65 | 318 | 630 | 638 | 76 | 747 |
| Sotus 0 isconved (mgh) | 16 | 798 | 691 | 659 | 620 | 716 | 601 | 818 | 1 | 4 | 6 | 2 | 5 | 16 | 3 | 0 | 66 | 63 |
| Conductivy (umnovem) | 68 | 1018 | 667 | 867 | 622 | 818 | 609 | 818 | 863 | 681 | 090 | 657 | 649 | 803 | 827 | 629 | 681 | 60 |
| Mardnasa (mgi as $\mathrm{CaCO3}$ ) | 2080 | 5280 | 3870 | 4100 | 3560 | 440 | 4070 | 3490 | 800 | 86 | 806 | 876 | 637 | 1037 | 803 | 13 | 82 | 01 |
| Ca Ditioned (mil) | 695 | 1390 | 1190 | 1240 | 1220 | 1320 | 1270 | 360 | 4140 | 4110 | 360 | 3030 | 3750 | 1310 | 4370 | 3000 | 3000 | 320 |
| Mg Discomed (mgl) | 112 | 250 | 187 | 134 | 202 | 240 | 160 | 11.7 | 1250 | 1310 | 1250 | 1290 | 1160 | 1470 | 1770 | 1180 | 110 | 1220 |
| Na Distomed (mgh) | 1870 | 3080 | 3400 | 3240 | 3300 | 2510 | 3320 | 3130 | 3250 | 173 | 198 | 16 | 171 | 204 | 204 | 186 | 235 | 103 |
| $K$ Oiseonod (met) | 413 | 50 | 188 | 76 | ${ }^{\infty}$ | ${ }^{\infty}$ | 36 | 1110 | 3250 | 113 | 3280 | 3310 | 2930 | 2310 | 2100 | 2800 | 3220 | 3009 |
| Ci Oissoned (mith) | 1500 | 2100 | 3100 | 2000 | 1550 | 1830 | 1000 | 230 | 1740 | 1930 | 224 | $\infty$ | 22 | $\infty$ | 154 | 47 | 2 m | 113 |
| A | 25 | 20 | 310 | 64 | 846 | 336 | 608 | 530 | 834 | 637 | 1810 | 1870 | 1730 | 1870 | 1610 | 1820 | 2670 | 1006 |
|  | 28 | 20 | 517 | 644 | 442 | 333 | 608 | 527 |  | 631 | 700 | 64 | 656 | 421 | $4{ }^{4}$ | 300 | 620 | 508 |
| SO4 Disconed (mpt) | 275 | 605 | 209 | 265 | 278 | 318 | 279 | 271 | 291 | 634 | 687 | 04 | 653 | 418 | 43 | 593 | 518 | 303 |
| Si Discoved (mot) | 1000 | 2000 | 1870 | 1580 | 3000 | 1020 | 1590 | 3450 | 291 | 2 N | 38 | 264 | 276 | 374 | 24 | 257 | 310 | 311 |
| St Dissonod (mgl) | 179 | 227 | 255 | 103 | 26 | 197 | 19 | 3450 | 1570 | 1700 | 4500 | 1600 | 1820 | 46 | 450 | 1800 | 2540 | 2012 |
| $\mathrm{DHH}_{(1 \mathrm{SU}}{ }^{\text {a }}$ | 54 | 57 | 16 | 63 | 78 | 78 | 67 | 239 | 14 | 202 | 260 | 202 | 16 | 23 | 165 | 10 | 20 | 217 |
| Ammona (mith as N ) | 15 | 24 | 12 | 02 | 02 | 03 | 0 | 0 | 02 | 77 | 03 | 15 | 78 | 79 | 70 | 70 | 18 | 74 |
| A Totes (mgh) | 4750 | 8130 | 256 | 000 | 000 | 3430 | 000 | 218 | 020 | 000 | 03 | 02 | 03 | 04 | 01 | 03 | 0 | 08 |
| A1 Oiseowed (m9t) | 805 | 1970 | 053 | 027 | 022 | 000 | 000 | 218 | 000 | 0000 | 157 | 000 | 000 | 304 | 000 | 000 | 659 | 1000 |
| Fo Tote (mgh) | 9510 | 17100 | 325 | 148 | 073 | 5300 | 000 | 204 | 000 | 000 | 056 | 000 | 000 | 000 | 001 | 000 | 125 | 103 |
| Fo Disounod (mer) | 805 | 1590 | 003 | 008 | 085 | 005 | 010 | 009 | 000 | 082 | cse | 018 | 238 | 1120 | 108 | 185 | 1240 | 2134 |
| Mn Total (mgl) | 780 | 1220 | 044 | 319 | 162 | 200 | 010 | ${ }_{008}$ | 000 | 012 | 100 | 000 | 072 | 301 | 031 | 010 | 134 | 200 |
| Mn Discomed (mor) | 651 | 934 | 027 | 424 | 160 | 140 | 056 | 039 | 015 | 270 | 597 | 008 | 230 | 277 | 117 | 359 | 768 | 340 |
| 2n Total (mgh) | 032 | 180 | 004 | 002 | 000 | 017 | 002 | 050 | 000 | 242 | 634 | 000 | 18 | 00 | 101 | 313 | 653 | 273 |
| 2n Diteomod (mol) | 052 | 123 | 010 | 003 | 011 | 000 | 002 | 000 | 000 | 002 | 000 | 000 | 002 | 004 | 014 | 000 | 000 | 019 |
| Ni fotel (mer) | 072 | 145 | 000 | 000 | 000 | 009 | 000 | 000 | 002 | ${ }_{0}^{003}$ | 0000 | 000 | 004 | 000 | 000 | 000 | 000 | 014 |
| N1. Discoinoe (mgl) | 033 | OSt | 000 | 000 | 000 | 000 | 000 | 000 | 002 | 003 | 000 | 000 | 000 | 008 | $\infty 00$ | 000 | 000 | 014 |
| Cu Potel (mar) | 006 | 031 | 000 | 002 | 000 | 005 | 003 |  | coo | 000 | 000 | 000 | 000 | 000 | 003 | 000 | 000 | 00 |
| Cu Dissonod (mol) | 000 | 000 | 000 | 000 | 000 | 000 | 000 | ${ }_{000}$ | 000 | 003 | 000 | 000 | 00 | 007 | 000 | 002 | 000 | 004 |
| Orparce Carion Total (mgl) | 77 | 35 | 275 | 111 | 120 | 114 | 0 | 200 | $\underline{60}$ | 1005 | 000 | 000 | 000 | 000 | $\infty$ | 000 | 000 | 000 |
| Touctiy Unts Toten (Tuts) | 18 | 30 | 0 | 1 | 20. | , | . | 200 | 6 | 10 | 360 | 92 | 261 | $\stackrel{1}{2}$ | 78 | 348 | 424 | 176 |
| Tapcry uma Diseoved (Tue) | 5 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 4 |
| Acceo Mopor ton Sumvai (\%) | 9097 | 9904 | 090\% |  | 9\%\% | $090 \%$ | ¢0\% | $098 \%$ | $090 \%$ | 09\% | $00 \%$ | 0 con | 09 | $\bigcirc$ | 4 | $\bigcirc$ | 0 | 1 |
| Cronce Mapor ion Simval (in) | 0880 | 7225 | 0104 | $610 \%$ | 612\% | $014 \%$ | 846\% | 883\% | 8159 | 7944 | $670 \%$ | \% 24 |  | com | ¢0\% | $0 \times$ | 0 OH | 0408 |
| C ouna Sumvan (in) | $\infty$ | $\infty$ | 100 | 100 | 100 | 100 | 100 | 100 | 100 |  |  | 24x | 6114 | nox | 1174 | 6778 | 7300 | 620\% |
| C ouve Reproouction (Neonmes) | 80 | 01 | 1430 | 2080 | 533 | 1550 | 1170 | 1000 | 100 | 1980 | 1020 | 1300 | 100 | 100 | 100 | $\infty$ | 100 | 87 |
| Fureso mimow Suruven (i) | 100 | $\infty$ |  | 1400 |  | 1200 | 680 |  |  | 1950 | 1020 | 1300 | 1700 | 110 | 100 | 20.5 | 1040 | 1135 |
| Furtesa minow Orominsumval (g) | 03 | $\infty$ |  | 40 |  | 30 | 650 |  | 425 | $\underline{50}$ |  | 125 | 1000 | 1278 |  | 1075 |  | 773 |
| Ferrese mimow 0 romitis (p) | 01 | $\infty$ |  | 38 |  | 31 | 20 |  | 13 | 29 |  | 35 | 52 | 41 |  | 42 |  | 36 |
|  |  |  |  |  |  | 31 | 20 |  | 13 | 22 |  | 17 | 32 | 37 |  | 30 |  | 22 |

## APPENDIX G

## LABORATORY QUALITY CONTROL PROTOCOL

# Alabama Power Company Environmental Affairs General Test Lab 

## LABORATORY STATEMENT OF QUALIFICATIONS

## Laboratory Certifications:

National Pollutant Discharre Elimination System: This laboratory is recognized as certified to analyze National Pollutant Discharge Elimination System (NPDES) samples for Environmental Protection Agency - Region IV. We participate in an annual proficiency examination. Past and present data is on file for inspection.

Drinking Water: This laboratory is certified to analyze drinking water which includes the determination of Inorganics, Total Trihalomethanes, Volatile Organic Chemicals, Synthetic Organic Chemicals by GC/MS, Synthetic Organic Chemicals by HPLC, Other Synthetic Organic Chemicals, Haloacetic Acids, and Total Organic Carbon.
\#2 Diesel Fuel Oil: This laboratory participates in a round robin study conducted by The American Society For Testing and Materiak (ASTM), three times per year. This study allows for the refinement of methods and a means of quality control with other laboratories.

Coal Testing: This laboratory participates in a quarterty round robin study conducted by Quality Associates Intermational of Canada. This study covers the anatysis of coal and coal ash and serves as a means of quality control through comparison with other participating laboratories.

## Analvtical Methods

This laboratory utilizes a variety of reference methods for amalyses performed, including ASTM, EPA, and Standard Methods. The majority of the methods utilize one or more

## Quality Control

This laboratory has a written Comprehensive Quality Assurance plan, which is available for inspection. This plan serves as a guide for quality laboratory operation and covers such aspects as general quality control measures, equipment maintenance and calibration, chemical controk, standards controls, sample handling and preservation, and corrective action plan. The general quality control measures include the analysis of blanks, duplicates, matrix spikes, blank spikes, surrogate standards, internal standards and historical cvaluation, as applicable, to assure generation of quality data.

## Data Reporting

This laboratory uses Labworks by Automated Analytical System for the collection, validation, tracking and reporting of laboratory data. Upon completion of analysis, the sample data is reported on hard copy and archived in an SQL database. Data may also be transferred via Internet.

## Sampling

This laboratory will prepare sampling kits for the convenience of our clients, at no additional charge. These kits may be obtained on demand or can be shipped on a schedule based upon applicable NPDES permits. These kits contain all necessary sampling containers, preservatives, sampling instructions and chain of custody forms. Return shipping fees are not included.

## Summary

In conclusion, this laboratory has the capability to perform a wide range of analytical testing on various matrices. As evidenced in the attachments of personnel and equipment, this laboratory is equipped to handle most any testing that may be deemed necessary to maintain a clean environment.
We offer:

1. Diversified chemical testing capability
2. Ongoing quality control program
3. Qualified chemical staff
4. Experience with many different matrices such as soil, water, coal and petroleum products

## Table - QA Targets for Precision, Accuracy and Method Detection Limits

| Method Reference | Analysis Name | Units | MDL | Precision (\%RSD) | $\begin{gathered} \text { Accuracy } \\ \text { Range } \\ (\% R) . \end{gathered}$ | Accuract Range (\%R) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| EPA 150.1 | pHI | SU |  |  |  |  |
| EPA 160.1 | Solids. Dissolved | $\mathrm{mg} / \mathrm{L}$ | 1 |  |  |  |
| EPA 160.2 | Solids - Suspended | $\mathrm{mg} / \mathrm{L}$ | 1 | 7.6 | 82 | 112 |
| EPA 160.3 | Non-Volatile Suspended Solids | $\mathrm{mg} / \mathrm{L}$ | 1 |  |  |  |
| EPA 160.3 | Solids. Inorganic (Fixed) | $\mathrm{mg} / \mathrm{L}$ | 1 |  |  |  |
| EPA 160.3 | Solids. Total | mg/L | 1 |  |  |  |
| EPA 160.4 | Solids. Organic | $\mathrm{mg} / \mathrm{L}$ | 1 |  |  |  |
| EPA 160.4 | Volatile Suspended Solids | $\mathrm{mg} / \mathrm{L}$ | 1 |  |  |  |
| EPA 160.5 | Solids. Setteable | $\mathrm{mL} / \mathrm{l}$. | 0.1 |  |  |  |
| EPA 1664 | Oil and Grease | $\mathrm{mg} / \mathrm{L}$ | 1.4 | 1.9 | 82 | 89 |
| EPA 180.1 | Turbidity | NTU | 0.30 |  |  |  |
| EPA 200.7 | Aluminum. Total | $\mathrm{mg} / \mathrm{L}$ | 0.006 | 6.2 | 76 | 101 |
| EPA 200.7 | Aluminum. Total | $\mathrm{mg} / \mathrm{L}$ | 0.006 | 6.2 | 76 | 101 |
| EPA 200.7 | Antimony. Total | mg/L | 0.002 | 1.0 | 70 | 74 |
| EPA 200.7 | Arsenic. Total | $\mathrm{mg} / \mathrm{L}$ | 0.005 | 1.6 | 97 | 103 |
| EPA 200.7 | Barium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.6 | 97 | 104 |
| EPA 200.7 | Barium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.6 | 97 | 104 |
| EPA 200.7 | Beryllium. Total | $\mathrm{mg} / \mathrm{l}$. | 0.001 | 0.4 | 90 | 91 |
| EPA 200.7 | Beryllium. Total | $\mathrm{mg} / \mathrm{L}$. | 0.001 | 0.4 | 90 | 91 |
| [EPA 200.7 | Bismuah. Toxal | $\mathrm{mg} / \mathrm{L}$ | 0.001 |  |  |  |
| EPA 200.7 | Boron. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 7.4 | 78 | 108 |
| EPA 200.7 | Cadmium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.1 | 95 | 99 |
| EPA 200.7 | Cadmium. Total | $\mathrm{mg} / \mathrm{l}$ | 0.002 | 1.1 | 95 | 99 |
| EPA 200.7 | Calcium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 21.8 | 52 | 139 |
| EPA 200.7 | Chromium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.001 | 1.1 | 93 | 97 |
| EPA 200.7 | Chromium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.001 | 1.1 | 93 | 97 |
| I:PA 200.7 | Coball Tokal | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 0.7 | 95 | 98 |
| I:PA 200.7 | Copper. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.4 | 92 | 97 |
| EPA 200.7 | Copper. Total | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 1.4 | 92 | 97 |
| EPA 200.7 | Iron. Total | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 1.0 | 97 | 101 |
| EPA 200.7 | Iron. Total | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 1.0 | 97 | 101 |
| EPA 200.7 | Lead. Total | $\mathrm{mg} / \mathrm{l}$. | 0.001 | 0.7 | 101 | 104 |
| EPA 200.7 | Lithium. Total | $\mathrm{mg} / \mathrm{l}$ | 0.002 | 0.9 | 74 | 78 |
| EPA 200.7 | Magnesium. Total | $\mathrm{mg} / \mathrm{l}$ | 0.01 | 1.7 | 93 | 100 |
| EPA 200.7 | Manganesc. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.6 | 94 | 100 |
| EPA 200.7 | Manganese. Total | mg/ | 0.002 | 1.6 | 94 | 100 |
| 1PA 200.7 | Molyhdenum. Total | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 0.7 | 77 | 80 |
| EPA 200.7 | Nickel. Total | $\mathrm{mg} / \mathrm{l}$. | 0.0012 | 1.4 | 97 | 102 |
| :PA 200.7 | Nickel. Toral | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 1.4 | 97 | 102 |
| :PA 200.7 | Phosphorus. Total | $\mathrm{mg} / \mathrm{L}$ | 0.005 | 2.8 | 54 | 65 |
| :PA 200.7 | Potassium. Toxal | $\mathrm{mg} / \mathrm{L}$. | 0.01 | 10.5 | 49 | 91 |
| [PA 200. 7 | Silicon. Dissolved | $\mathrm{mg} / \mathrm{l}$ | 0.005 | 4.5 | 59 | 77 |


| Method Reference | Analysis Name | Units | MDL | Precision (\%RSD) | $\begin{array}{\|c\|} \hline \text { Accuracy } \\ \text { Range } \\ (\% R) . \end{array}$ | Accuracy Range (\%R) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| EPA 200.7 | Silicon. Total | $\mathrm{mg} / \mathrm{l}$. | 0.005 | 4.5 | 59 | 77 |
| EPA 200.7 | Silver, Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.4 | 90 | 95 |
| EPA 200.7 | Silver. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 1.4 | 90 | 95 |
| EPA 200.7 | Sodium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 6.6 | 71 | 98 |
| EPA 200.7 | Strontium. Total | mg L | 0.002 | 1.1 | 87 | 91 |
| EPA 200.7 | Thallium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 2.2 | 92 | 101 |
| EPA 200.7 | Tin. Total | $\mathrm{mg} / \mathrm{L}$ | 0.005 | 1.1 | 88 | 93 |
| EPA 200.7 | Titanium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 0.8 | 94 | 98 |
| EPA 200.7 | Vanadium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 0.7 | 96 | 99 |
| EPA 200.7 | Zinc. Total | $\mathrm{mg} / \mathrm{l}$ | 0.002 | 4.9 | 80 | 99 |
| EPA 200.7 | Zinc. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 4.9 | 80 | 99 |
| EPA 200.9 | Antimony, Total | $\mathrm{mg} / \mathrm{L}$ | 0.003 |  |  |  |
| EPA 200.9 | Antimony. Total | $\mathrm{mg} / \mathrm{L}$ | 0.003 |  |  |  |
| EPA 200.9 | Antimony. Total | $\mathrm{mg} / \mathrm{L}$ | 0.003 |  |  |  |
| EPA 200.9 | Arsenic. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 |  |  |  |
| EPA 200.9 | Arsenic. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 |  |  |  |
| EPA 200.9 | Arsenic. Total | $\mathrm{mg} / \mathrm{l}$. | 0.001 |  |  |  |
| EPA 200.9 | Bismuth. Total | $\mathrm{mg} / \mathrm{L}$ | 0.005 |  |  |  |
| EPA 200.9 | Lead. Total | $\mathrm{mg} / \mathrm{L}$ | 0.001 |  |  |  |
| EPA 200.9 | Lead. Total | $\mathrm{mg} / \mathrm{L}$ | 0.001 |  |  |  |
| EPA 200.9 | Selenium. Total | mg/L | 0.002 |  |  |  |
| EPA 200.9 | Selenium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.002 |  |  |  |
| EPA 200.9 | Thallium. Total | $\mathrm{mg} / \mathrm{L}$ | 0.001 |  |  |  |
| EPA 200.9 | Thallium. Total | $\mathrm{mg} / \mathrm{l}$. | 0.001 |  |  |  |
| E.PA 218.5 | Ilexavalent Chromium | $\mathrm{mg} / \mathrm{l}$. | 0.010 |  |  |  |
| EPA 245.1 | Mercury. Total | $\mathrm{mg} / \mathrm{L}$ | 0.0002 |  |  |  |
| EPA 245.1 | Mercury. Total | mg/l. | 0.0002 | 3.2 | 93 | 106 |
| E:PA 2540G | Solids. Fixed | \% By Wt. | 0.001 |  |  |  |
| EPA 2540G | Solids. Total | \% By Wt. | 0.001 |  |  |  |
| E:PA 2540G | Solids. Volatile | \% By Wt. | 0.001 |  |  |  |
| EPA 300.0 | Acetate | $\mathrm{mg} / \mathrm{L}$ | 0.10 |  |  |  |
| IEPA 300.0 | Bromate | $\mathrm{mg} / \mathrm{L}$. | . 010 |  |  |  |
| EPA 300.0 | Bromide | $\mathrm{mg} / \mathrm{L}$ | 0.02 | 4.9 | 93 | 113 |
| EPA 300.0 | Bromide | $\mathrm{mg} / \mathrm{l}$. | 0.02 | 2.0 | 97 | 105 |
| EPA 300.0 | Bromide - Dissolved | $\mathrm{mg} / \mathrm{L}$ | 0.02 | 2.0 | 97 | 105 |
| EPA 300.0 | Chlorate | $\mathrm{mg} / \mathrm{L}$. | 0.10 |  |  |  |
| EPA 300.0 | Chloride | $\mathrm{mg} / \mathrm{l}$. | 0.10 | 1.2 | 98 | 102 |
| EPA 300.0 | Chloride | $\mathrm{mg} / \mathrm{L}$ | 0.10 | 1.2 | 98 | 102 |
| EPA 300.0 | Chloride - Dissolved | $\mathrm{mg} / \mathrm{l}$. | 0.10 | 1.2 | 98 | 102 |
| EPPA 300.0 | Chlorite | $\mathrm{mg} / \mathrm{l}$. | . 010 |  |  |  |
| EPA 300.0 | Fluoride - Dissolved | $\mathrm{mg} / \mathrm{l}$. | 0.01 |  |  |  |
| EPA 300.0 | Fluxride: Total | $\mathrm{mg} / \mathrm{l}$. | 0.01 | 9.8 | 75 | 114 |
| EPA 300.0 | Iodide | $\mathrm{mg} / \mathrm{l}$ | 0.10 | 2.0 | 96 | 104 |
| EPA 300.0 | lodide - Dissolved | $\mathrm{mg} / \mathrm{l}$. | 0.10 | 2.0 | 96 | 104 |
| 1:PA 300.0) | Nitrate (as N ) | $\mathrm{mg} / \mathrm{l}$. | 0.05 | 0.3 | 103 | 105 |


| Method Reference | Analysis Name | Units | MDL | Precision (\%RSD) | $\begin{aligned} & \text { Accuracy } \\ & \text { Range } \\ & \text { (\%R). } \end{aligned}$ | Accuracy Range (\%R) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| EPA 300.0 | Nitrate. Water Soluble | $\mathrm{mg} / \mathrm{l}$. | 0.01 |  |  |  |
| EPA 300.0 | Nitrogen. Nitrate | $\mathrm{mg} / \mathrm{L}$ | 0.1 |  |  |  |
| EPA 300.0 | Nitrogen. Nitrate | $\mathrm{mg} / \mathrm{L}$ | 0.1 |  |  |  |
| EPA 300.0 | Nitrogen-Nitrate. Dissolved | $\mathrm{mg} / \mathrm{L}$ | 0.1 |  |  |  |
| EPA 300.0 | Phosphaxe. Ortho | $\mathrm{mg} / \mathrm{L}$ | 10 | 0.3 | 98 | 100 |
| EPA 300.0 | Sulfate | $\mathrm{mg} / \mathrm{L}$ | 1.0 | 0.6 | 99 | 101 |
| EPA 300.0 | Sulfate - Dissolved | $\mathrm{mg} / \mathrm{L}$ | 1.0 | 0.6 | 99 | 101 |
| EPA 300.0 | Water Extractable Chlorides | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 300.0 | Water Extractable Fluoride | $\mathrm{mg} / \mathrm{kg}$ | 0.1 |  |  |  |
| EPA 300.0 | Water Extractable Sulfate | $\mathrm{mg} / \mathrm{kg}$ | 10 |  |  |  |
| EPA 3040 | Aluminum | $\mathrm{mg} / \mathrm{kg}$ | 3 |  |  |  |
| EPA 3040 | Aluminum | $\mathrm{mg} / \mathrm{kg}$ | 3 |  |  |  |
| EPA 3040 | Barium | mg/kg | 1 | 30.7 | 36 | 158 |
| EPA 3040 | Boron | mg/kg | 2 |  |  |  |
| EPA 3040 | Cadmium | mg/kg | 1 | 16.8 | 67 | 134 |
| EPA 3040 | Calcium | mg/kg | 1 |  |  |  |
| EPA 3040 | Chromium | $\mathrm{mg} / \mathrm{kg}$ | 1 | 13.1 | 81 | 133 |
| EPA 3040 | Copper | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3040 | Iron | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3040 | Lead | $\mathrm{mg} / \mathrm{kg}$ | 1 | 20.2 | 57 | 138 |
| EPA 3040 | Magnesium | $\mathrm{mg} / \mathrm{kg}$ | 3 |  |  |  |
| EPA 3040 | Molybdenum | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3040 | Nickel | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| IPPA 3040 | Phosphorus | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3040 | Silica | mg/kg | 1 |  |  |  |
| EPA 3040 | Silver | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3040 | Sodium | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3040 | Tin | $\mathrm{mg} / \mathrm{kg}$ | 3 |  |  |  |
| EPA 3040 | Zinc | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/200.9 | Gallium. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/200.9 | Indium. Total | $\mathrm{mg} / \mathrm{kg}$ | 2 |  |  |  |
| EPA 305I/245.1 | Mercury | $\mathrm{mg} / \mathrm{kg}$ | 0.02 |  |  |  |
| EPA 3051/6010 | Aluminum | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Aluminum. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Antimons | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| 1:PA 305 1/6010 | Arsenic | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Arsenic Oxide (As2O5) | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Barium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Barium. Tocal | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Beryllium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Buron. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Cadmium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Calcium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| LEPA 3051/6010 | Calcium. Toxal | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Chromium | mghg | 1.0 |  |  |  |

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| Method Reference | Analysis Name | Units | MDL | Precision (\%RSD) | $\begin{aligned} & \text { Accuracy } \\ & \text { Range } \\ & \text { (\%R). } \end{aligned}$ | $\begin{aligned} & \text { Accuracy } \\ & \text { Range } \\ & (\% R) \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| EPA 3051/6010 | Cobalt | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Copper | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Iron | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Lead | mg/kg | 1.0 |  |  |  |
| EPA 3051/6010 | Lead Oxide (PbO) | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Magnesium | mg/kg | 1.0 |  |  |  |
| EPA 3051/6010 | Magnesium. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Manganese | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Molytdenum | mg/kg | 1.0 |  |  |  |
| EPA 3051/6010 | Nickel | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Phosphorus | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 305 1/6010 | Phosphorus. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Potassium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Potassium. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Selenium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Selenium Oxide ( SeO 3 ) | $\mathrm{mg} / \mathrm{kg}$ | 2 |  |  |  |
| EPA 3051/6010 | Silicon | mg/kg | 1.0 |  |  |  |
| EPA 3051/6010 | Silicon | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| LEPA 3051/6010 | Silver | $\mathrm{mg} / \mathrm{kg}$ | 0.2 |  |  |  |
| EPA 3051/6010 | Sodium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Sodium. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Strontium | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Strontium. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Thallium | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Tin | mg/kg | 1.0 |  |  |  |
| EPA 3051/6010 | Titanium | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 3051/6010 | Titanium. Total | $\mathrm{mg} / \mathrm{kg}$ | 1 |  |  |  |
| EPA 3051/6010 | Vanadium | mg/kg | 1.0 |  |  |  |
| EPA 3051/6010 | Zinc | $\mathrm{mg} / \mathrm{kg}$ | 1.0 |  |  |  |
| EPA 335.3 | Cyanide Total | $\mathrm{mg} / \mathrm{L}$. | 0.005 |  |  |  |
| EPA 335.4 | Cyanide | $\mathrm{mg} / \mathrm{l}$. | 0.005 |  |  |  |
| EPA 340.2 | Fluoride | $\mathrm{mg} / \mathrm{L}$ | 0.02 |  |  |  |
| EPA 350.1 | Nitrogen. Ammonia | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 2.7 | 123 | 133 |
| EPA 351.2 | Nitrogen. Total Kjeldahl | $\mathrm{mg} / \mathrm{l}$. | 0.01 | 2.7 | 123 | 133 |
| EPA 353.2 | Nitrate (as N) | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 1.8 | 98 | 105 |
| EPA 353.2 | Nitrite (as N) | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 1.5 | 96 | 102 |
| EPA 353.2 | Nitrogen. Nitrate | $\mathrm{mg} / \mathrm{l}$. | 0.01 | 1.8 | 98 | 105 |
| EPA 353.2 | Nitrogen. Nitrate. Dissolved | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 1.8 | 98 | 105 |
| EPA 353.2 | Nitrogen. Nitrite | $\mathrm{mg} / \mathrm{l}$. | 0.01 | 1.5 | 96 | 102 |
| EPA 353.2 | Nitrogen. Nitrite-Dissolved | $\mathrm{mg} / \mathrm{L}$ | 0.01 | 1.5 | 96 | 102 |
| EPA 365.2 | Phosphatc-Otho | mg/l as P | 0.01 | 5.3 | 94 | 115 |
| EPA 365.2 | Phosphorux. Iotal | mg/las P | 0.001 |  |  |  |
| EPA 415.1 | Suspended (rganic Carton | $\mathrm{mg} / \mathrm{l}$. | 0.30 | 3.9 | 89 | 105 |
| EPA 415.1 | Total Organic Carton | $\mathrm{mg} / \mathrm{L}$. | 0.30 | 2.7 | 64 | 74 |
| EPA 624 | 1.1.1-Trichlorkethanc | $\mathrm{mg} / \mathrm{L}$. | 0.001 | 4.7 | 92 | 111 |


| Method Reference | Analysis Name |  |  |  |  |  |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |


| Mathod Reference | Analysis Name | Units | MDL | Precision (\%RSD) | $\begin{array}{\|c} \hline \text { Accuracy } \\ \text { Range } \\ \text { (\%R). } \end{array}$ | Accuracy Range (\%R) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| EPA 625 | 2-Chlorophenol | mg/L. | 0.004 | 11.6 | 31 | 77 |
| EPA 625 | 2-Methylnaphthalene | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.7 | 60 | 83 |
| EPA 625 | 2-Nitrophenol | $\mathrm{mg} / \mathrm{L}$ | 0.004 | 9.3 | 37 | 75 |
| EPA 625 | 3.3p-Dichlorobenzidine | $\mathrm{mg} / \mathrm{L}$ | 0.013 | 14.5 | 65 | 123 |
| EPA 625 | 3.4-Benzofluoranthene | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 6.9 | 69 | 96 |
| EPA 625 | 4.6-Dinitro-o-cresol | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 6.6 | 21 | 48 |
| EPA 625 | 4-Bromophenyl phenyl ether | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.6 | 71 | 93 |
| EPA 625 | 4-Chlorophenyl phenyl ether | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.5 | 63 | 85 |
| EPA 625 | 4-Nitrophenol | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.9 | 32 | 55 |
| EPA 625 | Acenaphthene | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 5.1 | 66 | 86 |
| EPA 625 | Acenaphthylene | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 3.9 | 52 | 68 |
| EPA 625 | Anthracene | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.0 | 58 | 78 |
| EPA 625 | Benzidine | $\mathrm{mg} / \mathrm{L}$ | 0.007 | 13.4 | 10 | 64 |
| EPA 625 | Benzo( a anthracene | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 8.4 | 95 | 129 |
| EPA 625 | Benzol a pyrene | $\mathrm{mg} / \mathrm{L}$. | 0.003 | 6.7 | 79 | 106 |
| EPA 625 | Benao(g.h.i)perylene | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.9 | 68 | 91 |
| EPA 625 | Benzo(k) fluoranthene | $\mathrm{mg} / \mathrm{l}$. | 0.003 | 8.0 | 89 | 121 |
| EPA 625 | Bis(2-chloroethoxy)methane | mg/L | 0.002 | 4.3 | 59 | 77 |
| EPA 625 | Bis(2-chloroethyl)ether | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.9 | 51 | 75 |
| EPA 625 | Bis(2-chloroisopropyl)ether | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.3 | 52 | 73 |
| EPA 625 | Bis(2-ethylhexyl)phthalate | $\mathrm{mg} / \mathrm{l}$. | 0.004 | 10.2 | 95 | 136 |
| EPA 625 | Butyl benzyl phthalate | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 8.6 | 91 | 126 |
| EPA 625 | Chrysene | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 7.1 | 86 | 114 |
| EPA 625 | Dibenzo( a h ) anthracene | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 7.2 | 82 | 111 |
| EPA 625 | Diethyl phthalate | $\mathrm{mg} / \mathrm{l}$. | 0.003 | 7.3 | 74 | 103 |
| EPA 625 | Dimethyl phthalate | $\mathrm{mg} / \mathrm{L}$ | 0.003 | 6.3 | 68 | 93 |
| EPA 625 | Di-n-butylphthalate | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 5.1 | 60 | 81 |
| EPA 625 | Di-n-octylphthalate | $\mathrm{mg} / \mathrm{L}$ | 0.004 | 9.6 | 83 | 121 |
| EPA 625 | Fluoranthene | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 5.5 | 64 | 86 |
| 1:PA 625 | Fluoreme | $\mathrm{mg} / \mathrm{l}$. | 0.003 | 6.1 | 68 | 93 |
| EPA 625 | I lexachlorobenzene | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 4.9 | 56 | 75 |
| I:PA 625 | Hexachlorobutadiene | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 4.8 | 37 | 56 |
| EPA 625 | Hexachlorocyclopentadiene | $\mathrm{mg} / \mathrm{L}$ | 0.001 | 1.5 | 55 | 61 |
| EPA 625 | Hexachloroethane | $\mathrm{mg} / \mathrm{L}$. | 0.002 | 5.9 | 34 | 57 |
| EPA 625 | Indeno( 1.2.3-cd)pyrene | $\mathrm{mg} / \mathrm{L}$. | 0.003 | 6.2 | 61 | 85 |
| EPA 625 | Isophorone | $\mathrm{mg} / \mathrm{L}$. | 0.002 | 5.5 | 67 | 89 |
| EPA 625 | Naphthalene | $\mathrm{mg} / \mathrm{l}$. | 0.003 | 6.3 | 67 | 92 |
| EPA 625 | Nitroherzenc | $\mathrm{mg} / \mathrm{L}$ | 0.002 | 4.7 | 45 | 64 |
| 1:PA 625 | N -Nitrosodimethylamine | $\mathrm{mg} / \mathrm{l}$ | 0.003 | 8.0 | 30 | 62 |
| 1:PA 625 | N-Nitrosodi-n-propylamine | $\mathrm{mg} / \mathrm{l}$. | 0.002 | 3.4 | 61 | 75 |
| E:PA 625 | N -Nitrosodiphenylamine | $\mathrm{mg} / \mathrm{L}$. | 0.003 | 8.5 | 97 | 131 |
| EPA 625  | Pentachlorophemol | $\mathrm{mg} / \mathrm{l}$. | 0.008 | 6.0 | 51 | 75 |
| EPA 625 P | Phenanthrene | $\mathrm{mg} / \mathrm{l}$. | 0.001 | 5.0 | 57 | 77 |
| EPA 625 P | Phenol | $\mathrm{mg} / \mathrm{L}$ | 0.001 | 6.6 | 22 | 48 |
| EPA 625 | Pyrene | $\mathrm{mg} / \mathrm{L}$. | 0.002 | 4.7 | 63 | 82 |


[^0]:    -The average event removal is hased on the total mass removal of contaminant (T-Al. T-F: T.Mn. and acidity) entering the system at the hase of the coal pile (A') during each ('PR treatment period.

[^1]:    ${ }^{\text {'Paper presented at the } 2001 \text { National Meeting }}$ of the American Society for Surface Mining and Reclamation, Albuquerque, New Mexico, June 3-7, 2001. Pub. by ASSMR, 3134 Montavesta Rd.. Lexington KY 40502.
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[^2]:    a Parameter = Chionde (mgl)

[^3]:    a. Parameter $=$ Siver. Total (mpl)

[^4]:    - Parameter = Alumixum. Dissolved (moll)

[^5]:    a Parameter $=$ Aurminum. Totel $(m g / 1)$

[^6]:    a. Pormater = Arsenic, Tolel (moll)

[^7]:    - Perameter $=$ Coucium. Totel $(\mathrm{mg} / \mathrm{I})$

[^8]:    a. Parmater = Cedimim. Dissolved (mp/l)

[^9]:    a. Paremeior a Cobell. Diseoked (mpl)

[^10]:    a. Parmmeter = Copper, Dissolved (mg/)

[^11]:    - Perameter = Menganese, Dissotved (ma/7)

[^12]:    a. Partmatior $=$ Nickel, Total (mol)

[^13]:    a. Permmeter $=$ Setentim, Totel $(m=1)$

[^14]:    a Parameter $=$ Thamum. Dessolved (mg/)

[^15]:    a. Partrineter $=$ Thamum. Totai $(\mathrm{mg} / \mathrm{f})$

[^16]:    a. Perameter $=$ Solids. Suspended $(\mathrm{mg} / \mathrm{I})$

[^17]:    a. Parameter = Biochemical Oxygen Demand. 5 Day (mg/)

[^18]:    a. Parmeter = Nitrogen. Nitrite (moll)

[^19]:    a. Parameter a Nitrogen. Ammonia (ma/l)

[^20]:    a. Parameter $=$ Nitrogen. Total Kieldahl (mg/)

[^21]:    a. Parameter $=$ Dissolved Phosphate. Ortho $(\mathrm{mg} / \mathrm{h})$

[^22]:    a. Parsmeter $=$ Total Phosphate. Ortho (mg/)

[^23]:    - Perameter $=$ Alunindy. Total. (man as CaCO3)

[^24]:    a. Permeter $=$ Carbonate Alnainity (mpl as CaCO3)

[^25]:    - Perameter $=$ Hydronde Allainity (moll es CaCO3)

[^26]:    a EVENT = CPR Runof Event :3

[^27]:    a EVENT = CPR Runof Event ${ }^{1 / 3}$

[^28]:    a EVENT = CPR Runof Evert *3

[^29]:    a EVENT = CPR Runof Event ${ }^{5}$

