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# Evaluation of a pilot-scale constructed wetland treatment system for ash basin water

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EVALUATION OF A PILOT-SCALE CONSTRUCTED WETLAND TREATMENT
SYSTEM FOR ASH BASIN WATER

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Presented to
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Lane Campbell Dorman
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# Abstract

This investigation examined the feasibility of using surface-flow constructed wetland treatment systems (CWTSs) to decrease the concentration and bioavailability of targeted constituents of concern (COC) in ash basin water. Ash basin water results from hydraulic transport (sluicing) of coal ash produced during thermoelectric power production. During the sluicing process, potentially toxic trace elements contained within coal ash may be transferred to the aqueous phase and subsequently introduced to aquatic receiving systems. COC in ash basin water were identified by a risk quotient method in order to determine biogeochemical conditions needed within wetland reactors for reducing the aqueous concentration and bioavailability of identified COC. Specific research objectives were: 1) characterize ash basin water from a risk-based perspective and identify COC; 2) evaluate pilot-scale CWTS performance for treating formulated ash basin water by measuring the concentration and bioavailability of COC in CWTS influent and effluent; 3) determine the effectiveness of using CWTSs to reduce reuse limiting parameters (scaling, biofouling, and corrosion); and 4) develop a mathematical model to describe the hydraulics of a pilot-scale reactor in a surface-flow CWTS.

Two pilot-scale CWTSs (i.e. series A and B) were designed to decrease concentrations of arsenic, chromium, mercury, selenium, and zinc through the following removal processes: precipitation as nonbioavailable sulfide minerals, co-precipitation with iron oxyhydroxides and sorption onto iron oxides. Concentrations of identified COC decreased as water moved through the wetland reactor series. In addition, the bioavailability of COC (evaluated by toxicity experiments) was successfully abated

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through treatment with the CWTSs. Treatment of simulated ash basin water by the CWTSs resulted in effluent concentrations of chromium, zinc, arsenic, selenium and mercury as low as 5.3, 4.8, 7.1, 37.3, 0.1 µg/L, respectively. Effluent concentrations of zinc, arsenic, and mercury were less than 120, 64, and 2 µg/L, respectively in all experiments. Effluent chromium concentrations were less than 11 µg/L in 2 of 9 experiments. The concentration of selenium in CWTS effluent was less than 50 µg/L in 3 of 9 experiments. Performance data suggest that removal of COC occurred in reactors designed to support dissimilatory sulfate reduction. Therefore, it is interpreted that removal of COC in these reactors occurred via precipitation as non-bioavailable sulfide minerals. Additionally, removal of chromium, arsenic, mercury, and zinc occurred in the oxidizing reactors. However, due to lower influent concentrations, less removal occurred in the oxidizing reactors than in the reducing reactors.

Biofouling in hydraulic transportation systems can reduce flow volume, thereby reducing efficiency. However, biofouling in series A and B effluent was 46 and 68%, respectively, less than biofouling in CWTS influent. Although, scale deposits on glass coupons indicate potential scale formation following treatment with CWTS, effluent scale formation was 80 and 40% less than influent scale formation for series A and B, respectively. Corrosion was not decreased in CWTS effluent as compared to influent.

The developed wetland flow and solute transport model simulated transport of a non-reactive tracer (bromide) in a pilot-scale reactor of a surface-flow constructed wetland treatment system. Two zones were identified with the solute transport model. The first zone is a relatively active flow region comprised of the main surface flow

channels (i.e. advective solute transport). The second zone is a no-flow (or relatively low flow) 'temporary storage' surface flow zone in which a solute may reside for a portion of time prior to re-entering the actively flowing region of the main surface flow channels. Because a maximum of 10% of CWTS influent entered the hydrosoil and the concentration of trace elements was decreased, the modeling study suggests that removal of trace elements by the surface-flow constructed wetland reactor occurred near the sediment water interface.

# Dedication

This thesis is dedicated to my wife, Anne. Your unwavering support made this possible.

# Acknowledgements

I would like to thank my advisor, Dr. Castle for his suggestions in preparing this thesis. I would like thank Dr. Rodgers for helping me to 'learn how to learn' and 'learn to manage my time wisely', I'm sure these concepts will be invaluable both in my professional and personal life. I'm grateful to Dr. Molz for always being available to help. I would like to thank Dr.Huddleston for providing insight into my research.

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# Chapter 1: Introduction

Lane C. Dorman and James W. Castle

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Thermoelectric power generation through combustion of coal converts chemical energy of coal into electrical energy (Woodruff *et al.*, 2004). Approximately one-half of the electricity generated in the United States results from coal combustion (EIA, 2006). Coal combustion wastes contain numerous trace elements such as arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, selenium, and zinc (Cherry and Guthrie, 1977; Walia and Mehra, 1998; Smith, 2003), all of which cause severe physiological effects to organisms exposed to certain elemental forms or species above tolerable concentrations (Chang, 1996). Coal combustion wastes include slag and bottom ash, fly ash, and flue gas desulfurization (FGD) scrubber sludge (Dvorak *et al.*, 1978). Fly ash is relatively fine grained and usually collected by a particulate control device. Bottom ash is coarser grained and falls from the combustion chamber into an ash hopper (Shorney, 1983). In 2005, combustion of coal in the United States produced 71.1 million short tons (64.5 million metric tons) of fly ash and 17.6 million short tons (16 million metric tons) of bottom ash (ACAA, 2006). Ash production will likely increase as power companies experience increased electricity demand due to development, economic growth, and human population increase. Current disposal techniques for fly and bottom ash include hydraulic transportation (sluicing) to a receiving basin followed by settling and removal to a landfill or removal for various reuse applications. These techniques provide minimal treatment of potentially toxic components. Toxic elements in ash may be transferred to the aqueous phase allowing introduction to aquatic receiving systems (Walia and Mehra, 1998). With the introduction of more stringent environmental laws, power companies are encountering increased disposal costs and growing environmental concerns.

Constructed wetland treatment systems (CWTSs) may provide a viable means of treating constituents of concern (COC) and increasing the reuse potential of ash basin waters. CWTSs are self-maintaining and provide a cost-effective alternative to traditional remediation approaches (LeDuc and Terry, 2005). Wetlands possess unique reactions not occurring in other aquatic or terrestrial systems. CWTS can be poised or buffered to ensure that desired reactions (transfers and transformations) affecting targeted constituents of concern proceed at predictable rates over long periods of time. Alternatives to treatment with a constructed wetland system, such as transportation to a water treatment facility, are not attractive due to high capital costs and continuing high costs associated with operation and maintenance (Bhamidimarri *et al.*, 1991). CWTS have been used to treat various wastewaters including municipal sewage wastes, industrial wastes, stormwater runoff, pulp and paper wastes, landfill leachates, and petroleum refinery wastes (Kadlec and Knight, 1996).

Research presented in this thesis addresses the potential use of CWTSs to treat ash basin water and has three major objectives: 1) characterize ash basin water and identify constituents of concern, 2) measure performance of a pilot-scale CWTS specifically designed to treat ash basin water, and 3) develop a mathematical model to simulate solute transport within a reactor of the pilot-scale CWTS.

The second chapter of this thesis focuses on characterizing ash basin water from a risk based perspective. The composition of ash basin water was determined by compiling data from publications and analyzing samples. The literature review included peer reviewed and non-peer reviewed publications. Chemical analyses were performed on 18 ash basin water samples. Concentrations of the following trace and major elements were

determined by inductively coupled plasma mass spectrometry (ICP-MS) according to USEPA method 200.8: Al, As, Ag, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn. Mercury analyses were conducted by cold vapor atomic absorption spectrometry (CVAAS) according to USEPA method 245.1. In addition to the trace and major element concentrations, general water chemistry parameters for six ash basin water samples were measured. Data collected (i.e. measured) in the characterization of ash basin water are included in the appendix.

The third chapter of this thesis focuses on the treatment effectiveness of specifically designed pilot-scale CWTSs. Determination of treatment effectiveness encompassed analytical, toxicological, and reuse parameters. Analytical techniques were used to assess the reduction in concentration of arsenic, chromium, mercury, selenium, and zinc (i.e. identified constituents of concern) in CWTS effluent. Toxicity experiments with CWTS influent and effluent identified the presence (or absence) of any unanticipated deleterious constituents and provided data concerning the bioavailability of COC. Due to stressed water resources, reuse of water traditionally considered wastewater has become an important alternative. Since reuse of ash basin water has the potential to reduce industrial water requirements, an investigation into the use of CWTSs to reduce reuse limiting parameters, such as scaling, biofouling, and corrosion was performed. Data collected in the performance evaluation are included in the appendix.

The fourth chapter of this thesis focuses on the development of a mathematical model to describe the hydraulics and hydrology of a portion of the pilot-scale surface-flow CWTS. A tracer test was performed on reactor A1 of the CWTS. Effluent samples

were collected over time and analyzed for tracer concentration. Data collected in the analysis of effluent samples are included in the appendix.

1.1    Organization of this thesis

This thesis is comprised of five chapters including the Introduction (Chapter 1) and the Summary and Conclusions (Chapter 5). The body of this thesis consists of three chapters formatted as independent manuscripts for submittal to scientific journals for peer review and publication. For this reason, some material may be repeated. The manuscripts and their targeted journals are:

Chapter 2: Characterization of ash basin water from a risk based perspective, prepared for submission to *Water, Air, and Soil Pollution.*

Chapter 3: Performance of a specifically designed pilot-scale constructed wetland treatment system for the remediation of simulated ash basin water, prepared for submission to *Bioresource Technology.*

Chapter 4: Development of a mathematical model for constructed wetland treatment system hydrology, prepared for submission to *Environmental Modeling & Assessment.*

Collectively, these manuscripts provide a knowledge base for the physicochemical characteristics of ash basin water, provide a treatment technique for ash basin water, and increase the understanding of solute transport within surface flow CWTSs.

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# Chapter 2: Characterization of Ash Basin Water from a Risk-Based Perspective

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2.1   <u>Abstract</u>

Historically, coal ash produced during thermoelectric power generation has been hydraulically transported (sluiced) to onsite ash ponds. Ash ponds provide minimal treatment (i.e. particulate settling) of potentially toxic components in ash basin water. Risks associated with introduction of ash basin water to aquatic receiving systems have not been thoroughly assessed. The purpose of this investigation is to characterize ash basin water by literature review and sample analysis and identify constituents of concern from a risk-based perspective. Ash basin water samples were collected from coal-fired power plants in the United States and analyzed for trace element concentrations and general water chemistry. A risk quotient method was utilized to identify constituents of concern in ash basin water. Identified constituents of concern in ash basin water include: aluminum, cadmium, chromium, copper, iron, lead, mercury, selenium, zinc, and pH. Ash basins for treating sluice water are rudimentary treatment systems, and often more effective treatment is required to decrease risk to receiving system biota.

2.2    Introduction

Thermoelectric power generation through combustion of coal converts chemical energy of coal into electrical energy (Woodruff *et al.*, 2004). Approximately one-half of the electricity generated in the United States results from coal combustion (EIA, 2006). Coal combustion wastes contain numerous trace elements such as arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, selenium, and zinc (Cherry and Guthrie, 1977; Walia and Mehra, 1998; Smith, 2003), all of which can cause severe physiological effects to organisms exposed to certain elemental forms or species above tolerable concentrations (Chang, 1996). Coal combustion wastes include slag and bottom ash, fly ash, and flue gas desulfurization (FGD) scrubber sludge (Dvorak *et al.*, 1978). Combustion of large quantities of coal generates copious volumes of ash, which may contain the aforementioned trace elements. Fly ash is relatively fine grained and usually collected by a particulate control device. Bottom ash is coarser grained and falls from the combustion chamber into an ash hopper (Shorney, 1983). In 2005, combustion of coal in the United States produced 71.1 million short tons (64.5 million metric tons) of fly ash and 17.6 million short tons (16 million metric tons) of bottom ash (ACAA, 2006). Ash production will likely increase as power companies experience increased electricity demand due to development, economic growth, and human population increase. Current disposal techniques for fly and bottom ash include hydraulic transportation (sluicing) to a receiving basin followed by settling and removal to a landfill or removal for various reuse applications. These techniques provide minimal treatment of potentially toxic components. Toxic elements in ash may be transferred to the aqueous phase allowing

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introduction to aquatic receiving systems (Walia and Mehra, 1998). With the introduction of more stringent environmental laws, power companies are encountering increased disposal costs and growing environmental concerns.

The purpose of this investigation was to determine the composition of ash basin water and risks that these waters may pose to aquatic receiving systems. Ash basin water contain concentrations of constituents (metals, metalloids, and total dissolved solids) in excess of National Pollutant Discharge Elimination System (NPDES) Clean Water Act discharge limits (Walia and Mehra, 1998). In addition, ash basin water contains constituents that limit reuse options (Chu and Ruane, 1978). Specific objectives of our study were to: 1) characterize ash basin water through a literature review, 2) chemically analyze ash basin water samples, and 3) use a risk-based approach to identify constituents of concern that may restrict surface discharge or reuse of ash basin water.

2.3     Materials and Methods

*2.3.1 Characterization of Ash Basin Water*

The composition of ash basin water was determined by compiling data from publications and analyzing samples of ash basin water. Data collected were analyzed using statistical software included with Microsoft Excel 2003©. This analysis included the number of values reported and the concentration minimum, maximum, mean, and standard deviation.

*2.3.1.1   Literature Review of Ash Basin Water Composition*

The literature review included peer reviewed and non-peer reviewed publications. Non-peer reviewed publications include government, academic, business, and industry

reports. Composition data from ash basin effluent and ash basin water supernatant were included in characterization of ash basin water. Ash basin supernatant was included in the analyses because it is likely that water with similar characteristics will discharge from ash basins. Data from fly ash basins and bottom ash basins were considered separately. Most coal fired power plants combine these waste streams into a single basin (Chu and Ruane, 1978; Rowe *et al.*, 2002). However, when data were provided for separate fly ash and bottom ash waste streams, we assumed separate ash basins for analysis purposes.

*2.3.1.2   Chemical Analysis of Ash Basin Water Samples*

Chemical analyses were performed on 18 ash basin water samples. Samples were collected in clean Nalgene® high density polyethylene (HDPE) bottles according to standard field sampling practices, placed on ice, and transported to the laboratory for analysis. Fourteen samples were collected from a coal-fired power plant in New Mexico and four samples were collected from two coal-fired power plants in North Carolina. Concentrations of the following trace and major elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) according to USEPA method 200.8: Al, As, Ag, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn. Mercury analyses were conducted by cold vapor atomic absorption spectrometry (CVAAS) according to USEPA method 245.1.

General water chemistry parameters for six ash basin water samples were measured. The samples were analyzed for pH, alkalinity, hardness, electrical conductivity (EC), dissolved oxygen (DO), sulfates, chlorides, and chemical oxygen demand (Table 2-1).

Table 2-1. Methods for determination of general water chemistry.

| Parameter | Method | MDL[1] |
|---|---|---|
| Temperature | Direct Instrumentation: YSI Model 52 | 0.5 °C |
| pH | Direct Instrumentation: Orion Model 420A | 0.01 |
| Conductivity | Direct Instrumentation: YSI Model 30 | 0.1 $\mu$S cm$^{-1}$ |
| Alkalinity | Standard Methods: 2320 B (Clesceri *et al.*, 1999) | 2 mg L$^{-1}$ as CaCO3 |
| Hardness | Standard Methods: 2340 C (Clesceri *et al.*, 1999) | 2 mg L-1 as CaCO3 |
| DO[2] | Direct Instrumentation: YSI Model 52 | 0.1 mg L$^{-1}$ |
| COD[3] | Closed reflux colorimetry (HACH- modified from Standard Methods: 5220 D) (Clesceri *et al.*, 1999) | 3 mg L$^{-1}$ |
| | High: HACH Drop Count Titration Method | 500 mg L$^{-1}$ |
| Chloride | Low: HACH colorimetric method 8207 | 25 mg L$^{-1}$ |
| Sulfate | Standard Methods: 4500 E (Clesceri *et al.*, 1999) | 1 mg L$^{-1}$ |

[1] Method Detection Limit
[2] Dissolved Oxygen
[3] Chemical Oxygen Demand

*2.3.2 Identification of Constituents of Concern by Risk Analysis*

Constituents of concern (COC) in ash basin water are those properties, elements, or compounds that pose risk to aquatic receiving system biota. These constituents were identified using the risk quotient (RQ) method (USEPA, 1992; Peterson, 2006) or by comparison of a toxic effects concentration to an environmental exposure concentration.

RQ is defined as the ratio of an environmental exposure concentration to a toxicity end point (equation 2.1).

$$RQ = \frac{EE}{LC_{50},\ EC_{50},\ NOEC,\ or\ LOEC} \tag{2.1}$$

where:   EE is the environmental exposure concentration (defined as the concentration of a constituent, present in ash basin water, to which organisms may be exposed);

$LC_{50}$ is the concentration of a material in water that causes 50% mortality in a test population within a specified time period;

$EC_{50}$ is the aqueous concentration effective in producing a sublethal response in 50% of test organisms;

NOEC (no observed effects concentration) is the highest concentration of a constituent that has no statistically significant adverse effect on an exposed population of test organisms compared with the controls; and

LOEC (lowest observed effects concentration) is the lowest concentration of a constituent that has a statistically significant adverse effect on the exposed population of test organisms compared with the controls.

Toxicity endpoints of sentinel species (e.g., *Ceriodaphnia dubia*, *Daphnia magna*, etc.) are used in the RQ calculation to assess risks to receiving system biota. The RQ method compares a calculated RQ to a predefined level of concern (LOC). The LOC depends on the toxicity endpoint (i.e. acute or chronic) utilized in the RQ calculation and the species for which risk is being assessed (USEPA, 2004). Acute toxicity endpoints, $LC_{50}$ and $EC_{50}$, employ a RQ of 0.5, while chronic toxicity endpoints, NOEC and LOEC, employ a RQ of 1. Accordingly, endangered species will have lower LOC values than species without this designation. When the RQ is equal to or greater than the LOC (USEPA, 2004), risk to receiving system biota is anticipated (equation 2.2).

$$RQ \geq LOC \Rightarrow \text{Potential risk to receiving system biota} \qquad (2.2)$$

Constituents in ash basin water that may be toxic but did not have sufficient toxicity data available (i.e. no values for $LC_{50}$, $EC_{50}$, NOEC, or LOEC are available) for the RQ calculation were identified as a constituent of concern by comparing the environmental exposure concentration to the toxic effects concentration published in

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Quality Criteria for Water 1986 (USEPA, 1986). The chronic toxicity to freshwater

aquatic life criterion (USEPA, 1986) was used as the toxicity endpoint in the RQ

calculation for constituents with insufficient toxicity data. The LOC value employed for

instances of insufficient toxicity data was 1. This LOC value corresponds to the LOC

used for chronic toxicity endpoints.

The maximum observed concentration of ash basin water constituents was used as

the environmental exposure concentration in the RQ calculation. While this approach

may seem conservative it should be realized that ash basins 'treat' sluice water by

dilution and homogenization. Since ash basin effluent concentrations are controlled by

ash basin volume, a smaller ash basin will result in higher effluent concentrations. An

additional measure of risks associated with ash basin water was gained by comparing

concentrations of identified constituents of concern to USEPA water quality criteria

(USEPA, 2006).

2.4    Results and Discussion

*2.4.1 Literature Review of Ash Basin Water Composition*

Results for general water chemistry parameters of ash basin water (Table 2-2)

include: pH, alkalinity, hardness, EC, dissolved solids, suspended solids, and sulfate

concentration. Limited data are available on temperature and dissolved oxygen. Data

collected in previous studies from 22 coal fired power plants reveal numerous potentially

toxic constituents in ash basin water (Table 2-3). The concentrations of trace and major

elements in such waters vary widely from site to site.

Table 2-2. Literature reported ash basin general water chemistry.

| Water Quality Parameter | Range[a,b,c,d,e] | | Mean[a] | Mean[b] | Mean[c] | Range[d] | Mean[e] |
|---|---|---|---|---|---|---|---|
| | Min | Max | n = 15 | n = 21 | n = 63 | n = 6 | n = 2 |
| pH (S.U.) | 4.2 | 11.2 | 8.7 [2] | 6.7 [0.38] | 6.8 [0.3] | 7.1 - 8 | 6.9 |
| Alkalinity (mg $L^{-1}$ as $CaCO_3$) | 8.5 | 141 | 75.4 [31] | 8.5 [3.1] | 8.5 [3.1] | 14 - 21 | NR |
| Hardness (mg $L^{-1}$ as $CaCO_3$) | 93 | 329 | 195 [81] | NR | NR | NR | NR |
| Conductivity ($\mu S\ cm^{-1}$) | 40 | 915 | 501 [232] | 109 [29] | NR | 40 - 180 | NR |
| Dissolved solids (mg $L^{-1}$) | 136 | 524 | 287 [124] | NR | NR | NR | NR |
| Suspended solids (mg $L^{-1}$) | 3.1 | 71 | 33 [19] | 4.4 [3.1] | 3.1 [2.3] | NR | NR |
| Temperature (°C) | 12.2 | 33 | NR | 19.7 [7.6] | NR | 12.2 - 33 | 25.1 |
| Dissolved Oxygen (mg $L^{-1}$) | 6.1 | 9.6 | NR | 9.6 [2.14] | NR | 6.1 - 9.5 | 8.6 |
| Sulfate (mg $L^{-1}$) | 45 | 346 | 131.4 [76] | NR | NR | NR | NR |

[a] USEPA (1980)
[b] Newman *et al.* (1985)
[c] Alberts *et. al.* (1985)
[d] Guthrie and Cherry (1976)
[e] Larrick *et al.* (1981)
Bracketed values represent one standard deviation from the mean
n = number of samples analyzed
NR = not reported

Table 2-3. Literature reported trace and major element concentration range (Min and Max), mean, standard deviation (S.D.), and number of samples analyzed (n) in ash basin water.

| Element | Min (mg L$^{-1}$) | Max (mg L$^{-1}$) | Mean (mg L$^{-1}$) | S.D. (mg L$^{-1}$) | n |
|---|---|---|---|---|---|
| Aluminum[a,e,f] | 1.40 | 20.86 | 4.58 | 6.24 | 17 |
| Antimony[f] | 0.08 | 0.08 | 0.08 | N/A | 1 |
| Arsenic[a,b,c,d,e,f,g] | 0.000027 | 0.25 | 0.06 | 0.07 | 24 |
| Barium[b,e,f] | 0.10 | 0.98 | 0.3 | 0.3 | 17 |
| Beryllium[d,e] | 0.00000020[1] | 0.010 | 0.01[2] | 0.002 | 16 |
| Boron[d] | 0.012 | 0.012 | 0.012 | N/A | 1 |
| Bromine[b,f] | 0.14 | 0.16 | 0.15 | 0.014 | 2 |
| Cadmium[a,b,c,d,e,f] | 0.0000010 | 0.17 | 0.02 | 0.05 | 20 |
| Calcium[b,e,f] | 9.28 | 152.0 | 66.82 | 41.61 | 17 |
| Cesium[b,f] | 0.020 | 0.030 | 0.03 | 0.01 | 2 |
| Chloride[b,e,f,] | 3.0 | 14.0 | 6.8 | 3.0 | 17 |
| Chromium[a,b,c,d,e,f] | 0.0000020 | 0.18 | 0.04 | 0.06 | 20 |
| Cobalt[a,b,c,f] | 0.00066 | 0.080 | 0.05 | 0.04 | 4 |
| Copper[a,b,c,d,e,f] | 0.0000030 | 0.56 | 0.1 | 0.2 | 20 |
| Iron[a,b,e,f] | 0.053 | 21.62 | 3.69 | 6.20 | 18 |
| Lead[a,e] | 0.00033 | 0.066 | 0.018 | 0.014 | 16 |
| Magnesium[b,e,f] | 0.30 | 14.0 | 5.5 | 3.7 | 17 |
| Manganese[a,b,c,e,f] | 0.010 | 0.49 | 0.1 | 0.1 | 19 |
| Mercury[b,c,e,f] | 0.00020 | 0.040 | 0.01 | 0.01 | 18 |
| Molybdenum[a,d] | 0.00017 | 0.085 | 0.04 | 0.06 | 2 |
| Nickel[a,e] | 0.0056 | 0.080 | 0.05 | 0.01 | 16 |
| Potassium[b] | 8.39 | 8.39 | 8.4 | N/A | 1 |
| Selenium[a,b,c,d,e,f,g] | 0.000057 | 0.24 | 0.07 | 0.08 | 26 |
| Silver[e] | 0.010[1] | 0.010[1] | 0.010[2] | N/A | 15 |
| Sodium[b,f] | 7.66 | 8.84 | 8.3 | 0.8 | 2 |
| Strontium[b] | 0.42 | 0.42 | 0.4 | N/A | 1 |
| Tin[b] | 0.15 | 0.15 | 0.2 | N/A | 1 |
| Titanium[b,c,f] | 0.98 | 1.35 | 1.2 | 0.2 | 3 |
| Vanadium[d] | 0.00013 | 0.00013 | 0.0001 | N/A | 1 |
| Zinc[a,b,c,d,e,f] | 0.00044 | 1.40 | 0.2 | 0.3 | 20 |

[1] Minimum detection limit.
[2] Mean calculated using minimum detection limits as values for samples with concentrations below detection limits.
[a] Evans and Horton (1980)
[b] Rodgers *et al.*, (1978)
[c] Cherry and Guthrie (1977)
[d] Dreesen *et al.* (1977)
[e] USEPA (1980)
[f] Cherry *et al.* (1979)
[g] Cumbie (1978)
N/A = not applicable

*2.4.2 Chemical Analysis of Ash Basin Water Samples*

Average general water chemistry parameters for ash basin water samples analyzed (Table 2-4) were within literature reported ranges, with the exception of hardness, which was below the minimum range of literature reported values. Concentrations of trace and major elements in ash basin water samples analyzed are listed in Table 2-5.

Table 2-4. General water chemistry of ash basin water samples analyzed in this study.

| Constituent | Mean | S.D. | n |
|---|---|---|---|
| Temperature[†] (°C) | 24.2 | 0.8 | 3 |
| Dissolved Oxygen (mg $L^{-1}$) | 8.4 | 0.4 | 3 |
| pH (S.U.) | 6.7 | 0.2 | 6 |
| Conductivity (µS $cm^{-1}$) | 161 | 35 | 6 |
| Hardness (mg $L^{-1}$ as $CaCO_3$) | 43 | 14 | 6 |
| Alkalinity (mg $L^{-1}$ as $CaCO_3$) | 13 | 7.8 | 6 |
| COD[1] (mg $L^{-1}$) | 15 | N/A | 1 |
| Sulfate (mg $L^{-1}$) | 51.4 | N/A | 1 |

[†] = Sample temperature at time of analysis; not indicative of effluent temperature at time of sampling
[1] = Chemical Oxygen Demand
S.D. = standard deviation
n = number of samples analyzed
N/A = not applicable

Table 2-5. Trace and major element concentration range (Min and Max), mean concentration (Mean), standard deviation (S.D.), and number of ash basin water samples (n) analyzed in this study.

| Element | Min (mg L$^{-1}$) | Max (mg L$^{-1}$) | Mean (mg L$^{-1}$) | S.D. (mg L$^{-1}$) | n |
|---|---|---|---|---|---|
| Aluminum | 0.062 | 6.62 | 1.13 | 1.92 | 16 |
| Antimony | 0.0050[1] | 0.019 | 0.008[2] | 0.0050 | 16 |
| Arsenic | 0.013 | 0.25 | 0.04 | 0.057 | 16 |
| Barium | 0.026 | 1.60 | 0.25 | 0.36 | 16 |
| Beryllium | 0.0010[1] | 0.022 | 0.002[2] | 0.005 | 16 |
| Cadmium | 0.0020[1] | 0.0020 | 0.0020[2] | N/A | 16 |
| Calcium | 13.7 | 37.6 | 18.3 | 6.0 | 16 |
| Chloride | 109 | 119 | 114 | 7 | 2 |
| Chromium | 0.0050[1] | 0.11 | 0.01[2] | 0.026 | 16 |
| Cobalt | 0.020[1] | 0.075 | 0.023[2] | 0.014 | 16 |
| Copper | 0.010[1] | 0.23 | 0.02[2] | 0.06 | 16 |
| Iron | 0.020 | 27.2 | 2.2 | 6.8 | 16 |
| Lead | 0.0020[1] | 0.12 | 0.01[2] | 0.03 | 16 |
| Magnesium | 4.8 | 5.0 | 4.9 | 0.1 | 2 |
| Manganese | 0.010[1] | 7.0 | 0.5[2] | 1.7 | 16 |
| Mercury | 0.00020[1] | 0.00032 | 0.00021[2] | 0.00003 | 16 |
| Nickel | 0.010[1] | 0.15 | 0.02[2] | 0.03 | 16 |
| Potassium | 11.7 | 11.8 | 11.8 | 0.1 | 2 |
| Selenium | 0.0070 | 0.069 | 0.022 | 0.023 | 16 |
| Silver | 0.0050[1] | 0.0050 | 0.0050[2] | N/A | 16 |
| Sodium | 14.6 | 32.8 | 19.4 | 5.3 | 16 |
| Thallium | 0.0020[1] | 0.0048 | 0.0020[2] | 0.0007 | 16 |
| Tin | 0.010[1] | 0.010 | 0.010[2] | N/A | 2 |
| Vanadium | 0.021 | 0.051 | 0.035 | 0.013 | 16 |
| Zinc | 0.010 | 0.099 | 0.027 | 0.023 | 16 |

[1] Minimum detection limit.
[2] Mean calculated using minimum detection limits as values for samples with concentrations below detection limits.
N/A = not applicable

*2.4.3 Identification of Constituents of Concern*

The greater of the two maximum values (i.e. literature reported or analyzed sample) was used for identification of constituents of concern in ash basin water (Table 2-6).

Table 2-6. Maximum literature reported concentration (Max Literature), maximum measured concentration in this study (Max Sample), associated toxicity endpoints (NOEC, $LC_{50}$ or $EC_{50}$, and USEPA QCW), risk quotients (RQ) (calculated from the greater of the two maximum concentrations), level of concern (LOC) values, and constituents of concern (COC). Constituents are identified as COC if the RQ exceeds the LOC.

| Constituent | Max Literature (mg $L^{-1}$) | Max Sample (mg $L^{-1}$) | NOEC (mg $L^{-1}$) | $LC_{50}$ or $EC_{50}$ (mg $L^{-1}$) | USEPA QCW (mg $L^{-1}$) | RQ | LOC | COC |
|---|---|---|---|---|---|---|---|---|
| Aluminum | 20.86 | 6.62 | | 2.880[a] | | 7.24 | 0.5 | Yes |
| Antimony | 0.08 | 0.019 | | | 1.600[q] | 0.05 | 1 | No |
| Arsenic | 0.25 | 0.25 | | 1.42[n] | | 0.18 | 0.5 | No |
| Barium | 0.98 | 1.60 | | 13.500[b] | | 0.12 | 0.5 | No |
| Beryllium | 0.010 | 0.022 | 0.25[m] | | | 0.09 | 1 | No |
| Boron | 0.012 | N/A | 10.0[c] | | | 0.00 | 1 | No |
| Bromine | 0.16 | N/A | 0.46[m] | | | 0.35 | 1 | No |
| Cadmium | 0.17 | 0.0020 | 0.01[d] | | | 17.00 | 1 | Yes |
| Calcium | 152.0 | 37.6 | | 499[e] | | 0.30 | 0.5 | No |
| Cesium | 0.030 | N/A | | 7.4[p] | | 0.00 | 0.5 | No |
| Chloride | 14.0 | 119 | 1296[f] | | | 0.09 | 1 | No |
| Chromium | 0.18 | 0.11 | 0.010[c‡] | | | 18.00 | 1 | Yes |
| Cobalt | 0.080 | 0.075 | | 1.620[b] | | 0.05 | 0.5 | No |
| Copper | 0.56 | 0.23 | 0.0037[g] | | | 151.35 | 1 | Yes |
| Iron | 21.62 | 27.2 | | 9.600[b] | | 2.83 | 0.5 | Yes |
| Lead | 0.066 | 0.12 | 0.0051[h] | | | 2.35 | 1 | Yes |
| Magnesium | 14.0 | 5.0 | | 322[b] | | 0.04 | 0.5 | No |
| Manganese | 0.49 | 7.0 | | 14.5[i] | | 0.48 | 0.5 | No |
| Mercury | 0.040 | 0.00032 | | 0.005[b] | | 8.00 | 0.5 | Yes |
| Molybdenum | 0.085 | N/A | | 79.7[n†] | | 0.00 | 0.5 | No |
| Nickel | 0.080 | 0.15 | | 1.120[b] | | 0.13 | 0.5 | No |
| Potassium | 8.39 | 11.8 | | 166.0[b] | | 0.07 | 0.5 | No |
| Selenium | 0.24 | 0.069 | 0.085[j] | | | 2.82 | 1 | Yes |
| Silver | 0.010 | 0.0050 | 0.00053[k] | | | 18.87 | 1 | Yes |
| Sodium | 8.84 | 32.8 | | 1820[b] | | 0.02 | 0.5 | No |
| Strontium | 0.42 | N/A | | 125[b] | | 0.00 | 0.5 | No |
| Thallium | N/A | 0.0048 | | | | 0.12 | 1 | No |
| Tin | 0.15 | 0.010 | | 55[b] | | 0.00 | 0.5 | No |
| Titanium | 1.35 | N/A | | 1000[o] | | 0.00 | 0.5 | No |
| Vanadium | 0.00013 | 0.051 | 0.940[o] | | | 0.11 | 1 | No |
| Zinc | 1.40 | 0.099 | 0.116[r] | | | 12.07 | 1 | Yes |

NOEC = no observed effects concentration
QCW = quality criteria for water
[‡] LOEC = lowest observed effects concentration
[†] $IC_{50}$ = reproductive inhibition of 50%
N/A = not available

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[a] Soucek *et al.* (2001)    [g] Suedel *et al.* (1996)    [m] LeBlanc  (1980)
[b] Biesinger and Christensen (1972)    [h] Jop *et al.* (1995)    [n] Naddy *et al.* (1995)
[c] Hickey (1989)    [i] Lasier *et al.* (2000)    [o] USEPA (2007)
[d] Suedel *et al.* (1997)    [j] Ingersoll *et al.* (1990)    [p] Baudouin and Scoppa (1974)
[e] Goodfellow *et al.* (2000)    [k] Rodgers *et al.*, (1997)    [q] USEPA (1986)
[f] Cowgill and Milazzo (1990)    [l] Soucek and Kennedy, (2005)    [r] unpublished data (2007)

Constituents of concern (Table 2-6) are those constituents having a RQ value greater than

the LOC value (equation 2.2). These constituents include aluminum, cadmium,

chromium, copper, iron, lead, mercury, selenium, and zinc. While silver is indicated as a

constituent of concern using the RQ method, it is not included in the list of COC because

each investigator reported the concentration of silver as less than the detection limit of the

analytical method used.

In addition to COC identified using the RQ method, other properties (or

measures) of ash basin effluents may cause toxicity. These properties include pH, total

dissolved solids (TDS), total suspended solids (TSS), EC, hardness, alkalinity,

temperature, and dissolved oxygen (DO). Due to potential toxicity resulting from either

an abundance or paucity, these properties were not classified using the RQ method. The

observed pH range for ash basin water was 4.2 – 11.2. This range is greater than the

range of 6.14 – 8.99 shown to cause neither reproductive nor survival impairment of the

cladoceran *C. dubia* (Belanger and Cherry, 1990). Therefore, pH is a potential constituent

of concern. The micro-crustacean *C. dubia* is accepted as a representative organism for

evaluation of the toxicity of effluents and receiving waters containing potentially toxic

materials (USEPA, 2002b). The potential toxicity of TDS, TSS, and EC are dependent on

the specific combination of ions contained within the water column. Consequently, TDS,

TSS, and EC are not adequate predictors of toxicity (Chapman *et al.*, 2000; Goodfellow

*et al.*, 2000). Accordingly, classification of these properties as COC was not appropriate.

Hardness is the concentration of divalent metallic ions, primarily calcium and magnesium, in solution. Hardness concentrations up to 638 mg/L as $CaCO_3$ have no observed effect on *C. dubia* (Cowgill and Milazzo, 1990). The maximum hardness observed in ash basin water was 329 mg/L as $CaCO_3$. Therefore, hardness is not considered a constituent of concern in ash basin water. Alkalinity, which is the concentration of constituents that elevate pH above approximately 4.5 (USEPA, 1976, 1986; Tchobanoglous *et al.*, 2003), may cause toxicity at concentrations less than 20 mg/L as $CaCO_3$ (USEPA, 1976, 1986). The minimum alkalinity observed in ash basin water was 93 mg/L as $CaCO_3$, well above the minimum concentration of 20 mg/L as $CaCO_3$. For this reason alkalinity should not be considered a constituent of concern. Temperatures of ash basin effluents range from 12.2 – 33 °C (Guthrie and Cherry, 1976). The upper limit of this range, which is influenced by coal fired power plant discharge, corresponds to normal stream temperatures observed in the southeastern United States (Mohseni *et al.*, 2002). Therefore, the temperature of ash basin effluents is not considered a constituent of concern. DO is a measure of the concentration of gaseous diatomic oxygen dissolved in the water column. DO concentrations less than 4.0 mg/L may have deleterious effects on aquatic biota (USEPA, 1986, 2002b). However, the minimum observed DO concentration in ash basin water was 6.1 mg/L, above the 4.0 mg/L deleterious effects threshold. Since the DO concentration is in excess of the concentration at which adverse effects are expected, this parameter is not considered a constituent of concern in ash basin water.

Other studies have examined the concentrations of trace and major elements in ash basin water, however, risks to aquatic receiving system biota were assumed on a qualitative basis (Coutant *et al.*, 1978; Evans and Giesy, 1978; Larrick *et al.*, 1981). Although constituents have been reported in ash basin water similar to those reported in this study, risks associated with this water have not been previously determined. The present study applied a quantitative method to determine constituents of concern in ash basin water and the risks associated with each constituent. This quantitative analysis of risks identifies the most problematic constituents and provides a basis for the development of remediation strategies. The results can be used to assess potential effects on aquatic biota as a consequence of exposure to ash basin effluents.

Certain identified constituents of concern present a greater problem to aquatic receiving system biota than other constituents. The mean concentration from combined data sets (literature and analyzed samples) revealed concentrations of the following elements to be greater than USEPA's freshwater criterion for a continuous concentration (FWCCC) (USEPA, 2006): aluminum, cadmium, chromium (form dependent), copper, iron, lead, mercury, and selenium (Table 2-7). Additionally, the pH range of ash basin water was greater than USEPA FWCCC. These constituents are consistently detected in ash basin effluents in concentrations greater than USEPA FWCCC (Cherry and Guthrie, 1977; Cherry *et al.*, 1984; Reash, 2004).

Table 2-7. Mean observed concentration of identified constituents of concern (COC) in ash basin water greater than USEPA freshwater criterion for a continuous concentration (FWCCC).

| Element | Mean (mg L$^{-1}$) | USEPA FWCCC (mg L$^{-1}$) |
|---|---|---|
| Aluminum | 2.9 | 0.087 |
| Cadmium | 0.013 | 0.00025 |
| Chromium | 0.025 | 0.074[a] or 0.011[b] |
| Copper | 0.078 | 0.009 |
| Iron | 3 | 1 |
| Lead | 0.014 | 0.0025 |
| Mercury | 0.004 | 0.00077 |
| Selenium | 0.045 | 0.005 |

[a] Chromium (III)
[b] Chromium (VI)

### 2.4.4 Identification of Reuse Limiters

Ash basin water may be reused within the power plant (e.g., resluicing ash) or for other purposes (e.g., stream flow augmentation or irrigation). However, reuse of these waters for irrigation or stream flow augmentation may require a decrease in concentration of identified COC to prevent toxicity to biota. Reuse options within the power plant may require decreasing concentrations of scale forming constituents (calcium, magnesium, silica, and sulfate) and corrosion promoters (primarily acidic pH) (Chu and Ruane, 1978). Additionally, biofouling may contribute to buildup of material on hydraulic transport systems, thereby reducing transport efficiency.

### 2.5   Conclusions

The results of this study identify potential risks associated with ash basin water and the need for efficient and effective remediation strategies. Constituents of concern in ash basin water were identified by the risk quotient method or by comparing an

environmental exposure concentration to the toxic effects concentration published by

USEPA (1986). Constituents of concern identified by the risk quotient method include:

aluminum, cadmium, chromium, copper, iron, lead, mercury, selenium, zinc, and pH.

Constituents of greatest concern due to mean concentrations being greater than USEPA

FWCCC (USEPA, 2006) are aluminum, cadmium, chromium (form dependent), copper,

iron, lead, mercury, and selenium. Also, the pH range of ash basin water is not within the

range suggested by USEPA FWCCC. The identification of these constituents of concern

necessitates development of efficient and effective treatment techniques for ash basin

effluents.

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# Chapter 3: Performance of a Specifically Designed Pilot-Scale Constructed Wetland Treatment System for Ash Basin Water

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3.1 <u>Abstract</u>

In order to assess the role of a constructed wetland treatment system (CWTS) in the reuse of ash basin water, a pilot-scale system was designed to decrease concentration and toxicity of identified constituents of concern (COC) by precipitation as non-bioavailable sulfides, co-precipitation with iron oxyhydroxides, and adsorption onto iron oxides. Effective reduction of COC concentrations to less than USEPA recommended water quality criteria was accomplished. The concentration of chromium in CWTS effluent was less than 11 μg/L in 4 of 18 experiments. Zinc concentrations in CWTS effluent were less than 120 μg/L in all 18 experiments. CWTS effluent concentrations of arsenic were less than 64 μg/L in all 18 experiments. Selenium concentrations in CWTS effluent were less than 50 μg/L in 3 of 18 experiments. Mercury concentrations in CWTS effluent were less than 2 μg/L in all 12 experiments with mercury. The removal efficiency (defined as the percent concentration decrease from influent to effluent) was observed to be dependent on the influent constituent of concern concentration, while the extent of removal (defined as the concentration of a constituent of concern in effluent) was observed to be independent of the influent constituent of concern concentration. Toxicity experiments showed that the CWTS removed toxicity of influent with regard to survival in all 10 experiments. In 4 of 10 experiments the CWTS removed influent toxicity with regard to reproduction. Additionally, a reduction in the potential for scale formation and biofouling was achieved through treatment with the pilot-scale CWTS. Results suggest that specifically designed CWTSs will decrease the concentration and toxicity of COC and reduce reuse limiting parameters.

3.2     Introduction

Thermoelectric power generation through combustion of coal converts chemical energy into electrical energy (Woodruff *et al.*, 2004). Approximately one-half of the electricity generated in the United States results from coal combustion (EIA, 2006). Coal combustion wastes contain numerous trace elements such as arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, selenium, and zinc (Cherry and Guthrie, 1977; Walia and Mehra, 1998; Smith, 2003), all of which cause severe physiological effects to organisms exposed to certain elemental forms or species above tolerable concentrations (Chang, 1996). Coal combustion wastes include slag and bottom ash, fly ash, and flue gas desulfurization (FGD) scrubber sludge (Dvorak *et al.*, 1978). Fly ash is fine grained and usually collected by a particulate control device. Bottom ash is coarser grained and falls from the combustion chamber into an ash hopper (Shorney, 1983). In 2005, combustion of coal in the United States produced 71.1 million short tons of fly ash and 17.6 million short tons of bottom ash (ACAA, 2006). Ash production will likely increase as power companies experience escalating electricity demands due to development, economic growth, and increased human population. Current disposal techniques for fly and bottom ash include hydraulic transportation (sluicing) to a receiving basin followed by settling and subsequent disposal in a landfill or removal for various reuse applications. These techniques provide minimal treatment of potentially toxic components. Toxic elements in ash, transferred to the aqueous phase, may be introduced to aquatic receiving systems (Walia and Mehra, 1998). Power companies are encountering increased disposal costs and growing environmental concerns.

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Constructed wetland treatment systems (CWTSs) may provide a viable means of removing constituents of concern (COC) and reuse limiters from ash basin water. CWTSs are self-maintaining and provide a cost-effective alternative to traditional remediation approaches (LeDuc and Terry, 2005). Alternatives to treatment with a constructed wetland system, such as transportation to a water treatment facility, are not attractive due to high capital costs and continuing high costs associated with operation and maintenance (Bhamidimarri *et al.*, 1991).

Based upon previous CWTSs designed to treat targeted constituents, such as those in ash basin water, sediments in CWTSs are likely repositories for precipitated or settled COC (Ye *et al.*, 2003; LeDuc and Terry, 2005; Murray-Gulde *et al.*, 2005a). Many targeted constituents precipitate as sulfide minerals (Webb *et al.*, 1998) reducing their bioavailability (Griethuysen *et al.*, 2002). Thus, it is important to ensure that the sedimentary environment in a CWTS is conducive to formation of sulfides (Hsu and Maynard, 1999; Gillespie *et al.*, 2000). Formation of sulfides in wetland sediments requires a carbon and energy source (organic matter), a sulfur source (as a terminal electron acceptor), presence of sulfate-reducing bacteria, a physical means of retaining sulfide precipitates (sediments), a pH above 5, and absence of diatomic oxygen (Dvorak *et al.*, 1992). These are crucial components contributing to the performance of the CWTS for ash basin water remediation and may be reliable predictors of performance.

Pilot-scale reactors were used in our investigation to assess CWTS remediation of simulated ash basin water. Simulating ash basin water allowed a reduction in associated transport and storage costs. In addition, inputs to the system could be controlled more

accurately than if using transported ash basin water. Pilot-scale reactors provided benefits over full-scale trials. The use of pilot-scale reactors allowed concurrent replication of experiments and establishment of an analogue to indigenous wetland environments. Pilot-scale reactors utilized in this investigation provided time efficient and cost effective results.

The overall purpose of this research was to assess the treatability of ash basin water utilizing specifically designed CWTSs. Specific objectives of this research were to measure performance of CWTSs for: 1) decreasing the concentration of COC in ash basin water; 2) reducing toxicity associated with COC in ash basin water; and 3) reducing reuse-limiting parameters of ash basin water. Performance assessment encompassed analytical, toxicological, and reuse parameters. Analytical techniques were used to assess the concentration of COC in CWTS influent and effluent. Toxicity testing of CWTS effluent identified unanticipated deleterious constituents and provided data concerning bioavailability of COC. The reuse of water traditionally considered wastewater is becoming an important alternative due to stressed water resources. The reuse of ash basin water has the potential to reduce industrial water requirements.

## 3.3    Materials and methods

### 3.3.1 Constituents of Concern in Ash Basin Water – Concentration Reduction

#### 3.3.1.1   Constituents of Concern – Identification

In order to design a CWTS capable of decreasing the concentration and toxicity of COC in ash basin water, COC were identified by a risk quotient (RQ) method as outlined in Chapter 2. The RQ method uses a sentinel species (e.g. *Ceriodaphnia dubia*) to assess

risks to receiving system biota. A RQ is the ratio of an environmental exposure concentration to a toxicity endpoint (e.g. NOEC, $LC_{50}$, $EC_{50}$ etc.). When the RQ is equal to or greater than a predefined level of concern (LOC) (USEPA, 2004), risks to receiving system biota are likely (equation 3.1) and the constituent is identified as a constituent of concern.

$$RQ \geq LOC \Rightarrow \text{Potential risk to receiving system biota} \qquad (3.1)$$

The LOC is the maximum acceptable risk quotient (Rand and Clark, 2000). Accordingly, endangered species will have lower LOC values than non-endangered species.

### 3.3.1.2 *Pilot-Scale Constructed Wetland Treatment System – Design and Construction*

The CWTS was designed based on biogeochemical treatment processes that transfer or transform identified COC by promoting conditions that produce these processes (Rodgers and Castle, 2007), thus decreasing constituent of concern aqueous concentrations. To incorporate desired biogeochemical processes, two specifically designed pilot-scale wetland reactor series were built. Each reactor series (A and B) consisted of an initial 150-gallon (568 L) reactor (Rubbermaid® Utility Tank) (i.e. reactor 1), followed by two 70-gallon (265 L) reactors (i.e. reactors 1, 2, and 3), and a final 150-gallon (568 L) reactor (i.e. reactor 4). Reactor 4 of series A and B included a rock cascade near the influent position (Figure 3-1). The nominal hydraulic retention time (HRT) of reactor 1 in each series was 48 hours, and the nominal HRT of reactors 2, 3, and 4 in each series was 24 hours per reactor. Total system HRT was 120 hours (5 days).

Simulated ash basin water was formulated by addition of high purity salts (Fisher Scientific Inc., Fair Lawn, NJ) of COC to a 1000-gallon (3785 L) detention basin

(polypropylene tank). Simulated ash basin water was transferred from the detention basin to the CWTS via Fluid Metering Inc. (FMI)® piston pumps.
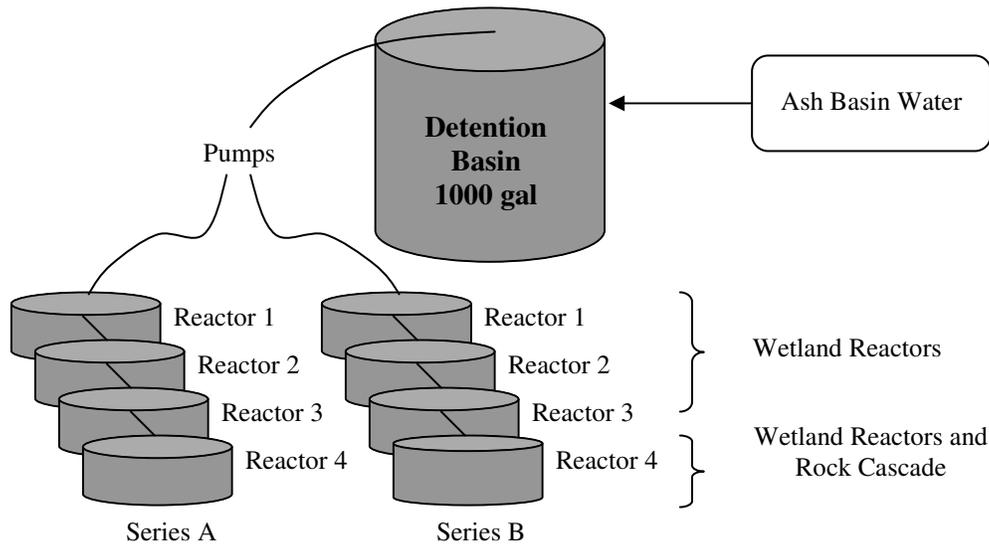


Figure 3-1. Schematic of the CWTS designed for remediation of ash basin water. Two reactor series (A and B) were used.

Hydrosoil composition (quartz sand) was selected to promote dissimilatory sulfate reduction and formation of ferric oxides and ferric hydroxides. Hydrosoil for each reactor was collected from a nearby creek (18 Mile Creek, near Clemson, South Carolina) and amended with organic matter. The same hydrosoil composition was used for each reactor. Kanagy *et al.* (2007) described particle size distribution, organic matter content, pH, Eh, and acid volatile sulfide concentration in hydrosoil collected from the same location. The hydrosoil was amended with organic matter because organic matter is a carbon and energy source for microbial activity (Dvorak *et al.*, 1992; Murray-Gulde *et al.*, 2005b), contributes to ambient dissolved oxygen concentrations (Kadlec and Knight, 1996), decreases hydrosoil oxidation-reduction potential (Eh) (Sobolewski, 1999), and provides

sorption and/or exchange sites for COC (Sobolewski, 1999). The target hydrosoil Eh range for each reactor was based on Eh-pH diagrams of the S-H-O system (Brookins, 1988), COC-S-O-H system (Brookins, 1988), and Fe-O-$H_2O$ system (Drever, 1988).

Reactors 1, 2, and 3 in series A and B were designed to promote dissimilatory sulfate reduction. Based on equilibrium biogeochemistry, Eh less than -50 mV should promote dissimilatory sulfate reduction (Brookins, 1988). Therefore, the target Eh range for reactors 1, 2, and 3 in series A and B was -250 to -50 mV (i.e. reducing reactors). Sulfide ions produced during dissimilatory sulfate reduction may combine with arsenic, chromium, mercury, selenium, and zinc (all present in ash basin water, see Chapter 2) to precipitate as non-bioavailable metal/metalloid-sulfide minerals (Murray-Gulde *et al.*, 2005b). Reducing reactors were planted with *Schoenoplectus californicus*. The *Schoenoplectus* genus (viz. *Schoenoplectus robustus*) has been shown to phytovolatilize selenium (Lin and Terry, 2003) and previous studies have shown that *Schoenoplectus californicus* C. promotes reducing hydrosoil conditions (Hawkins *et al.*, 1997; Gillespie *et al.*, 1999, 2000) required for dissimilatory sulfate reduction.

Reactor 4 in series A and B was designed to promote formation of ferric oxides and ferric hydroxides. A target hydrosoil Eh range (-50 to 250 mV) of reactor 4 in series A and B (i.e. oxidizing reactors) was selected to promote co-precipitation of COC with iron oxyhydroxides and sorption of COC onto iron oxides (Drever, 1988). Oxidizing reactors were planted with *Typha angustifolia* L. because it was abundantly available and the *Typha* genus (viz. *Typha latifolia*) readily transfers oxygen to the water column (Hammer, 1989) and root horizons (Moshiri, 1993), potentially increasing hydrosoil Eh

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(Jacob and Otte, 2003) forming ferric oxides and hydroxides. Iron oxides have a strong affinity for cations that are of similar size to ferric and ferrous cations (Sinicrope *et al.*, 1992). The following cations, present in ash basin water (see Chapter 2), have similar physical dimensions as ferric and ferrous cations: zinc, cadmium, copper, and nickel (Kabata-Pendias and Pendias, 1984). Therefore, these cationic metals may combine with iron oxides in the CWTS forming metal-oxide complexes (Benjamin and Leckie, 1981). Soluble arsenic, present in ash basin water (see Chapter 2), may be removed from the water column by adsorbing onto amorphous iron hydroxides (Pierce and Moore, 1980) or co-precipitating with iron oxy-hydroxides such as goethite (Manning *et al.*, 1998), ferrihydrite (Raven *et al.*, 1998), and scorodite (Johnson and Hallberg, 2005). Ferric oxides and hydroxides, such as goethite, are adsorbents for selenate (Se(VI)) (Peak and Sparks, 2002) and selenite (Se(IV)) (Zhang and Sparks, 1990).

*3.3.1.3   Hydrosoil Characteristics – Monitoring*

Monitored hydrosoil characteristics included organic matter content and Eh. Organic matter content was determined from grab samples collected within the CWTS and analyzed by the difference on ignition method (Luczak *et al.*, 1997). Eh was determined by placing platinum tipped Eh probes in hydrosoil of each reactor. Eh probes remained *in-situ* for the duration of experiments. Eh measurements were made against an Accumet® calomel reference electrode using a Fluke® 77 voltage meter (Faulkner *et al.*, 1989).

*3.3.1.4   Water Chemistry - Sampling and Analysis*

In order to determine the ability of CWTSs to decrease concentration of COC in ash basin water, aqueous samples were collected from multiple locations within the CWTS and analyzed for general water chemistry parameters (Table 3-1) and concentration of COC. The sampling period for COC included active growth (i.e. spring/summer) and dormant (i.e. winter) stages of macrophyte development.

Table 3-1. Methods for determination of general water chemistry.

| Parameter | Method | MDL[1] |
|---|---|---|
| Temperature | Direct Instrumentation: YSI Model 52 | 0.5 ºC |
| pH | Direct Instrumentation: Orion Model 420A | 0.01 |
| Conductivity | Direct Instrumentation: YSI Model 30 | 0.1 µS/cm |
| Alkalinity | Standard Methods: 2320 B (Clesceri *et al.*, 1999) | 2 mg/L as $CaCO_3$ |
| Hardness | Standard Methods: 2340 C (Clesceri *et al.*, 1999) | 2 mg/L as $CaCO_3$ |
| DO[2] | Direct Instrumentation: YSI Model 52 | 0.1 mg/L |

[1] Method Detection Limit          [2] Dissolved Oxygen

Sampling for COC and general water chemistry was initiated in December 2006 with the exception of mercury sampling, which was initiated in February 2007. Sampling was completed in June 2007. Samples for analysis of arsenic, chromium, selenium, and zinc were collected in 250-mL Nalgene® high-density polyethylene (HDPE) bottles. Samples were immediately transported to the laboratory and acidified to pH ≤ 2 using trace metal grade concentrated (15.8 N) nitric acid (Fisher Scientific Inc., Fair Lawn, NJ). Samples were stored at a controlled temperature (4 ± 1 °C) until analysis. Samples for mercury analysis were collected in 30 mL glass vials with Teflon lined tops. After collection, mercury samples were immediately transported to the laboratory and preserved with bromine monochloride (USEPA, 2002a).

Samples were analyzed for arsenic, chromium, selenium, and zinc by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (SPECTROFLAME-EOP, Spectro Analytical Instruments, Kleve, Germany) according to EPA method 200.7. Mercury analyses were performed at the Laboratory for Environmental Analysis at the University of Georgia using a Sciex Elan 9000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Perkin-Elmer, Norwalk, CT). The four main isotopes of mercury ($^{199}$Hg, $^{200}$Hg, $^{201}$Hg, and $^{202}$Hg) were quantified and averaged. A laboratory fortified blank (LFB), non-fortified blank (NFB), and sample duplicate were run after every five samples. Additionally, a quality control sample prepared from a different stock solution was run after every twenty samples. Sample analyses were considered acceptable if LFB recovery was within the recommended range of 85-115% (USEPA, 1994), the relative percent difference (RPD) (calculated from equation 3.2) between the calibration blank and subsequent NFB readings was less than 10%, and RPD between duplicate samples was less than 20%.

$$RPD = \left( \frac{|X\text{-}Y|}{Mean\ (X,Y)} \right) *100 \qquad (3.2)$$

where:   X = sample concentration (µg/L)

Y = duplicate sample concentration (µg/L)

Removal efficiency, which is the percent decrease in concentration of a constituent of concern from influent to effluent, was calculated using equation 3.3:

$$removal\ efficiency\ (\%) = \left( \frac{I\text{ - }O}{I} \right) 100 \qquad (3.3)$$

where:    I is the concentration (µg/L) of a constituent of concern in the influent and O is the concentration (µg/L) of the constituent in the effluent.

*3.3.2 Toxicity - Sampling and Experiments*

In order to determine the ability of CWTSs to reduce toxicity associated with COC in ash basin water, the influent and effluent of each CWTS reactor series were sampled at least every two months for aqueous toxicity testing. Toxicity samples were collected in 1-L Nalgene® HDPE bottles, transported to the laboratory, and stored at a controlled temperature (4 ± 1 °C) until test initiation.

Five toxicity experiments were performed to assess toxicity abatement by specifically designed CWTSs. Toxicity experiments were conducted according to EPA method 1002.0 (USEPA, 2002b). Seven-day chronic toxicity experiments were conducted using a control, CWTS influent, and four concentrations of CWTS effluent. The microcrustacean *Ceriodaphnia dubia*, commonly used in NPDES permit testing (Gillespie *et al.*, 2000), served as a sentinel (i.e. for aquatic receiving system biota) testing species. Water used for CWTS influent and 100% effluent concentrations was collected directly from the source (i.e. pump discharge or CWTS effluent). Aliquots of CWTS effluent were diluted with moderately hard water (Sawyer *et al.*, 1994) to produce the following concentrations of CWTS effluent: 100, 50, 25 and 10%. Moderately hard water was also used for the control solution. General water chemistry analyses (Table 3-1) were conducted on days 1, 3, and 7 of toxicity experiments. Toxicity experiments were initiated by placing one *C. dubia* (<24 hours old) in each of 10 replicates containing 15 mL of each concentration of effluent, influent, and control. *C. dubia* were fed 100 µL

of *Selenastrum capricornutum* and 100 µL of yeast-cerophyll-trout chow (YCT) each day. In order to accurately assess exposures of *C. dubia* to COC, samples for aqueous toxicity testing were collected concurrently with samples collected for analytical analysis.

Statistical analyses of *C. dubia* survival and reproduction were performed to determine whether differences existed between a laboratory control group, a group exposed to CWTS influent, and a group exposed to CWTS effluent. Data normally distributed with homogeneous variance were analyzed with a one-way ANOVA ($\alpha=0.05$). Data not meeting these criteria were analyzed with a one-way ANOVA on ranks. Appropriate post-hoc tests were used to determine where differences existed.

Lowest observed effect concentrations (LOECs) were determined as the lowest concentration of CWTS effluent eliciting a response significantly different from that of controls. No observed effect concentrations (NOECs) were determined as the lowest concentration of CWTS effluent eliciting a response not significantly different from that of controls. Toxicity data were analyzed with SigmaStat® 3.1.

*3.3.3 Reuse – Sampling and Analysis*

Reuse of ash basin effluents within power plants may require reducing the concentration of soluble salts (e.g. calcium sulfate, calcium carbonate, or magnesium and silca compounds) and corrosion promoters (primarily high or low pH) (Chu and Ruane, 1978). Soluble salts may precipitate on hydraulic transportation systems, forming a scale (Flemming, 2002) which decreases efficiency.  In addition to possible scale formation and corrosion of hydraulic transportation systems, biofouling (Flemming, 2002) can reduce the efficiency of hydraulic transportation systems. Therefore, reuse limiting

parameters in ash basin water include biofouling, scaling, and corrosion. Remediation of these parameters was assessed by measuring accretion of mass on glass coupons (i.e. biofouling and scaling) and loss of mass of copper coupons (i.e. corrosion) placed in the detention basin (influent) and each CWTS series effluent. One copper coupon (Alabama Specialty Products, Inc) and three glass coupons were weighed and placed in the detention basin (influent) and each CWTS effluent stream for 30 days. This period has been shown to allow a significant degree of accretion while avoiding loss due to sloughing or browsing by organisms (Azis *et al.*, 2001). All coupons were placed parallel to one another and horizontal to the water surface in each CWTS effluent stream. Upon removal, glass coupons were dried in an oven at 105°C for 24 hours, removed, allowed to cool in a desiccator, and weighed. Biofouling, the dry weight gain of organic material per unit area, was determined by the difference on ignition method (Luczak *et al.*, 1997). Scale was the remaining dry weight gain of inorganic material per unit area. Corrosion, measured as the decrease in mass of the copper coupon, was assessed following the American Society for Testing Materials (ASTM) method D 2688-05 (ASTM, 2007). After removal from influent and effluent locations, copper coupons were dried in an oven at 105°C for 24 hours, removed, allowed to cool in a desiccator, and weighed.

3.4    Results

*3.4.1 Constituents of Concern in Ash Basin Water – Concentration Reduction*

*3.4.1.1    Constituents of Concern – Identification*

COC identified by the RQ method are: aluminum, cadmium, chromium, copper, iron, lead, mercury, selenium, and zinc (see Chapter 2). In addition, arsenic was included

as a constituent of concern because arsenic has been implicated in observed toxic effects to amphibians inhabiting areas contaminated by coal combustion waste (Hopkins *et al.*, 1998) and because of multiple detections in ash basin water samples (Cherry and Guthrie, 1977; Dreesen *et al.*, 1977; Chu and Ruane, 1978; Turner, 1981; Alberts *et al.*, 1985).

Arsenic, chromium, mercury, selenium, and zinc were included in the simulated ash basin water used to evaluate CWTS performance. Aluminum solubility varies with pH (Kadlec and Knight, 1996), with low solubility at near-neutral pH (5 to 8 S.U.) and higher solubility at pH outside the near-neutral range (Kabata-Pendias and Pendias, 1984). Since the pH of CWTS effluent is generally near-neutral (Kadlec and Knight, 1996),  it was reasoned that aluminum would be sequestered within the CWTS. Zinc was considered a proxy for cadmium, copper, and iron because they have similar physical dimensions and are present in the environment as divalent (or trivalent; in the case of iron) cations, the factors controlling zinc mobility in soil are similar to those controlling copper mobility, and cadmium geochemistry is strongly associated with zinc geochemistry in that neither element undergoes a valence reduction in the presence of sulfide (Kabata-Pendias and Pendias, 1984; Gammons and Frandsen, 2001). Lead removal by CWTSs has been extensively studied (Kadlec and Knight, 1996) and was therefore not included in simulated ash basin water. Chromium may predict aluminum and iron behavior in CWTSs since there are similarities between the ionic size and geochemical properties of the trivalent forms of these metals (Kabata-Pendias and Pendias, 1984).

*3.4.1.2   Constructed Wetland Treatment System – Hydrosoil Characteristics*

Organic matter content of CWTS hydrosoil ranged from 0.10 to 0.42% (Table 3-2). Hydrosoil Eh was measured in September 2006, February 2007, and May 2007 (Figure 3-2). The average of the three hydrosoil Eh measurements with time in each reactor planted with *S. californicus* (viz. reactors A1, A2, A3, B1, B2, and B3) was within the targeted range (-250 to -50 mV) for precipitation of COC as insoluble sulfides (Brookins, 1988; Mitsch and Gosselink, 2000) (Figure 3-2, C). For each reactor planted with *T. angustifolia* (viz. reactors A4 and B4) the average of the three hydrosoil Eh measurements with time was within the targeted range (-50 to 250 mV) for formation of ferric oxides and ferric hydroxides (Drever, 1988) (Figure 3-2, C). The variation of Eh with time was greatest in reactors A1, A4, B1, and B4 (Figure 3-2, A and B). The Eh of reactor A1 varies between a maximum of 66 mV and a minimum of -153 mV (Figure 3-2, A). The Eh of reactor B1 varies between a maximum of -19 mV and a minimum of -165 mV (Figure 3-2, B). The Eh of reactor A4 decreased 192 mV over the experimental period (Figure 3-2, A and B).

Table 3-2. Measured organic matter
    content of CWTS reactors.

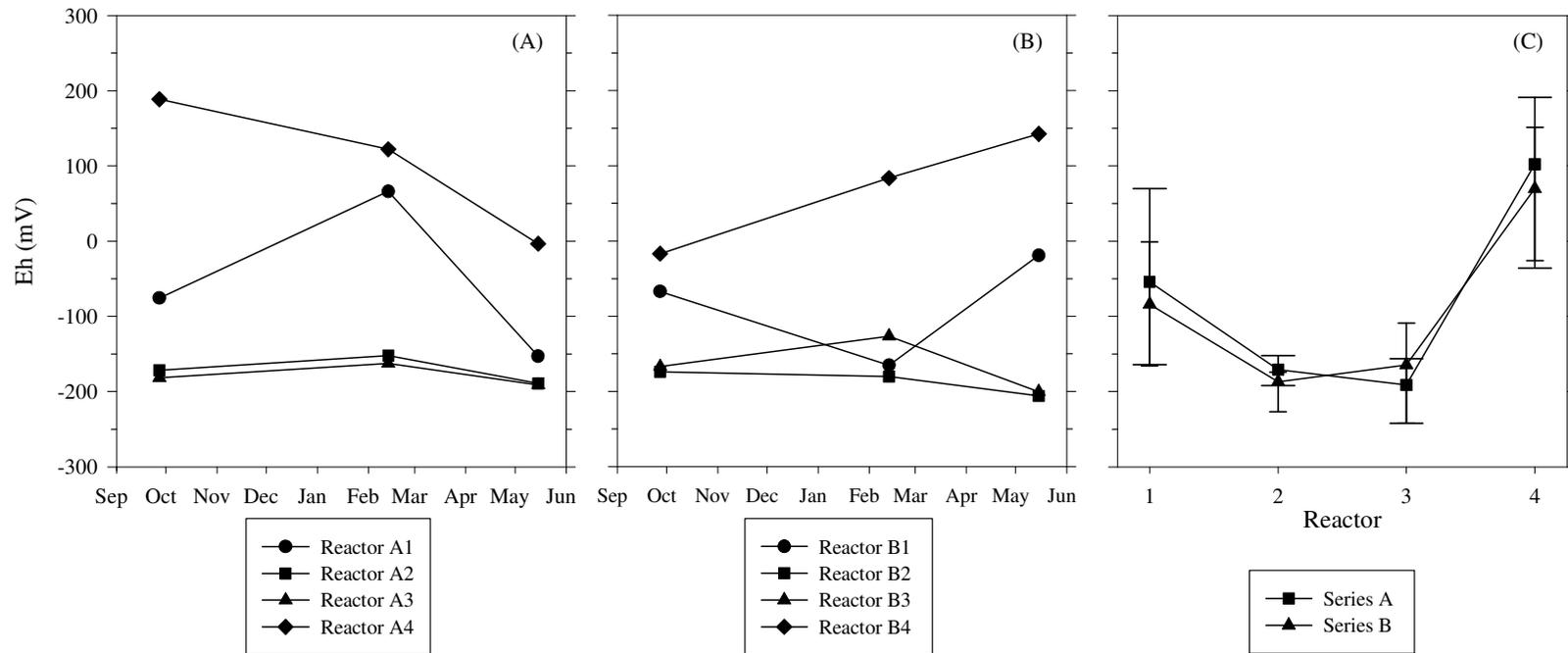| Reactor | Series A Organic matter %, by weight | Series B Organic matter %, by weight |
|---|---|---|
| 1 | 0.10 | 0.12 |
| 2 | 0.42 | 0.24 |
| 3 | 0.36 | 0.25 |
| 4 | 0.19 | 0.18 |

Figure 3-2. Eh of wetland reactors. (A) series A. (B) series B. (C) Eh averaged from September 2006, February 2007, and May 2007; error bars represent the range of triplicate measurements in each reactor on each measurement date; series A error bars are shown with extended end caps.

*3.4.1.3    Water Chemistry - Sampling and Analysis*

Values of general water chemistry parameters in the effluent from each reactor varied as water moved through the CWTS during the experiments (Table 3-3). A controlling factor for metal/metalloid-sulfide precipitation is pH of the aqueous medium (Brookins, 1988). Of the 72 measured reactor effluent pH values during the experiments, 97% were within the range required by sulfate reducing bacteria (5-8 S.U.) (Brown *et al.*, 1973).

Table 3-3. General water chemistry of influent to the CWTS and effluent from each reactor. Each value represents an average of 9 measurements taken on different dates over the course of experiments (December 2006 to June 2007).

| Location in CWTS | Temperature C | D.O.[†] mg $L^{-1}$ | Conductivity µS $cm^{-1}$ | pH S.U. | Alkalinity[‡] mg $L^{-1}$ | Hardness[‡] mg $L^{-1}$ |
|---|---|---|---|---|---|---|
| Influent | 22.0 (16.8-28.7) | 8.7 (8.1-9.5) | 675 (604-757) | 6.7 (5.8-7.1) | 15 (10 - 20) | 196 (122-226) |
| A1 Effluent | 21.9 (15.9-28.7) | 8.6 (8.0-9.9) | 660 (583-720) | 6.3 (5.8-7.0) | 11 (10-12) | 198 (114-240) |
| A2 Effluent | 21.5 (16.7-27.8) | 8.3 (7.8-9.8) | 681 (599-748) | 6.4 (5.5-8.2) | 17 (5-44) | 203 (118-290) |
| A3 Effluent | 21.3 (16.8-27.2) | 8.2 (7.3-9.7) | 688 (610-765) | 6.0 (5.3-7.0) | 14 (10-20) | 194 (122-250) |
| A4 Effluent | 22.0 (17.3-26.9) | 8.5 (7.9-10.1) | 682 (572-772) | 6.3 (5.8-7.0) | 12 (10-16) | 192 (116-270) |
| B1 Effluent | 21.5 (16.9-24.3) | 8.3 (7.2-9.4) | 674 (598-764) | 6.4 (5.7-7.0) | 14 (5-20) | 198 (126-250) |
| B2 Effluent | 21.2 (14.7-23.9) | 8.5 (7.8-9.8) | 660 (547-770) | 6.2 (5.8-6.8) | 15 (5-24) | 196 (124-250) |
| B3 Effluent | 21.2 (16.5-23.2) | 8.3 (7.9-9.6) | 697 (618-785) | 6.3 (5.8-7.0) | 16 (10-22) | 209 (128-320) |
| B4 Effluent | 22.1 (17.1-28.1) | 8.5 (7.7-10.2) | 700 (619-796) | 6.6 (5.9-8.4) | 19 (10-40) | 207 (132-280) |

Values in parenthesis represent the range of measurements.
[†] D.O. = dissolved oxygen
[‡] as $CaCO_3$

CWTS effluent concentrations of arsenic, chromium, mercury, and zinc were less than or equal to influent concentrations for each measured sample during the December 2006 to June 2007 experimental period (Table 3-4). CWTS effluent concentrations of selenium were lower than influent concentrations in 7 of 9 effluent samples from series A and B.

Table 3-4. Influent and effluent concentrations and removal efficiency (%) of constituents of concern.

| Material Experiment | Influent (µg/L) | Effluent (µg/L) A | B | Removal (%) A | B |
|---|---|---|---|---|---|
| **Chromium** | | | | | |
| 12-06-06 | 46.6 | 14.3 | 11.7 | 69.4 | 75.0 |
| 12-20-06 | 59.0 | 18.0 | 14.9 | 69.5 | 74.8 |
| 01-11-07 | 51.5 | 19.1 | 16.3 | 62.9 | 68.3 |
| 02-13-07 | 55.4 | 26.4 | 19.3 | 52.3 | 65.2 |
| 03-06-07 | 53.9 | 18.2 | 11.8 | 66.2 | 78.1 |
| 03-22-07 | 45.4 | 11.7 | 11.9 | 74.2 | 73.9 |
| 04-26-07 | 17.2 | 15.4 | 17.2 | 10.6 | NR |
| 05-15-07 | 69.9 | 5.3 | 8.0 | 92.4 | 88.6 |
| 06-11-07 | 36.0 | 8.6 | 9.1 | 76.2 | 74.7 |
| **Zinc** | | | | | |
| 12-06-06 | 135.3 | 19.2 | 8.5 | 85.8 | 93.7 |
| 12-20-06 | 145.4 | 29.1 | 9.8 | 80.0 | 93.2 |
| 01-11-07 | 127.4 | 23.6 | 14.4 | 81.5 | 88.7 |
| 02-13-07 | 144.1 | 89.4 | 49.4 | 38.0 | 65.7 |
| 03-06-07 | 98.9 | 89.4 | 33.1 | 9.6 | 66.5 |
| 03-22-07 | 98.2 | 79.4 | 18.5 | 19.2 | 81.1 |
| 04-26-07 | 125.3 | 60.5 | 35.1 | 51.7 | 72.0 |
| 05-15-07 | 39.3 | 4.8 | 7.5 | 87.8 | 80.8 |
| 06-11-07 | 15.6 | 6.3 | 16.7 | 59.4 | NR |
| **Arsenic** | | | | | |
| 12-06-06 | 180.9 | 8.6 | 21.8 | 95.3 | 87.9 |
| 12-20-06 | 276.6 | 21.9 | 7.1 | 92.1 | 97.4 |
| 01-11-07 | 239.9 | 12.2 | 30.5 | 94.9 | 87.3 |
| 02-13-07 | 325.4 | 59.0 | 57.2 | 81.9 | 82.4 |
| 03-06-07 | 296.1 | 33.4 | 26.1 | 88.7 | 91.2 |
| 03-22-07 | 281.7 | 26.3 | 27.0 | 90.7 | 90.4 |
| 04-26-07 | 88.4 | 35.7 | 35.5 | 59.6 | 59.8 |
| 05-15-07 | 174.0 | 18.7 | 14.8 | 89.3 | 91.5 |
| 06-11-07 | 207.7 | 16.4 | 23.6 | 92.1 | 88.6 |
| **Selenium** | | | | | |
| 12-06-06 | 271.7 | 292.0 | 286.0 | NR | NR |
| 12-20-06 | 307.2 | 275.4 | 283.7 | 10.4 | 7.6 |
| 01-11-07 | 291.5 | 272.4 | 258.4 | 6.5 | 11.3 |
| 02-13-07 | 124.1 | 145.8 | 142.3 | NR | NR |
| 03-06-07 | 147.8 | 125.3 | 122.4 | 15.2 | 17.2 |
| 03-22-07 | 158.9 | 124.3 | 132.7 | 21.7 | 16.4 |
| 04-26-07 | 301.4 | 200.7 | 217.3 | 33.4 | 27.9 |
| 05-15-07 | 353.3 | 37.3 | 48.3 | 89.4 | 86.3 |
| 06-11-07 | 102.1 | 58.0 | 42.3 | 43.2 | 58.6 |
| **Mercury** | | | | | |
| 02-13-07 | 33.2 | 1.7 | 1.2 | 94.9 | 96.3 |
| 03-06-07 | 20.3 | 1.0 | 1.3 | 95.2 | 93.6 |
| 03-22-07 | 19.4 | 1.0 | 1.8 | 94.9 | 91.0 |

| 04-26-07 | 14.1 | 0.1 | 0.2 | 99.1 | 98.7 |
| 05-15-07 | 1.2 | 0.2 | 0.4 | 81.1 | 67.3 |
| 06-11-07 | 2.4 | 0.3 | 0.3 | 88.5 | 87.9 |

NR = no removal

Because effluent concentrations of COC are limited by the amount that can be removed (solubility limits and background concentrations), effluent concentrations are independent of influent concentrations (Table 3-4). Influent concentrations of chromium ranged from 17.2 to 59.0 µg/L. However, effluent concentrations of chromium ranged from only 5.3 to 26.4 µg/L. The range of influent concentrations of zinc, 15.6 to 145.4 µg/L, was larger than the range of effluent concentrations, 4.8 to 89.4 µg/L. The range of arsenic influent concentrations, 88.4 to 325.4 µg/L, was larger than the range of effluent concentrations, 7.1 to 59.0 µg/L. Influent concentrations of mercury, 1.2 to 33.2 µg/L, were greater than effluent concentrations of mercury, 0.1 to 1.8 µg/L.

Representative plots of the decrease in concentration of COC as water moved through the CWTS show the greatest removal efficiency occurring in the first three reactors (i.e. reducing reactors), with minor removal associated with reactor 4 (i.e. oxidizing reactors) (Figure 3-3, A, B, C, D).
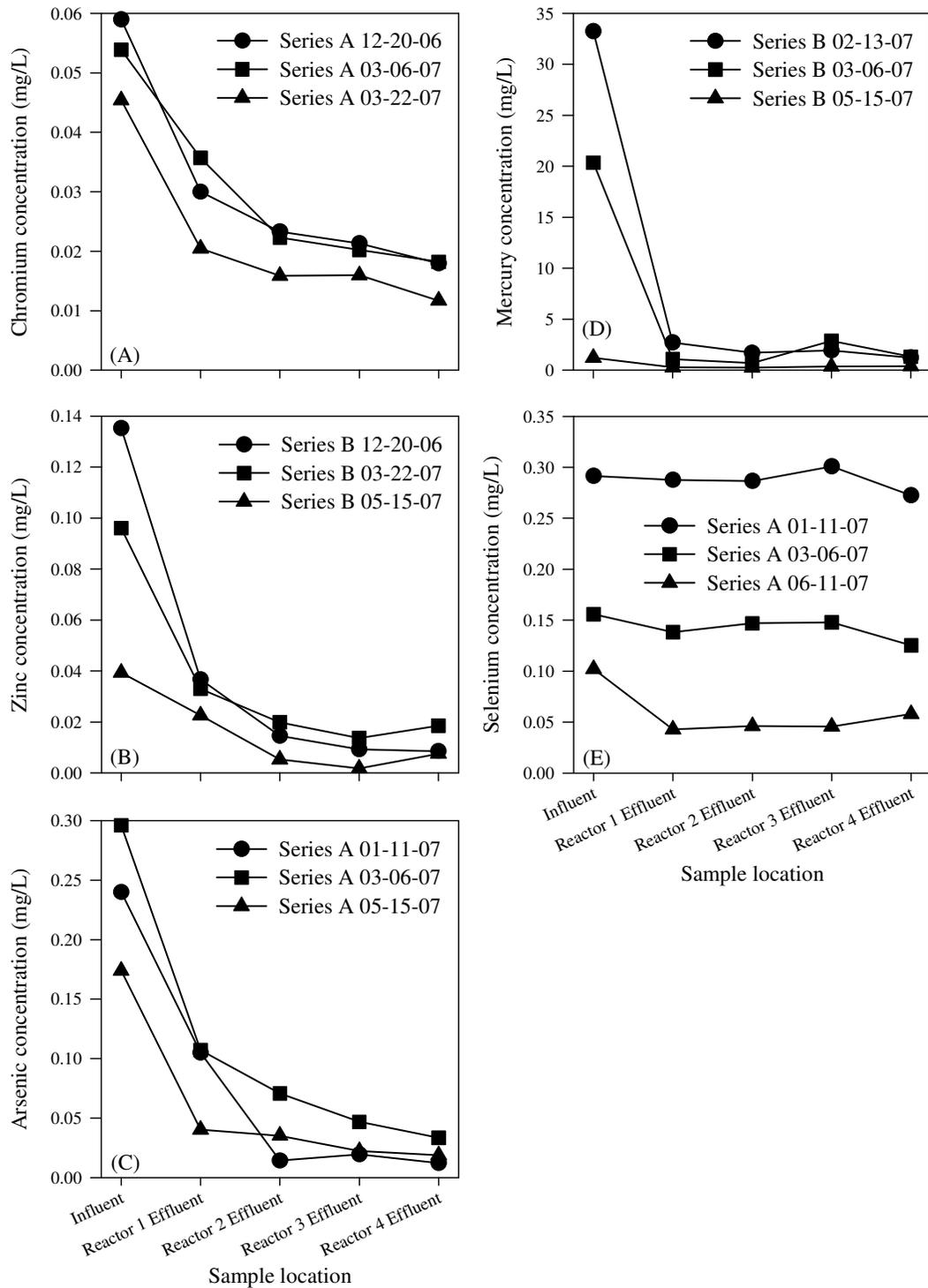
Figure 3-3. Constituent of concern concentrations in influent and effluent for each pilot-scale constructed wetland reactor. In both series A and B, reactors 1, 2, and 3 were reducing and reactor 4 was oxidizing.

*3.4.2 Toxicity - Sampling and Experiments*

Toxicity experiments served as a measure of performance for the pilot-scale CWTS, which was designed to reduce bioavailability of identified COC in ash basin water. In all five 7-day aqueous toxicity experiments, survival of *C. dubia* exposed to undiluted influent was significantly less than that of controls. Survival LOECs were >100% CWTS effluent for all toxicity experiments in both series A and B. In addition, undiluted (100%) CWTS effluent of both series A and B had no observed effect on *C. dubia* survival. *C. dubia* reproduction was slightly more sensitive than survival. Organisms exposed to 100% influent had statistically significant decreased reproduction as compared to control organisms for all five toxicity experiments. In 6 of the 10 effluents, *C. dubia*'s reproduction LOEC was the undiluted (100%) effluent. In 4 of the 10 effluents, *C. dubia*'s reproduction NOEC was the undiluted (100%) effluent (Table 3-5).

Table 3-5. LOECs and NOECs for *C. dubia* in 7-day aqueous toxicity experiments with influent[a] and effluent collected from the pilot-scale CWTS[b].

| Toxicity Experiment | Parameter | Series A Effluent | | Series B Effluent | |
|---|---|---|---|---|---|
| | | LOEC, % | NOEC, % | LOEC, % | NOEC, % |
| December 7, 2006 | Survival | >100 | 100 | >100 | 100 |
| February 14, 2007 | | >100 | 100 | >100 | 100 |
| April 30, 2007 | | >100 | 100 | >100 | 100 |
| May 19, 2007 | | >100 | 100 | >100 | 100 |
| June 21, 2007 | | >100 | 100 | >100 | 100 |
| | | | | | |
| December 7, 2006 | Reproduction | 10 | <10 | 100 | 50 |
| February 14, 2007 | | >100 | 100 | >100 | 100 |
| April 30, 2007 | | 25 | 10 | 50 | 25 |
| May 19, 2007 | | 100 | 50 | 25 | 10 |
| June 21, 2007 | | >100 | 100 | >100 | 100 |

[a] Influent survival and reproduction were significantly less than that of the effluent for all toxicity experiments.
[b] Results are expressed as a percentage of effluent (i.e. the concentration of CWTS effluent in the testing solution) to illustrate toxicity abatement by the CWTS.

### 3.4.3 Reuse – Sampling and Analysis

Factors limiting reuse of ash basin water within a coal-fired power plant include scaling, biofouling, and corrosion. Scale formation and biofouling were less in CWTS effluent compared to influent (Figure 3-4). Scale formation in series A and B effluent was 80 and 40%, respectively, less than influent scale formation. Series A and B effluent had 46% and 68%, respectively, less biofouling than influent biofouling. Corrosion was greater in CWTS effluent than in influent. Corrosion of copper coupons in series A and B effluent was 296% and 436%, respectively, greater than influent corrosion.
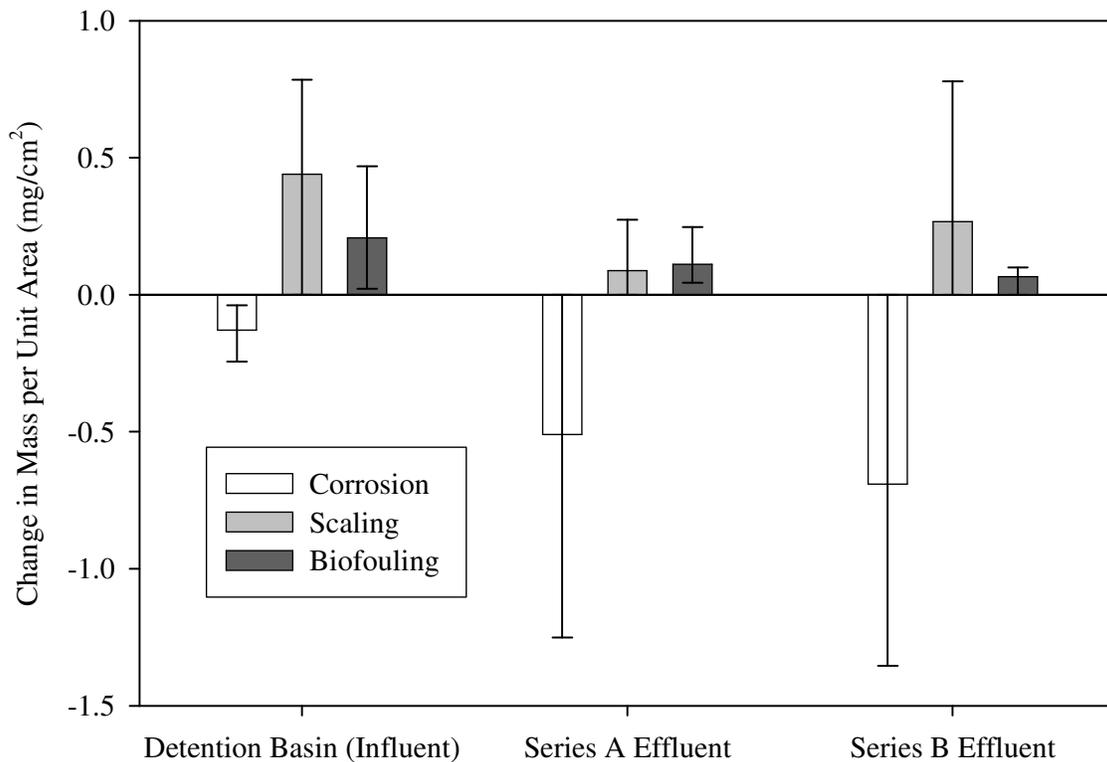
Figure 3-4. Influent and effluent scaling, biofouling, and corrosion per unit area. Values were averaged from experiments initiated in December 2006, March 2007, May 2007, and June 2007. Error bars represent the range of data.

3.5    Discussion

The pilot-scale CWTS was designed to decrease the concentration and toxicity associated with ash basin water by establishing biogeochemical conditions which promote dissimilatory sulfate reduction and formation of ferric oxides and ferric oxyhydroxides. Targeted constituent of concern removal processes were precipitation as non-bioavailable sulfide minerals, sorption onto iron oxides, and co-precipitation with iron oxyhydroxides. Treatment levels used to evaluate the use of CWTSs for treating ash basin water were based on USEPA recommended water quality criteria and USEPA drinking water standards (Table 3-6). The extent of removal (i.e. concentration of a

constituent of concern in effluent) and removal efficiency (the percent concentration decrease from influent to effluent) were used to evaluate performance of the CWTSs. Removal rates for a CWTS can be calculated by dividing removal efficiency for the CWTS by 5 days (i.e. the hydraulic retention time of the CWTS in our study). The removal rate was not constant over the 5 day HRT. For chromium, zinc, arsenic, and mercury the removal rate was greatest in the first 3 days of treatment, corresponding to the first two reactors (Figure 3-3, A, B, C, D).

The concentration of chromium in CWTS influent was effectively decreased by CWTS reactors (Figure 3-3, A). Total chromium concentration in series A and B effluent in the 5-15-07 and 6-11-07 experiments was less than the national recommended freshwater criterion for a continuous concentration (FWCCC) for hexavalent chromium and for trivalent chromium (Tables 3-4 and 3-6). Removal efficiencies for chromium ranged from 74.7 to 92.4% for the 5-15-07 and 6-11-07 experiments. For the other experiments, removal efficiencies ranged from no removal to 75%.

Aqueous zinc concentrations were effectively decreased by CWTS reactors 1, 2, and 3 (i.e. reducing reactors) (Figure 3-3, B). For experiments in which zinc concentrations in the influent exceeded the FWCCC (120 µg/L), concentrations in the effluent ranged from 8.5 to 89.4 µg/L and removal efficiencies ranged from 38.0 to 93.7% (Tables 3-4 and 3-6).

Table 3-6. Treatment levels used to evaluate constructed wetland treatment system performance.

| | Treatment level ($\mu g\ L^{-1}$) | |
|---|---|---|
| Element | FWCCC[a] | Drinking water standard[b] |
| Chromium | 74[c] or 11[d] | 100 |
| Zinc | 120 | 5000 |
| Arsenic | 64 | 10 |
| Selenium | 5 | 50 |
| Mercury | 0.77 | 2 |

[a] freshwater criterion for a continuous concentration (USEPA, 2006)
[b] national primary drinking water standard (USEPA, 2003)
[c] Chromium (III)
[d] Chromium (VI)

Series A reducing reactors (i.e. reactors 1, 2, and 3) removed 220.4, 249.3, and 151.6 µg/L of arsenic in the 1-11-07, 3-6-07, and 5-15-07 experiments, respectively, while the oxidizing reactor of series A (i.e. reactor 4) removed 7.3, 13.4, and 3.7 µg/L of arsenic during the same experiments (Figure 3-3, C).The concentration of arsenic in series A and B effluent was less than the FWCCC (64 µg/L) in all 9 experiments (Tables 3-4 and 3-6). Removal efficiencies for arsenic ranged from 59.6 to 95.3%.

Mercury was consistently and effectively treated in the first wetland reactor of each series. Removal efficiencies in the first wetland reactor ranged from 51.7 to 97.3%, and removal efficiencies for the entire system ranged from 67.3 to 99.1%. Mercury concentrations in series A and B effluent were less than the national primary drinking water standard (2 µg/L) in all 6 experiments and less than FWCCC (0.77 µg/L) in 3 experiments (Tables 3-4 and 3-6).

The removal efficiency of selenium was less than that of other COC (Figure 3-3, E). Seventy eight percent of the selenium concentrations in series A and B effluent were

greater than the drinking water standard (50 µg/L) (Table 3-4), which was the higher

treatment level (Table 3-6) used to evaluate performance. However, selenium

concentrations in the 5-15-07 effluent sample from series A and the 5-15-07 and 6-11-07

effluent samples from series B were less than the drinking water standard (Tables 3-4 and

3-6). The efficiency of selenium removal in the 5-15-07 and 6-11-07 experiments was

greater than the efficiency of selenium removal in earlier experiments. This increase in

selenium removal indicates that conditions necessary for decreasing selenium

concentrations, such as effective microbial populations, may have changed over the

course of experiments. Previous studies (e.g. Kashiwa *et al.*, 2000) have attributed

treatment of soluble selenium (i.e. selenate and selenite) to microbial reduction of soluble

selenium to insoluble elemental selenium.

      The removal efficiency for chromium, zinc, arsenic, and mercury in the reducing

reactors was greater than in the oxidizing reactors (Figure 3-3; A, B, C, D). The reducing

reactors were designed to promote biogeochemical conditions favorable for dissimilatory

sulfate reduction, particularly through establishment of a reducing hydrosoil. Measured

Eh demonstrated that targeted values were achieved (Figure 3-2). Therefore, it is

interpreted that dissimilatory sulfate reduction occurred in the reducing reactors, which

resulted in removal of chromium, zinc, arsenic, and mercury by precipitation as non-

bioavailable sulfides. Oxidizing reactors were designed to promote biogeochemical

conditions favorable for co-precipitation of COC with iron oxyhydroxides and sorption of

COC by iron oxides. Since measured Eh indicated that targeted values were achieved

(Figure 3-2), it is interpreted that oxidizing conditions within these reactors supported co-

precipitation of COC with iron oxyhydroxides and sorption of COC by iron oxides. Because influent constituent of concern concentrations to oxidizing reactors were much less than influent constituent of concern concentrations to reducing reactors, the high rates of removal observed in the reducing reactors were not possible in the oxidizing reactors.

The CWTS under study was designed to remove COC from the aqueous phase by precipitation as non-bioavailable sulfide minerals, sorption by iron oxides, and co-precipitation with iron oxyhydroxides. However, we recognize that plants and sediments within the CWTS have organic and inorganic ligands of differing strengths. Therefore, it is interpreted that removal of COC from the aqueous phase is occurring through additional biogeochemical processes, which may include uptake by wetland vegetation (Lin and Terry, 2003) and sorption to organic matter (Phillips, 1999), detritus and mineral phases (Deaver and Rodgers, 1996), and plant surfaces (Sinicrope *et al.*, 1992).

The concentrations of COC in CWTS effluent were consistently less than concentrations in CWTS influent (Table 3-4). Experiments using a range of influent concentrations provide evidence that the extent of removal was independent of influent concentrations. However, removal efficiency and removal rate were dependent on influent concentrations. Based on constituent of concern removal through time (Table 3-4), the extent of removal was also independent of the stage of macrophyte development (i.e. consistent removal in both winter and summer months). Effective treatment of simulated ash basin water during winter months provides encouragement that treatment of ash basin water in a full-scale CWTS will continue during winter months.

In addition to decreasing the concentration of COC, the CWTS effectively decreased toxicity associated with the bioavailable fraction of COC. In all toxicity experiments, aqueous CWTS influent samples were toxic to *C. dubia*. While reproduction NOECs of 6 effluent samples were less than that of undiluted (100%) effluent, 6 reproduction LOECs were undiluted (100%) effluent. Additionally, in all toxicity experiments there was no toxicity with regard to survival of *C. dubia* (Table 3-5). The decrease in toxicity of effluent samples as compared to influent samples indicates that COC in the aqueous phase were transformed or transferred within the system, resulting in less bioavailable forms.

With adequate treatment, reuse of wastewater for industrial applications can reduce the amount of water used (defined as water withdrawn for some application and subsequently discharged to a water body) and consumed (defined as water used but not returned to a water body). Within a power plant, parameters that determine the extent to which ash basin water can be reused include corrosion, biofouling, and scaling. While the corrosion of copper coupons placed in series A and B effluent was 296 and 436% greater than that of copper coupons placed in the influent (Figure 3-4), hydraulic transportation systems constructed from corrosion resistant materials (e.g., polyvinyl chloride [PVC]) should limit corrosion of ash basin water transportation systems (Schweitzer, 1989). Biofouling of hydraulic transportation systems can reduce flow volume, thereby reducing efficiency. Biofouling in series A and B effluent was 46 and 68%, respectively, less than biofouling in CWTS influent (Figure 3-4). Although scale deposits on glass coupons indicate potential scale formation following treatment with CWTS, series A effluent scale

formation was 80% less than influent scale formation, and series B effluent scale formation was 40% less than influent scale formation. The observed reduction of biofoul and scale deposits on hydraulic transportation systems as a result of treatment with a CWTS should allow more efficient effluent reuse.

3.6    Conclusions

Data from our study indicate reduction in concentration and bioavailability of arsenic, chromium, mercury, and zinc using pilot-scale CWTSs. Treatment of simulated ash basin water by CWTSs resulted in effluent concentrations as low as 7.1 µg/L arsenic, 5.3 µg/L chromium, 0.1 µg/L mercury, 37.3 µg/L selenium, and 4.8 µg/L zinc. While series A and B effluent concentrations of zinc were less than the FWCCC in all but one experiment, series A and B effluent concentrations of arsenic and mercury were less than the FWCCC in all experiments. Effluent chromium concentrations in series A and B were less than the FWCCC for hexavalent chromium (11 µg/L) in 2 of 9 experiments. The concentration of selenium in CWTS effluent was less than the drinking water standard (50 µg/L) in 3 experiments.

Performance data from the pilot-scale CWTS suggest that removal of arsenic, chromium, mercury, and zinc occurred in reactors designed to support dissimilatory sulfate reduction. Additionally, removal of arsenic, chromium, mercury, and zinc occurred in the oxidizing reactors. However, due to lower influent concentrations to the oxidizing reactors the rate of removal observed in the reducing reactors was not possible. The concentrations of chromium, zinc, arsenic, and mercury in CWTS effluent were consistently less than that of influent, regardless of influent concentration and stage of

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macrophyte development. The concentration of selenium in CWTS series A and B effluent was less than that of influent in 7 of 9 experiments.

Performance data concerning the decrease in concentration of COC also demonstrate the inadequacy of describing CWTS performance based solely on percent removals. The efficiency and rate of removal by the CWTS were dependent on influent concentrations, while the extent of removal was independent of influent concentration.

As illustrated by *C. dubia* toxicity experiments, toxicity associated with CWTS influent was removed upon transit through the system. Toxicity abatement by the pilot-scale CWTS resulted in undiluted effluents that had no effect on survival or reproduction of *C. dubia*. Ash basin effluents governed by the National Pollutant Discharge Elimination System (NPDES) must meet certain toxicity requirements to avoid permit violations. Results presented here indicate treatment of ash basin water with a CWTS may alleviate permit violations due to effluent toxicity because toxicity was effectively removed by the CWTS.

Biofouling and scaling in CWTS effluent were less than that of influent, which should allow more efficient reuse of ash basin water within a power plant. Since biofouling and scaling potential can be reduced by CWTS, future research should focus on specific biogeochemical processes responsible for the reduction and methods to optimize the processes.

As indicated by the results of this research, CWTSs can be designed to promote specific processes that transfer and transform COC to less bioavailable forms. In this study, the CWTS was designed to promote conditions favorable for dissimilatory sulfate

reduction (hydrosoil Eh between -250 to -50 mV) and promote the formation iron oxides and oxyhydroxides (hydrosoil Eh greater than -50 mV). These design parameters resulted in a treatment system that effectively decreased the concentration and bioavailability of arsenic, chromium, mercury, and zinc. By replicating the specific conditions responsible for the biogeochemical treatment processes in this pilot-scale CWTS, similar treatment effectiveness can be expected at a full-scale CWTS.

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# Chapter 4: Development of a Mathematical Model for Hydraulic Analysis of a Pilot-Scale Reactor in a Surface-Flow Constructed Wetland Treatment System

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4.1     <u>Abstract</u>

The present work evaluated transport of a conservative tracer (bromide) in a pilot-scale reactor of a surface-flow constructed wetland treatment system using the groundwater flow model, MODFLOW, coupled with the solute transport model, MT3DMS. Results suggest that a maximum of 10% of influent to the pilot-scale reactor entered the hydrosoil.

4.2    Introduction

Constructed wetland treatment systems (CWTSs) are natural treatment systems

that provide an efficient, low cost (construction and operation and maintenance), and

reliable alternative to conventional treatment systems (Scholes *et al.*, 1998; LeDuc and

Terry, 2005). CWTSs have been used for treating numerous types of polluted water,

including those derived from municipal, industrial, and agricultural sources; stormwaters

and polluted surface waters entering or leaving rivers and lakes (Kadlec and Knight,

1996; Lin *et al.*, 2005). CWTSs are capable of treating  a variety of aqueous pollutants

through a combination of physical, chemical, and biological processes (i.e. transfers or

transformations) (Rodgers and Castle, 2007). CWTSs are designed to remove targeted

contaminants through controlled processes. By manipulating biogeochemical conditions

within the wetland, processes effective for removal of targeted contaminants can be

utilized to decrease their concentration and bioavailability. There are two types of

CWTSs: surface-flow and subsurface flow (Mitsch and Gosselink, 2000). Surface-flow

CWTSs have flowing water above the ground surface (free-surface water) as well as

subsurface flow components, while subsurface flow CWTSs have no surface flow; all

flow is below the ground surface. To different degrees, flow through the soil (hydrosoil)

is important for effective treatment in both surface-flow and subsurface-flow CWTSs.

Macrophytes are selected to promote specific biogeochemical conditions within the

hydrosoil including oxidation/reduction potential, pH, and organic matter content. The

pilot-scale CWTS used in the present study was a surface-flow wetland.

CWTS hydraulics are a critical factor for realization of remediation goals (Lewis *et al.*, 1999; Mitsch and Gosselink, 2000; Persson and Wittgren, 2003). Inadequate attention given to CWTS hydraulics has resulted in failed performance goals (Mitsch and Gosselink, 2000). The most common method of analyzing or predicting constructed wetland treatment performance assumes plug-flow (Carleton, 2002). Plug-flow neglects a range of variables, including non-ideal flow patterns. Plug-flow conditions result in an instantaneous spike of conservative tracer injected as the influent exiting the wetland cell as an identical spike one hydraulic residence time (ratio of system volume to flow-rate) later (Martinez and Wise, 2003a). While assumptions of plug-flow conditions dominate CWTS treatment performance prediction, perfect plug-flow can not exist due to the presence of velocity heterogeneities (Lightbody *et al.*, 2007). Alternatively, constructed wetland performance may be analyzed assuming that completely mixed conditions prevail [i.e. a continuously stirred tank reactor (CSTR)]. Introduction of a conservative tracer in a CSTR would result in all parcels of water in the constructed wetland instantaneously having the same evenly distributed concentration of tracer (Martinez and Wise, 2003a). A variation of the CSTR analysis, the tanks-in-series model (TIS), which has been used with some degree of success by Kadlec (1994) and Chazarenc *et al.* (2003), can be conceptualized as a number of CSTR in series. Although the above methods have provided some insight into CWTS hydraulics, the primary aim of these models was prediction of treatment performance. CWTS hydraulics have been successfully assessed through tracer tests (Martinez and Wise, 2003a; Holland *et al.*, 2004) and numerical modeling techniques (Martinez and Wise, 2003b; Carleton and

Montas, 2007). Replication of tracer test results by a physically based numerical model will provide insight into CWTS hydrology. While numerical models have been applied to previous CWTS studies (Martinez and Wise, 2003a; Wang and Jawitz, 2006) few studies have applied a physically based three dimensional modeling scheme. Therefore, objectives of this manuscript are to: 1) apply the USGS modular groundwater flow model (MODFLOW) coupled with the US Army Corps of Engineers modular three-dimensional multispecies solute transport model MT3DMS to wetland hydraulics using selected property measurements and experimental results from a tracer test performed in a pilot-scale surface-flow constructed wetland reactor and 2) quantify physical and chemical processes governing solute transport in the pilot-scale reactor under study.

## 4.3    Materials and Methods

### 4.3.1 Design and Construction of a pilot-scale constructed wetland treatment system

Two pilot-scale surface-flow wetland reactor series were constructed. Each reactor series, A and B, consists of a 150-gallon (568 L) container (Rubbermaid® Utility Tank) planted with *Schoenoplectus californicus* C., two 70-gallon (265 L) containers planted with *S. californicus* C., and one 150-gallon (568 L) container planted with *Typha angustifolia* L. (Figure 4-1). The 150-gallon containers planted with *T. angustifolia* include a rock cascade near the influent position. Reactors 1, 2, and 3 of each series were
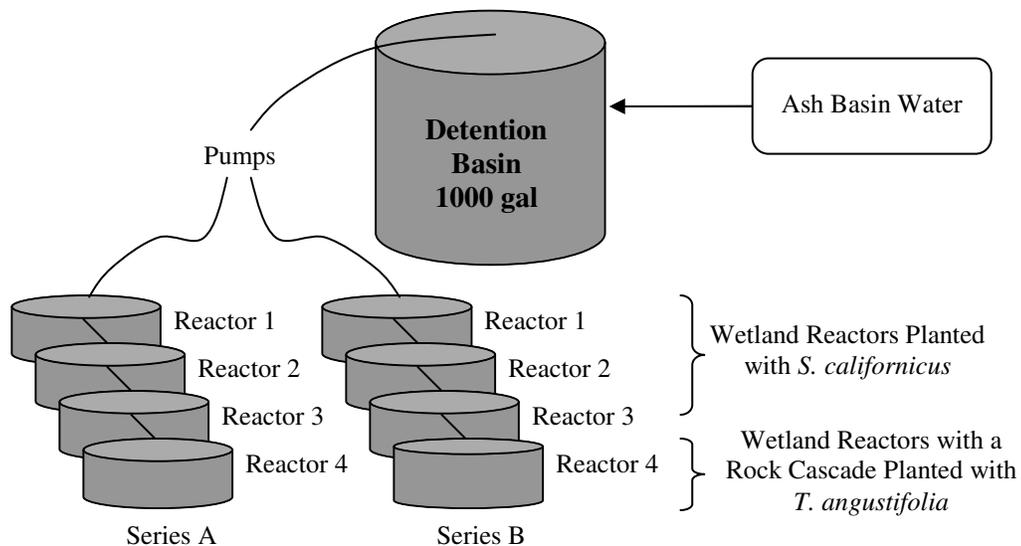


Figure 4-1. Schematic diagram of the CWTS designed for remediation.

designed to establish conditions within the reactors conducive for dissimilatory sulfate reduction (primarily an oxidation/reduction potential [Eh] between -250 and -50 mV). Reactor 4 of each series was designed to promote biogeochemical conditions favorable for the formation of iron oxides and oxyhydroxides (primarily and Eh greater than -50

mV). Hydrosoil for each reactor was collected from a nearby creek (18 Mile Creek, SC) and amended with organic matter. Influent to reactor 1 of each series was maintained by an FMI® piston pump. Reactors 1, 2, and 3 contained approximately 30 centimeters of hydrosoil (quartz sand), a 15 centimeter free-surface water zone, and wetland macrophytes. Reactor 4 of each series contained a rock cascade, 35 centimeters of hydrosoil, and a 10 centimeter free-surface water zone. The free-surface water zone in reactors 2, 3, and 4 was maintained by gravity flow from reactor 1. The nominal hydraulic retention time (ratio of system volume and influent flow rate multiplied by porosity) of reactor 1 in each series was 48 hours and the nominal hydraulic retention time of reactors 2, 3, and 4 in each series was 24 hours, corresponding to a total system hydraulic retention time of 120 hours.
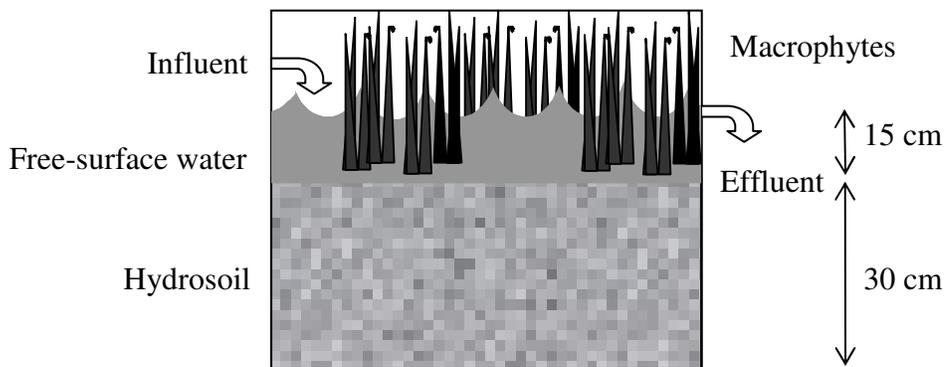


Figure 4-2. Schematic diagram of a pilot-scale constructed wetland reactor.

### 4.3.2 Tracer Testing

A potassium bromide tracer test was conducted in CWTS reactor A1 (Figure 4-1). Axial dimensions of reactor A1 are 63.5 cm in height, 147.3 cm in length, and 99.1 cm in width. Technical-grade potassium bromide (Fisher Scientific Inc., Fair Lawn, NJ) was mixed with municipal water in a 113 L (30-gallon, nominal) high-density polyethylene

(HDPE) barrel. The average influent bromide tracer concentration was 232 mg/L, which was well in excess of the measured 5 mg/L background effluent bromide concentration. The influent tracer flow-rate, 90 mL/min, was maintained by a calibrated Fluid Metering Inc. (FMI)® piston pump throughout the tracer test. During the tracer test, grab samples of reactor effluent were collected in 30-mL HDPE vials sealed with a snap top lid. Samples were transported to the laboratory and stored at a constant temperature ($20 \pm 5°C$) for 24 hours. This period allowed sample temperature to equilibrate.

Reactor effluent bromide concentrations were determined by a Thermo Orion (Beverly, MA) Model 290A portable pH and ISE meter coupled with a Thermo Orion 96-35 ionplus® series bromide electrode.

### 4.3.3 Determination of CWTS hydrosoil saturated hydraulic conductivity

The saturated hydrosoil hydraulic conductivity ($K_s$) of reactor A1 was estimated with a 7.6 cm inside diameter (3-inch, nominal) constant-head permeameter (Fetter, 2001). A grab sample of hydrosoil from reactor A1 was collected and packed (i.e. tamped with a rubber mallet) into a column screened above and below the sample. Constant hydraulic head gradients of 0.1, 0.25, 0.4, and 1 were applied to the hydrosoil sample while monitoring effluent flow rate. $K_s$ was determined through a variation of Darcy's law:

$$K_s = \frac{VL}{At\Delta h} \tag{4.1}$$

where $K_s$ = saturated hydraulic conductivity (cm/min), $V$ = volume of water (cm$^3$) discharging from the permeameter in time $t$ (min), $L$ = length of hydrosoil sample

interval (7.6 cm), $A$ = cross-sectional area of hydrosoil sample (cm$^2$), $t$ = time (min), and

$\Delta h$ = hydraulic head differential through hydrosoil sample (cm). At least 3 replicate

measurements of $K_s$ were made at each hydraulic head gradient.

*4.3.4 Determination of CWTS hydraulic head differential*

The hydraulic head differential in the free-surface water of reactor A1 (Figure

4-1) was determined using a manometric technique. An inverted U-tube differential air-

water manometer (Winter *et al.*, 1988) is a device for measuring a pressure differential

(e.g. hydraulic head) between two points in a system (King *et al.*, 1948). However, when

pressure differentials fall below the accuracy of available measurement devices,

amplification (by a known amount) of the pressure differential is required. A simple

amplification method replaces air in an air-water manometer with a fluid immiscible in

water (e.g. oil) having a specific gravity greater than air but less than water (Kelly and

Murdoch, 2003).

Vegetable oil was used as the immiscible fluid because it had the desired

properties (i.e. immiscible in water and density between air and water). The oil-water

manometer was constructed from two 2.5 m sections of vinyl tubing connected by a
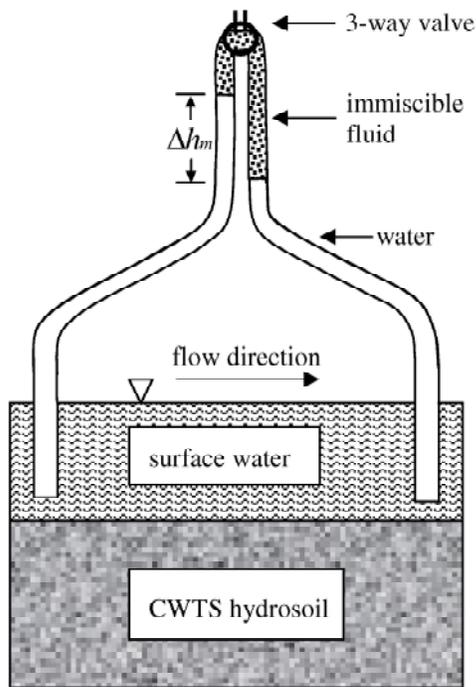
three-way valve (Figure 4-3).

Figure 4-3. Oil-water manometer used to measure the hydraulic head differential of reactor A1.

### 4.3.4.1 Oil Water Manometer Calibration

Laboratory experiments were performed to determine the accuracy and precision of the oil-water manometer. Following suggestions by Kelly and Murdoch (2003), a period of at least 10 minutes between each hydraulic head measurement of differing magnitude allowed the oil-water manometer to equilibrate. Five replicate laboratory measurements were made at each of seven hydraulic head differentials. Resultant hydraulic head differentials measured with the oil-water manometer ($\Delta h_m$) were plotted as a function of actual hydraulic head differentials ($\Delta h_a$). A linear calibration curve was calculated, using the method of least squares, from the plot of $\Delta h_m$ as a function of $\Delta h_a$. The average (n=7) relative error ([approximate-exact]/exact) associated with all laboratory hydraulic head differentials was <0.033 with a range of 0.008-0.120.

*4.3.4.2   Oil Water Manometer Field Measurements*

The calculated calibration curve equation generated from laboratory experiments was used to infer $\Delta h_a$ from $\Delta h_m$ in field experiments. One end of each section of vinyl tubing was inserted into the constructed wetland free-surface water near influent and effluent locations (Figure 4-3). The opposing end of vinyl tubing was connected to a 3-way valve. A screw-on syringe was fitted on the third leg of the 3-way valve (i.e. the leg not connected to a vinyl tube) in order to fill the vinyl tubing with water. After filling each tube with water, the valve was closed to all openings and the syringe removed. The syringe was filled with vegetable oil and reattached to the 3-way valve, the valve was opened and vegetable oil was introduced to each vinyl tube simultaneously. The oil-water manometer was allowed to equilibrate in field experiments for at least 12 hours prior to measuring the hydraulic head differential. Hydraulic head differential measurements were made early in the day to circumvent dampened hydraulic head differentials resulting from elevated evapotranspiration.

*4.3.5 Model Construction*

The modular three-dimensional physically based USGS developed model, MODFLOW (McDonald and Harbaugh, 1988), was utilized to simulate both surface and sub-surface flow in the CWTS. MODFLOW was combined with the US Army Corps of Engineers modular three-dimensional solute transport model MT3DMS (Zheng and Wang, 1999) to simulate solute transport in reactor A1. The MODFLOW-MT3DMS linkage used MODFLOW-96 v.3.3 (McDonald and Harbaugh, 1988) and MT3DMS v.4.5 (Zheng and Wang, 1999).

MODFLOW is a fully distributed model available free of charge from the USGS (http://water.usgs.gov/nrp/gwsoftware/modflow.html) that calculates groundwater flow from aquifer characteristics. The groundwater flow equation is represented using finite-difference approximations, which require the aquifer be divided into cells with uniform aquifer characteristics. MODFLOW calculates the unknown head at a node centered in the cell. Governing equations assume saturated-flow conditions exist, Darcy's Law applies, the density of groundwater is constant, and the selected coordinate system points along the principal directions of anisotropy in anisotropic materials.

MT3DMS is a fully distributed model available free of charge from the University of Alabama (http://hydro.geo.ua.edu/mt3d/) that can simulate advection, dispersion, dual-domain mass transfer, and chemical reactions of dissolved constituents (Zheng and Wang, 1999).

*4.3.5.1  Grid*

The model grid consists of 2 stratigraphic units (i.e. free-surface water and hydrosoil) represented by 19 layers, 39 rows, and 29 columns. A total of 16,089 active cells were used in the simulation. Nineteen (i.e. rather than two) layers should increase resolution and accuracy of model predictions. The dimensions of a basic cell were 4 cm by 4 cm by 3.2 cm with gradually refined cell dimensions of 2 cm by 1.3 cm by 3.2 cm near influent and effluent locations, and maximum cell dimensions of 6 cm by 4 cm by 3.2 cm. Dimensions of cells did not exceed 1.5 times the dimensions of neighboring cells.

*4.3.5.2   Calibration*

$K_s$, $\Delta h_a$, and temporal constructed wetland effluent tracer concentrations, $C(t)$, were available for model calibration. The model was calibrated in steady-state flow conditions. MODFLOW was used to solve the groundwater flow equation for the hydraulic head distribution. The hydraulic head distribution and Darcy's law were calculated cell-by-cell by MODFLOW to establish the groundwater flow field. This information was then used by MT3DMS to calculate the tracer concentrations as a function of position and time.

*4.3.5.2.1   Groundwater Flow Model*

Free-surface water hydraulic conductivity ($K_{fsw}$) was estimated by 'trial and error' calibration. The hydraulic head differential of the model, which is controlled by $K_{fsw}$, was calibrated using the average of three $\Delta h_a$ values. Varying $K_{fsw}$ allowed comparison between simulated hydraulic head differentials ($\Delta h_{mod}$) and $\Delta h_a$. $K_{fsw}$ was assumed to be representative of the actual free-surface water hydraulic conductivity when the relative percent difference (RPD) (equation 4.2) between $\Delta h_{mod}$ and $\Delta h_a$ was less than 10%. The average of all measured values of $K_s$ was used as the hydrosoil hydraulic conductivity of the model. The results of this calibration were used as starting conditions for solute transport modeling.

$$\text{RPD} = \left( \frac{|\Delta h_{mod} - \Delta h_a|}{\text{Mean}\ (\Delta h_{mod}, \Delta h_a)} \right) * 100 \qquad (4.2)$$

*4.3.5.2.2   Solute Transport Model*

The dual-domain solute transport model (DDM), recommended for modeling heterogeneous porous media (Zheng and Wang, 1999), was used to simulate solute transport in the free-surface water region of reactor A1. The DDM allows transfer of material between mobile (advective transport is dominant) and immobile (advective transport does not occur or is relatively small) domains and is characterized by a mass (i.e. solute) transfer relationship driven by a concentration difference between domains (Zheng and Wang, 1999). The homogenous hydrosoil of reactor A1 was represented by the conventional single-domain mass transport modeling capability of MT3DMS. Therefore, the only parameter required for mass transport in the hydrosoil was porosity, which was assumed to be 0.3.

It was reasoned that a much greater percentage of water would move through the free-surface water region than the hydrosoil region, so free-surface flow would control the time of first tracer breakthrough in the CWTS effluent. The mobile porosity of the free-surface water region ($\Phi_m$) was estimated by 'trial and error' calibration. $\Phi_m$ approximated the actual free-surface water mobile porosity when simulated tracer breakthrough occurred at approximately the same time as measured initial tracer breakthrough. Previous authors (Hammer and Kadlec, 1986; McKillop *et al.*, 1999; Bolster and Saiers, 2002) have assumed the total porosity of the free-surface water region (sum of mobile and immobile domain porosities) to be in the range 0.8 to 0.95. For the present work we adopted a free-surface water region total porosity of 0.9. Therefore, the immobile domain porosity ($\Phi_{im}$) was 0.9 minus $\Phi_m$. The mass-transfer coefficient of the

free-surface water region, $\zeta_{fsw}$, was varied systematically to reduce the sum of squares between observed and modeled constructed wetland effluent tracer concentrations. An additional input parameter for the DDM is dispersivity (longitudinal and transverse). While dispersivity would be an ambiguous scale dependent parameter required for the classical advection-dispersion model (Gelhar *et al.*, 1992), the DDM introduces differential advection (a type of solute spreading exclusive to the DDM) through transfer of a solute between mobile and immobile domains (Flack *et al.*, 2004). Differential advection dominates mechanical dispersion and mixing in the dual-domain model (Feehley *et al.*, 2000). Following the approach of Harvey and Gorelick (2000), dispersivity was omitted in the present dual-domain model.

## 4.4    Results

### 4.4.1 Tracer Testing

Effluent bromide tracer concentrations with time (Figure 4-4) had a peak concentration of 64 mg/L after only 995 minutes. This peak concentration was followed by a drop in concentration and an extended tracer 'tail'. Sample collection was terminated 6540 minutes after injection began. Therefore, an exponential fit to late time data (i.e. 2165 to 6540 minutes after tracer injection began) extended the $C(t)$ curve. The exponential fit to late time data (Figure 4-4) has a Pearson product-moment correlation coefficient (Glantz, 1992) of 0.987, supporting theorized exponential decrease of constructed wetland effluent tracer concentrations with time.
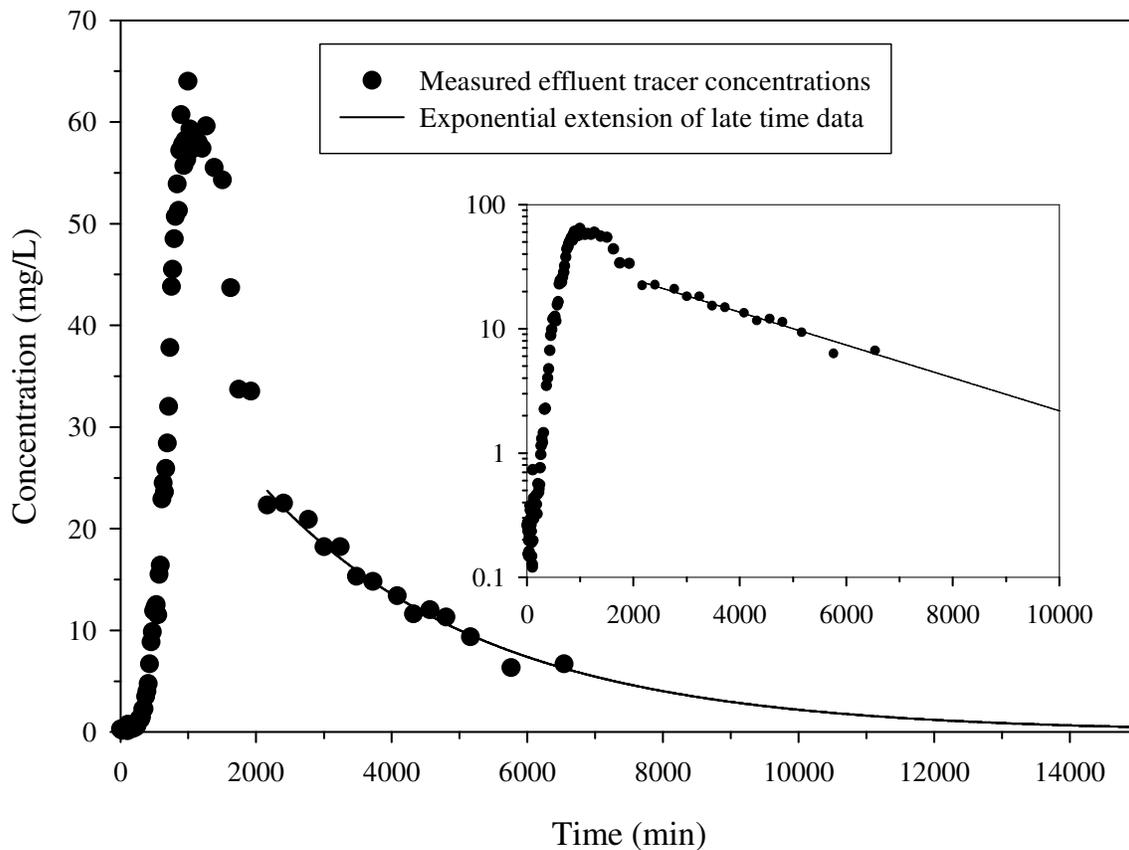
Figure 4-4. Measured (filled circles) and exponential extension of late time (lines) constructed wetland effluent tracer concentrations with time. Concentrations are shown on a log-scale inset to highlight measured late time exponential concentration decrease.

Rainfall entering the reactor and evapotranspiration leaving the reactor were minimized by placing a 10x10x12 ft canopy over the reactor. Effluent flow-rate was found to be approximately equal to influent flow-rate (data not shown), therefore, water loss through evapotranspiration and water gain through precipitation were considered negligible. Of the 12.7 grams of injected tracer, 99.1% was collected in CWTS reactor A1 effluent (Figure 4-5).
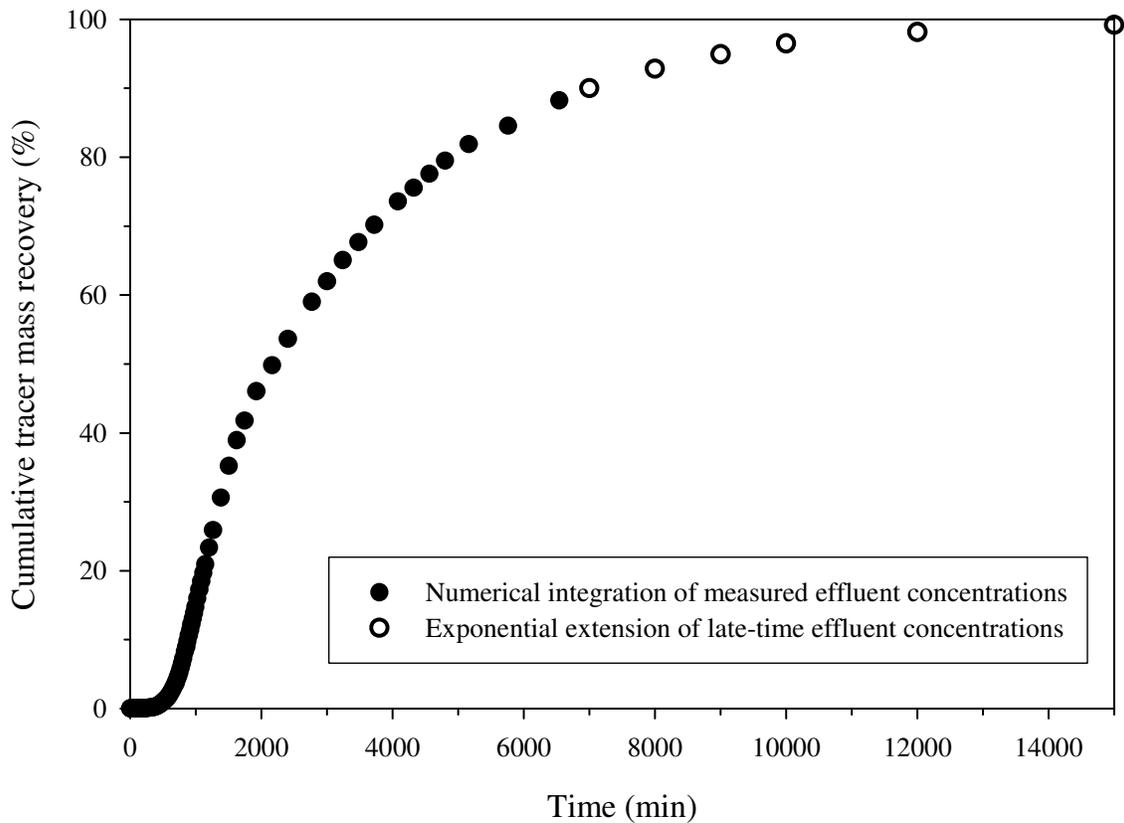
Figure 4-5. Cumulative mass recovery of 99.1% injected tracer in constructed wetland reactor A1 effluent validates conservancy of tracer and supports accurate tracer analysis and flow quantitation.

*4.4.2 Determination of Saturated Hydraulic Conductivity*

Measured values of $K_s$ (Table 4-1) decreased as hydraulic head gradient increased. However, a Kruskal-Wallis one-way ANOVA on ranks ($p<0.05$) revealed no significant differences between measured hydraulic conductivity values determined at different head gradients.

Table 4-1. Saturated hydraulic conductivity of reactor A1 hydrosoil.

| Head gradient (units) | Hydraulic conductivity (cm/min) |
|---|---|
| 0.30 | 12.1 (11.7-12.5) |
| 0.75 | 10.8 (10.5-10.9) |
| 1.20 | 10.2 (10.0-10.4) |
| 3.00 | 9.9 (9.4-10.4) |

Values in parenthesis represent the range of replicate measurements.

*4.4.3 Determination of CWTS hydraulic head differential*

Using the oil-water manometer, a total of 60 hydraulic head differential measurements were made over an 8 day period. Values of $\Delta h_a$ are remarkably consistent, varying by a maximum factor of ~1.8 (i.e. trials 2 and 3) (Table 4-2).

Table 4-2. Hydraulic head differential of reactor A1. Values were averaged for all measurements taken during each trial.

| Trial | Actual hydraulic head differential (cm) |
|---|---|
| 1 | 0.021 (0.018-0.022) |
| 2 | 0.017 (0.016-0.018) |
| 3 | 0.027 (0.026-0.028) |

Values in parenthesis represent the range of replicate measurements.

*4.4.4 Model*

Model parameters used to simulate observed constructed wetland effluent tracer concentrations are listed in Table 4-3.

Table 4-3. Parameters used to simulate solute transport in reactor A1 were measured or result from the calibration process.

| Parameter | Free-surface water | Hydrosoil |
|---|---|---|
| Hydraulic conductivity[‡] (cm min$^{-1}$) | 800 | 11 |
| Mobile Domain Porosity | 0.25 | 0.3 |
| Immobile Domain Porosity | 0.65 | N/A |
| Mass-transfer coefficient (min$^{-1}$) | 0.0004 | N/A |

[‡]Hydrosoil hydraulic conductivity is the average of 15 hydrosoil hydraulic conductivity measurements.
N/A = not applicable

The groundwater flow model MODFLOW calculates the volumetric rate of entry and exit of water into each layer. The hydrosoil hydraulic conductivity used in the model (11 cm/min) allowed ~3% of influent to enter the constructed wetland hydrosoil. The sensitivity of the rate of water entering constructed wetland hydrosoil to $K_s$ was determined by plotting the rate of water entering the hydrosoil as a function of differing $K_s$ values (Figure 4-6). Increasing model $K_s$ values by 50% resulted in 4.5% of influent entering constructed wetland hydrosoil, while decreasing model $K_s$ values by 50% resulted in 1.5% of influent entering constructed wetland hydrosoil.
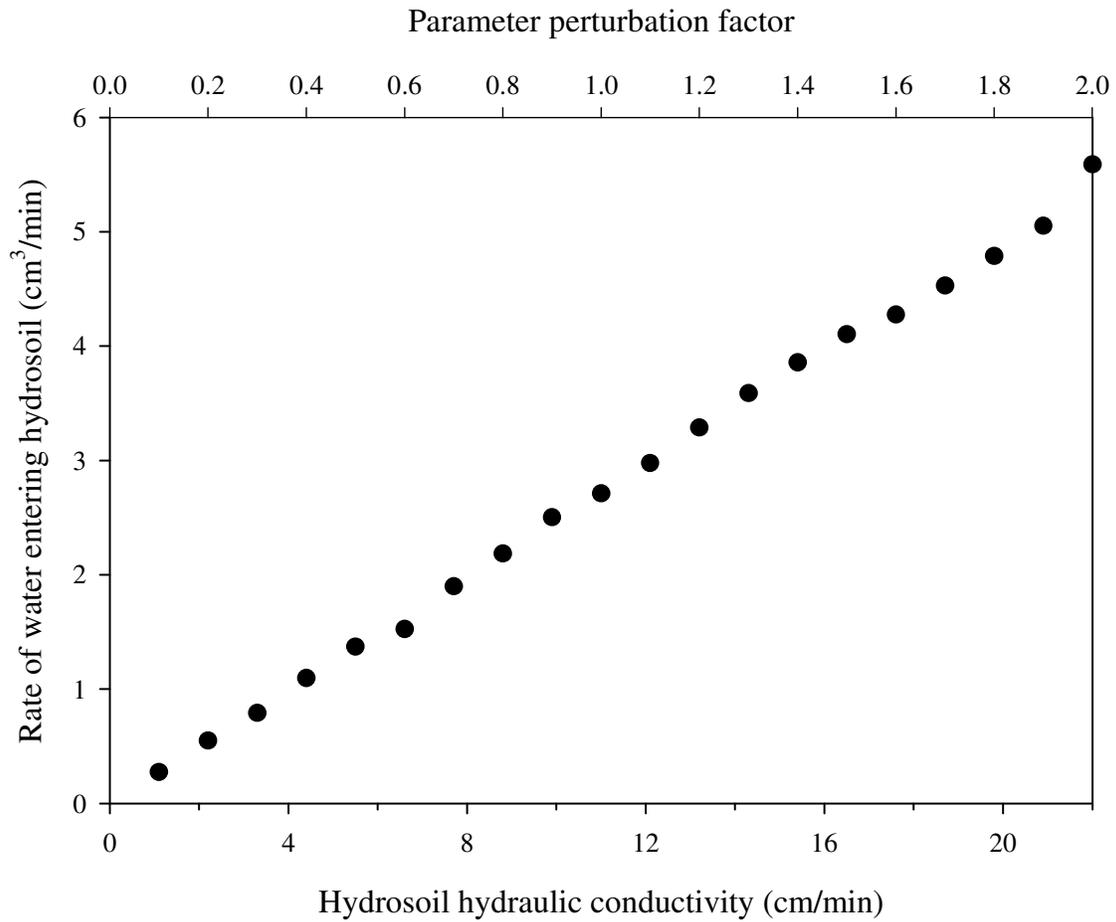
Figure 4-6. Effect of hydrosoil hydraulic conductivity on the rate of water entering constructed wetland hydrosoil.

The groundwater flow model MODFLOW and coupled solute transport model MT3DMS accurately reproduced effluent tracer concentrations with time (Figures 4-6 and 4-7). Measured (including exponential extension of late time data) and simulated effluent tracer concentrations had a Pearson product-moment correlation coefficient in excess of 0.98.
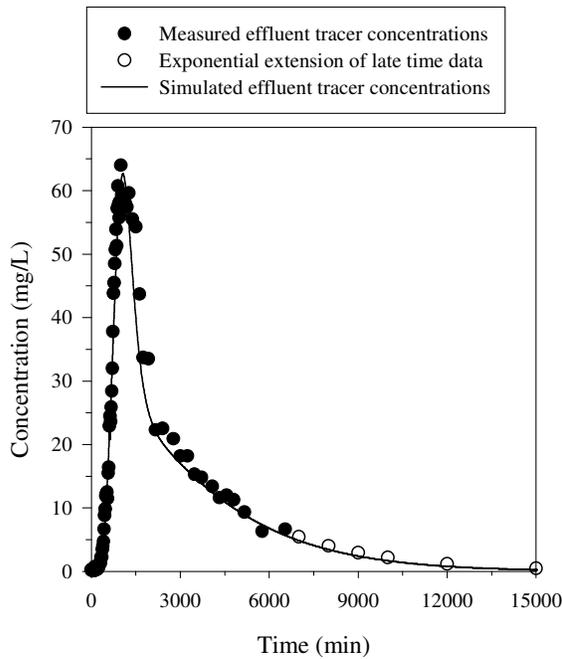
Figure 4-7. Model effluent tracer concentrations superimposed on measured and exponentially extended effluent tracer concentrations.
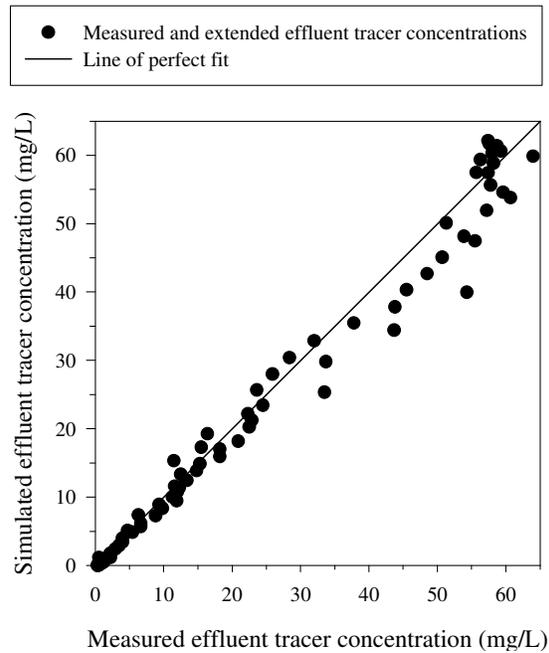
Figure 4-8. Simulated effluent tracer concentrations as a function of observed effluent tracer concentrations display an excellent fit with a correlation coefficient of 0.98.

Variation of $\Phi_m$, $\Phi_{im}$, and $\zeta_{fsw}$ were made to assess the importance of each parameter in solute transport. The mobile porosity of the free-surface water region has a notable effect on the time of simulated tracer breakthrough. As $\Phi_m$ increased, the time of simulated effluent tracer concentration breakthrough decreased (Figure 4-9). A mobile porosity of 0.25 resulted in a first breakthrough time similar to that measured in constructed wetland effluent. Mobile porosity values greater than or less than 0.25 resulted in breakthrough times that were later and earlier, respectively, than those of measured tracer breakthrough concentrations.
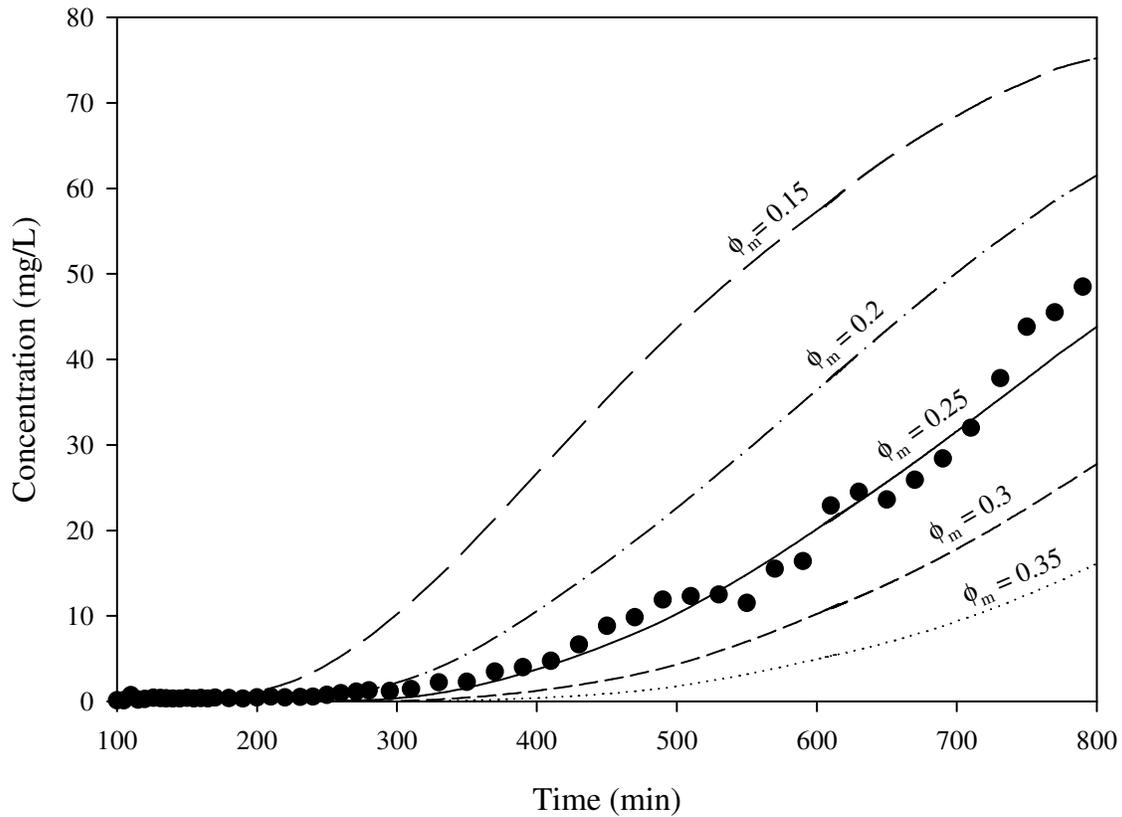
95

Figure 4-9. Effect of mobile porosity on tracer breakthrough in constructed wetland effluent. Filled circles represent measured effluent concentrations with time; lines represent mobile porosity values.

Variations of $\Phi_{im}$ (0.6 to 0.7) between bounds appropriate for the constructed wetland under study had a less pronounced effect on simulated effluent tracer concentrations than variations in $\Phi_m$ (Figures 4-8 and 4-9). As $\Phi_{im}$ increased over the interval 1000 to 4500 minutes simulated effluent tracer concentrations decreased. As $\Phi_{im}$ increased over the interval 4500 minutes to 15000 minutes simulated effluent tracer concentrations increased. An immobile porosity of 0.65 provided an effective fit to late time data extending over the entire simulation interval (4500 to 15000 minutes).
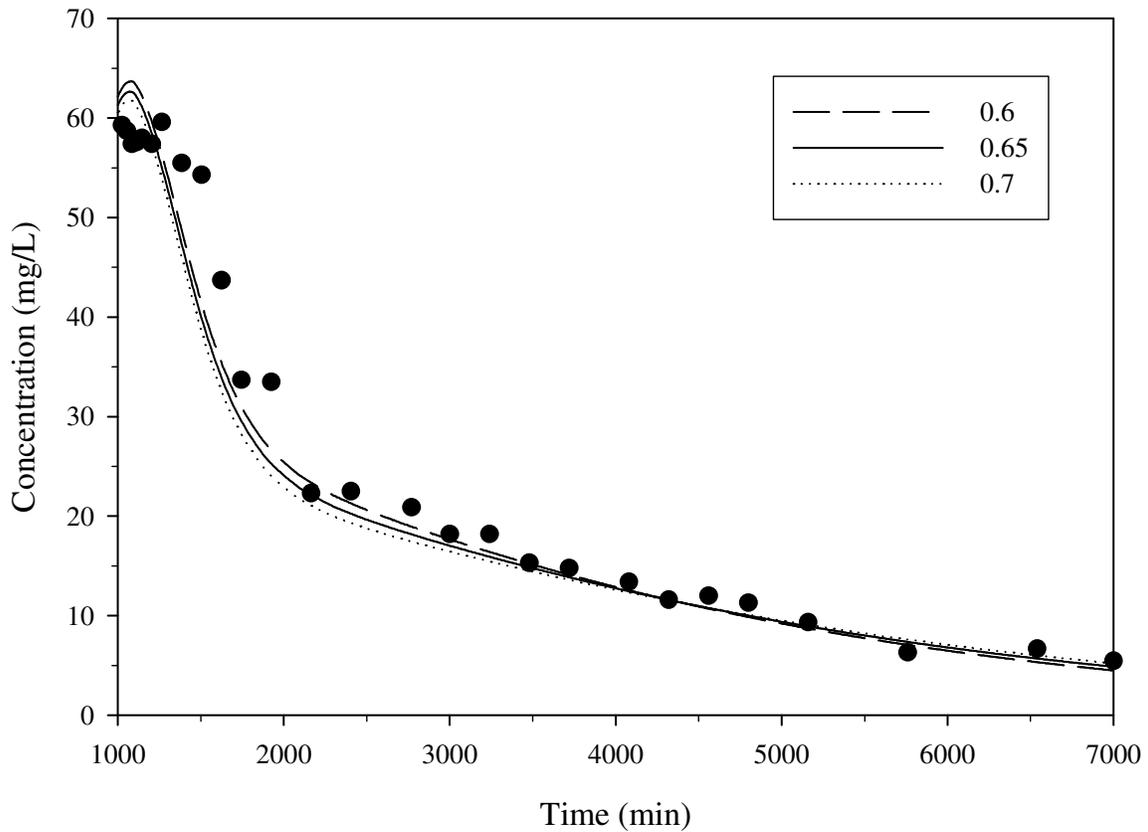
Figure 4-10. Effect of immobile porosity on simulated late time concentrations (lines). Measured effluent tracer concentrations are shown with filled circles.

The model predicted the peak effluent tracer concentration to be greater than that of the measured peak effluent tracer concentration when $\zeta_{fsw}$ was less than 0.0004/min and predicted the peak effluent tracer concentration to be less than that of the measured peak effluent tracer concentration when $\zeta_{fsw}$ was greater than 0.0004/min (Figure 4-11). In the interval 2000 to 8000 minutes, the model predicted effluent tracer concentrations greater than measured effluent tracer concentrations when values of $\zeta_{fsw}$ were less than 0.0004/min and less than measured effluent tracer concentrations when values of $\zeta_{fsw}$ were greater than 0.0004/min. A mass transfer coefficient of 0.0004/min provided an

effective fit to measured effluent tracer concentrations over the entire interval of

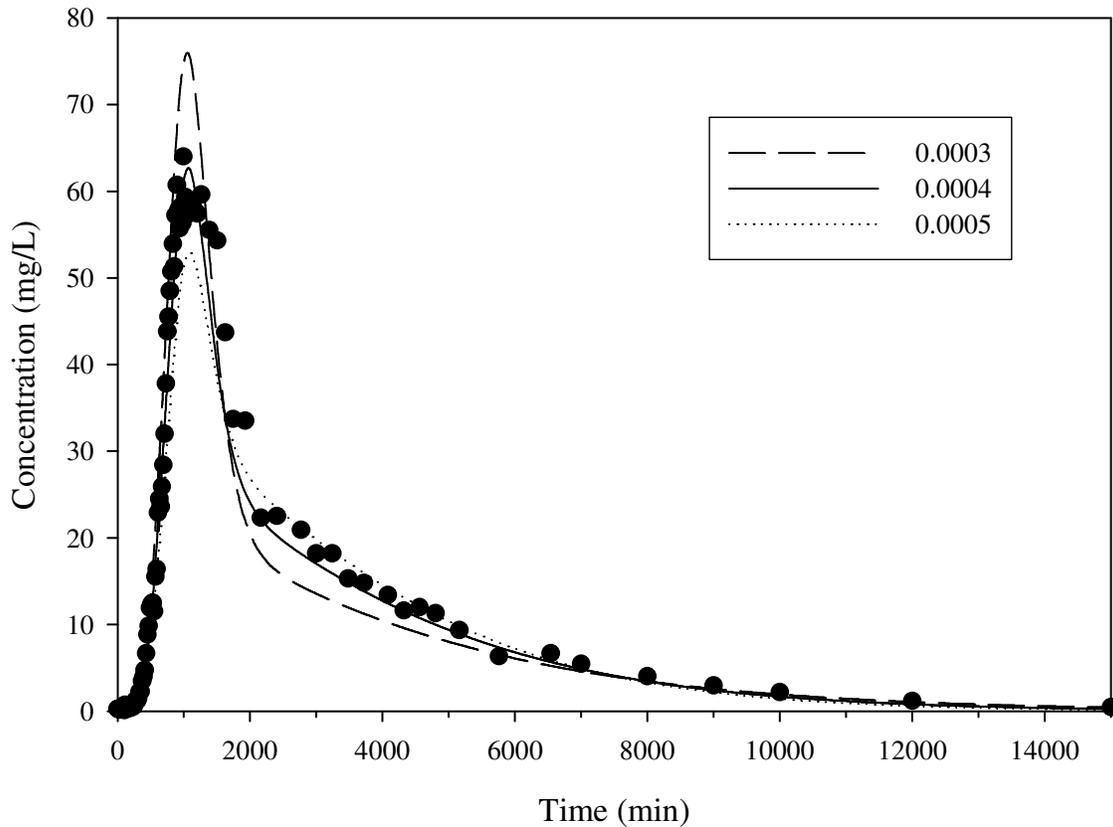measured and exponentially extended concentrations with time (Figure 4-11).



Figure 4-11. Effect of mass transfer coefficient (min$^{-1}$) on simulated effluent tracer
concentrations (lines). Measured effluent tracer concentrations are shown with filled
circles.

## 4.5    Discussion

Similar constructed wetland tracer test responses to those observed in this study

have been observed in other surface-flow wetland hydrologic studies (Lin *et al.*, 2003;

Martinez and Wise, 2003a; Holland *et al.*, 2004; Wang and Jawitz, 2006). Recovery of

99.1% injected tracer validates conservancy of the tracer used, indicates water loss was

negligible, and supports accurate effluent tracer analysis and flow quantification (Figure 4-4).

Influent entering the uppermost hydrosoil layer during the 15,000 minute steady-state simulation was 2.7 $cm^3$/min (Figure 4-6), when using the average of the measured hydraulic conductivity values (11 cm/min). This rate of entry into the hydrosoil represents approximately 3% of the total volume of influent to reactor A1. Due to potential errors associated with $K_s$ measurements, model $K_s$ values were increased to 22 cm/min, 100% greater than that measured. This increase in $K_s$ results in an increase in the volume of influent entering constructed wetland hydrosoil to 6.2%. An additional influx of water into the hydrosoil likely results from transpiration by macrophytes. Measurement of the rate of evapotranspiration (ET) occurring over a 48 hour period in April 2007 (data not shown) and modeling results presented here indicate the maximum volume (i.e. assuming transpiration fully accounts for measured ET and $K_s$ is 22 cm/min) of water that entered the pilot-scale surface-flow constructed wetland hydrosoil during the tracer test was 9 $cm^3$/min (i.e. 10% of influent).

Current theory on trace element removal by constructed wetlands suggests removal occurs primarily in the hydrosoil, thus maximizing contact time with hydrosoil components results in increased treatment efficiency (Kadlec and Knight, 1996). The constructed wetland considered here has been shown to effectively decrease the concentration and bioavailability of trace elements (see Chapter 3). However, modeling results presented here suggest only a small percentage (<10%) of influent entered the constructed wetland hydrosoil. Others (e.g., Donahoe and Liu, 1998; Gao *et al.*, 2000)

have noted what is interpreted to be a similar trend by measuring a dramatic decrease in concentration of sequestered trace elements with increasing hydrosoil depth. Since treatment (i.e. a reduction in concentration of trace elements) occurred within the surface-flow constructed wetland reactor under study (Chapter 3) under hydrologic conditions similar to those described here (i.e. less than 10% of CWTS influent entering the hydrosoil), modeling results presented in the present study suggest that the sediment water interface plays a major role in the treatment of trace elements by CWTSs. The sediment-water interface has been shown to control the distribution of trace elements adsorbed to iron and manganese oxyhydroxides (Donahoe and Liu, 1998). Therefore, biogeochemical processes occurring at the sediment-water interface are likely responsible for a portion of the observed reduction in concentration of trace elements.

4.6    Conclusions

The developed wetland flow and solute transport model successfully simulated transport of a non-reactive tracer (bromide) in a pilot-scale reactor of a surface-flow constructed wetland (Figures 4-6 and 4-7). Two zones were identified with the solute transport model. The first zone is an actively flowing region of the main flow channels (i.e. advective solute transport). The second zone is a no-flow 'temporary storage' region in which a solute may reside for a portion of time prior to re-entering the actively flowing region of the main flow channels. The identification of the two zones is a facet of the dual domain model, which assumes that a porous media may be conceptually divided into two interacting sub-media; a mobile domain (actively flowing region) and an immobile domain (no-flow 'temporary storage' region).

The rate of water entering hydrosoil of the surface-flow wetland reactor was shown to increase as the hydraulic conductivity of the hydrosoil increased (Figure 4-6). However, since the effective hydraulic conductivity of the free-surface water was so high (Table 4-3), increasing the hydraulic conductivity of the hydrosoil by a factor of 2 greater than that measured (Table 4-1) had an insignificant effect on the rate of water entering the hydrosoil (Figure 4-6). Therefore, the rate of influent entry into hydrosoil of the pilot-scale reactor, determined from modeling results presented here, suggests observed treatment (Chapter 3) within the hydrosoil of the surface-flow reactor occurs near the sediment water interface.

## 4.7    Symbols used

CWTSs—constructed wetland treatment systems
CSTR—continuously stirred tank reactor
TIS—tanks in series
USGS—United States Geological Survey
MT3DMS—modular 3-dimensional transport multi-species
COC—constituents of concern
Eh—oxidation/reduction potential
FMI—fluid metering, inc.
HDPE—high density polyethylene
ISE—ion selective electrode
$K_s$—saturated hydraulic conducitivity
$V$ —volume of water discharging from the constant-head permeameter
$L$— length of hydrosoil sample interval
$A$—cross-sectional area of hydrosoil sample
$t$—time
$\Delta h$— hydraulic head differential through hydrosoil sample
$\Delta h_m$— hydraulic head differential measured with the oil-water manometer
$\Delta h_a$— actual hydraulic head differential
$C(t)$—temporal constructed wetland effluent tracer concentrations
$K_{fsw}$—free-surface water hydraulic conductivity
$\Delta h_{mod}$—simulated hydraulic head differentials
RPD—relative percent difference

DDM—dual domain solute transport model
$\Phi_m$—mobile porosity of the free-surface water region
$\Phi_{im}$—immobile domain porosity
$\zeta_{fsw}$ —mass-transfer coefficient of the free-surface water region
ANOVA—analysis of variance

4.8    References

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# Chapter 5: Conclusions

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Ash basin water which results from sluicing coal ash may contain numerous toxic trace elements. Toxic trace elements commonly found in ash basin water include: arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, selenium, and zinc. With more stringent discharge limits imposed on low level contaminants, the disposal of ash basin waters has become increasingly expensive. Treatment and reuse of ash basin water has the potential to reduce industrial water consumption, thereby decreasing disposal costs. Constructed wetland treatment systems (CWTSs) offer a low-cost alternative to traditional 'concrete-and-steel' remediation techniques. Research presented here investigated the use of pilot-scale CWTSs to treat (i.e. transfer or transform) identified constituents of concern and reduce the formation of reuse limiting parameters in ash basin water and investigate processes responsible for treatment.

The focus of the second chapter of this thesis was to characterize ash basin water and identify constituents of concern (COC) in ash basin water from a risk-based perspective. This was accomplished through the completion of the following objectives: 1) compile data on the composition of ash basin water from published literature investigations, 2) measure the concentration of trace elements in ash basin water samples, and 3) apply risk quotient (RQ) method to identify COC in ash basin water. Through completion of these objectives, it was determined that ash basin water contains numerous potentially toxic elements including: aluminum, cadmium, chromium, copper, iron, lead, mercury, selenium, and zinc, and pH.

The focus of the third chapter of this thesis was to determine the role a constructed wetland treatment system may play in treatment of ash basin water. This was

accomplished through completion of the following objectives: 1) determine the ability of CWTSs to decrease the concentration of COC in ash basin water, 2) determine the ability of CWTSs to reduce toxicity associated with COC in ash basin water, and 3) determine the ability of CWTSs to reduce reuse-limiting parameters of ash basin water. The concentration of arsenic, chromium, mercury, and zinc in all CWTS effluent samples was less than that of influent samples. The concentration of selenium in each CWTS series (A and B) effluent was less than that of influent in 7 of 9 samples. The reduction in concentration of COC in ash basin water was accomplished by establishing biogeochemical conditions which occur naturally in wetlands. These natural biogeochemical conditions were achieved by selecting certain criteria (e.g. plant species, hydrosoil, organic matter content, etc.) to yield an environment conducive for the following removal processes: precipitation as nonbioavailable sulfide minerals, co-precipitation with iron oxyhydroxides and sorption onto iron oxides. Reducing the concentration and bioavailability of COC in ash basin water will allow discharge of ash basin water to aquatic receiving systems with little risk to aquatic receiving system biota.

Within a power plant, reuse controlling parameters in ash basin water include corrosion, biofouling, and scaling. Corrosion of copper coupons placed in CWTS effluent increased as compared to influent. Biofoul in hydraulic transportation systems can reduce flow volume, thereby reducing efficiency. However, biofoul formation in CWTS effluent was less than biofoul in CWTS influent. Scale deposits on glass coupons indicate potential scale formation following treatment with CWTS. Effluent scale formation was less than influent scale formation. The observed reduction of biofoul and scale deposits

on hydraulic transportation systems as a result of treatment with a CWTS should allow more efficient effluent reuse due to lower transport costs.

The fourth chapter of this thesis focused on the development of a mathematical model to describe the hydraulics of a pilot-scale reactor in a surface-flow CWTS. This was accomplished through the following objectives: 1) apply the USGS modular groundwater flow model (MODFLOW) coupled with the US Army Corps of Engineers modular three-dimensional multispecies solute transport model MT3DMS to wetland hydraulics using experimental tracer results from a pilot-scale constructed wetland reactor and 2) quantify physical and chemical processes governing solute transport in the pilot-scale CWTS reactor under study. The developed wetland flow and solute transport model simulated transport of a non-reactive tracer (bromide) in a pilot-scale reactor of a surface-flow constructed wetland. Two main zones (surface flow and subsurface flow) were identified with the solute transport model. Surface-flow was subdivided into two parts. The first part was an actively flowing region of the main flow channels (i.e. advective solute transport). The second part was a no-flow (or very low-flow) 'temporary storage' zone in which a solute may reside for a portion of time prior to re-entering the actively flowing region of the main flow channels. Since treatment of trace elements was observed in the reactor studied in Chapter 4 (see Chapter 3) under hydrologic conditions similar to those present during the tracer test, modeling results suggest that treatment at the sediment water interface plays a major role in treatment of trace elements.

Based on the results of our study, CWTSs are a viable option for treating ash basin water. CWTSs can be designed to promote specific biogeochemical treatment

processes that transfer and transform targeted COC to less bioavailable forms. In this study the CWTS was designed to promote conditions (primarily a hydrosoil Eh range of -250 to -50 mV) favorable for dissimilatory sulfate reduction and promote the formation of iron oxides and iron hydroxides (primarily a hydrosoil Eh greater than -50 mV). These design parameters resulted in a treatment system that effectively decreased the concentration and bioavailability of chromium, arsenic, zinc, and mercury. By replicating the specific conditions responsible for the biogeochemical treatment processes in this pilot-scale CWTS, similar treatment effectiveness can be expected at a full-scale CWTS.