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# CONSTRUCTED WETLAND TREATMENT SYSTEM: AN APPROACH FOR MITIGATING RISKS OF FLUE GAS DESULFURIZATION WATERS

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CONSTRUCTED WETLAND TREATMENT SYSTEM: AN APPROACH FOR  
MITIGATING RISKS OF FLUE GAS DESULFURIZATION WATERS

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A Dissertation  
Presented to  
the Graduate School of  
Clemson University

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In Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy  
Environmental Toxicology

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by  
Derek Anderson Eggert  
May 2009

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Accepted by:  
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## ABSTRACT

Federal laws regarding ambient air quality are currently requiring industries to reduce emissions of sulfur dioxides (SO<sub>2</sub>). Coal-fired power plants have therefore begun implementing flue gas desulfurization (FGD) scrubbers that utilize a highly oxygenated water stream (calcium carbonate saturated water) to transform sulfur gases into soluble anion species (e.g. sulfite and sulfate). This FGD process also transfers potentially toxic constituents including arsenic, cadmium, chemical oxygen demand, copper, mercury, selenium, chloride, sulfates, and zinc into the scrubbing water. These scrubber waters, referred to as FGD waters, present an industrial problem due to the large volumes produced (378,000 to 1,900,000 L/day) and regulations regarding their discharge such as National Pollutant Elimination and Discharge System (NPDES) permits. Constituents that exceed NPDES permit discharge limits or can adversely affect sentinel toxicity testing species must be treated before discharge and were referred to as constituents of concern (COC) in our research. A plausible treatment alternative for FGD waters is remediation utilizing constructed wetland treatment systems (CWTS). Problematic constituents including metals, metalloids, nutrients (i.e. nitrogen and phosphorus), herbicides, pesticides, and generic organics (e.g. oil and grease compounds) have been decreased to acceptable discharge limits using CWTS. In order to design pilot-scale CWTS for FGD waters, we measured and identified the COC for all FGD waters used in this research. COC in these FGD waters were cadmium (Cd), chlorides (Cl), nickel (Ni), mercury (Hg), and selenium (Se) (Chapter Two), arsenic (As), Cd, chemical oxygen demand (COD), Cl, copper (Cu), Hg, Se, and zinc (Zn) (Chapter Three), Hg and Se

(Chapter Four), and Se (Chapter Five). While the design of pilot-scale CWTS differed during this research, all systems targeted the removal of metals (Cd, Cu, Hg, Ni, and Zn) and metalloids (Se and As) through microbial reductive pathways in reducing reactors (-200 to 0 mV) and targeted oxidative pathways in the oxidizing reactors (0 to +150 mV). Pilot-scale CWTS are shown to decrease the identified COC in these FGD waters and provided removal rates in order to understand the scaling potential of these systems. Additionally, it was confirmed that pilot-scale CWTS were successful for decreasing the toxicity of FGD waters with co-management techniques for chlorides. Since FGD waters can differ based on site of production and can contain elements or compounds that limit the treatment of COC such as selenium and mercury, organic carbon additions were evaluated for enhancing the performance of CWTS for Se and Hg in two FGD waters. Organic carbon (e.g. molasses, glucose, and trypticase soy broth) additions can enhance the reduction and removal of Se forms in surface waters, but required testing for its application to remediate Se and Hg in FGD waters. Data indicated that sucrose and yeast culture additions could significantly increase the removal of Se in FGD waters using pilot-scale CWTS. Based on these results and laboratory experiments with organic carbon additions, we amended a full-scale CWTS with additions of sucrose and yeast culture. To understand if Se removal was enhanced with these additions, Se measurements were compared between the amended CWTS series and an un-amended CWTS series. This study confirmed that Se and nitrate removal could be significantly enhanced with additions of sucrose. Based on measurements of biochemical oxygen demand, microbial activity was also enhanced and suggests this was an important removal pathway for Se

and nitrate. Data presented in this dissertation provide strategies to not only decrease risks associated with FGD waters, but can be applied and transferred to other waters contaminated with metals and metalloids. By increasing our knowledge of approaches to mitigate risks in contaminated waters, we may improve the capture and sequestering of problematic constituents.

## DEDICATION

This dissertation is dedicated to my wife Lisa Mae Ferguson Eggert. Without her love, devotion, and many years of patience, this degree would not have been achieved. I would also like to thank my parents Del and Barbara, my other parents Lew and Joyce, my brother Damon, the Boston Fergusons, the Raleigh Fergusons, and the Cincinnati Alkires for their support and love throughout this process.

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## CHAPTER ONE

### INTRODUCTION

Sulfur dioxide was identified as a criterion pollutant by the United States Environmental Protection Agency (U.S. EPA) due to adverse effects it can cause on human health and welfare (Rubin et al., 2004). In an effort to mitigate this potentially toxic air emission, coal-fired power plants have begun to decrease sulfur dioxide and nitrous dioxide emissions to levels that were emitted during the 1980s or specifically defined for a particular geographical location (USDOE, 2006). For example, coal-fired power plants located in North Carolina are required by the U.S. EPA to reduce sulfur dioxide emissions by 70% of the total permitted limit of 1998 under the “Clean Smokestacks Legislation.” In response to this identified problem, flue gas desulfurization (FGD) processes were developed and can include various designs such as fluid bed reactors (dry scrubbing) and wet lime or limestone scrubbing (Rubin et al., 2004).

Of these designs, wet scrubbing processes are a common treatment approach (i.e. 87% of all FGD scrubber designs in 2000) with high efficiency (95-99%) for removing sulfur dioxide emissions from the flue gas (Jones, 1999; Berland et al., 2003). Wet FGD scrubbers contact flue gases with saturated calcium carbonate water allowing oxidation of  $\text{SO}_2$  gases and formation of calcium sulfite ( $\text{CaSO}_3$ ) and calcium sulfate ( $\text{CaSO}_4$ ) (Soud, 1994; Berland et al., 2003). Oxidation of  $\text{SO}_2$  is typically assisted through introduction of force air in scrubbing towers. FGD scrubber waters can be re-circulated within the scrubber tower for short periods (2-6 hr), but require removal once the chloride

concentrations exceed the corrosion limits of the system (EPRI, 2009). Additional treatment processes for the flue gas can be conducted pre- and post-wet scrubbing to enhance the removal of nitrous oxides, fly ash, total suspended solids, and gaseous elemental mercury ( $\text{Hg}^0$ ) (USDOE, 2006). Pre-scrubbing processes including removal of nitrous oxides using selective catalytic reactors (SCR) and removal of oxidized and partly-oxidized coal components (e.g. fly ash) using electrostatic precipitators (ESP) (EPRI, 2006). Due to the high concentrations (0.3 to 170 g/L) of total suspended solids (TSS) in FGD scrubber waters, hydrocyclones are used as the primary treatment process and removal approximately 80 to 90% of the total TSS (EPRI, 2006). Gypsum ( $\text{CaSO}_4$ ) accounts for the majority (10% w/w) of the TSS in FGD scrubber waters and can be sold as wallboard precursors depending on its purity (USDOE, 2006). The residual 10 to 20% of the TSS is removed using chemical additions (ferric chloride, cationic, anionic, and non-ionic polymer) to attract and/or flocculate the TSS and is typically assisted using a clarifier for gravity settling. Settling basins have also been used to decrease the residual TSS through gravity settling.

In addition to the calcium sulfate salts, FGD waters can contain a multitude of problematic constituents including arsenic, boron, cadmium, chromium, chloride, copper, lead, mercury, nitrate, selenium, and zinc (Mierzejewski, 1991). The forms and concentrations of these contaminants in FGD waters can, however, vary from site to site due to differences in coal source, burner design, burning rate, scrubber design and operation, selection of post-treatment processes (chemical, physical, or combination) for the removal of TSS, and source of water used in wet scrubbing (Mierzejewski, 1991).

FGD waters can pose several environmental challenges. FGD waters are produced in large volumes (0.756 to 3.78 million L/d), vary widely in composition, and contain constituents in concentrations and forms that are toxic to freshwater receiving system biota. Due to the potential risks of FGD waters, discharged effluents must comply with National Pollution Discharge Elimination System (NPDES) permits under the Clean Water Act (CWA). NPDES permits for the discharge of FGD waters are site-specific but can include monitoring and reporting or limits for identified contaminants (e.g. maximum daily concentrations or average monthly concentrations), whole effluent toxicity (WET) testing using waters with percentage of the discharged effluent (1.9 to 100%), and monitoring and reporting of contaminants in biota sampled from the receiving system (USEPA, 1985). In review of current NPDES permits for FGD effluents, the discharge limitations for many constituents are “monitor and report”, meaning there is no quantitative regulation for concentrations of these constituents discharged from a site. Narrative limits on NPDES permits (i.e. WET tests) can indicate the presence of a toxicant, but are not useful for determining the source of the toxic effects and therefore, a risk-based approach is needed, in addition to actual or anticipated NPDES permits, to determine the contaminants of concern in a FGD water.

Constituents of concern (COC) are defined as elements, compounds, or parameters observed in FGD waters that 1) exceed current NPDES permit limits or are lower/greater than the specified range (e.g. pH), 2) can exceed anticipated NPDES permit limits (e.g. for sites without or renewed NPDES permits), and 3) can adversely affect receiving system biota, due to their concentrations and forms.

For criterion 1, COC would be identified as constituents measured in the FGD water with concentrations that were greater than the NPDES permit limit (maximum daily concentration or average monthly concentration). For criterion 2, anticipated NPDES permit limits can be calculated using reasonable potential analysis (RPA) (USEPA, 1985). This calculation requires knowledge of the water quality criteria or regulatory limits (e.g. chronic toxicity values) for constituents in a wastestream to be treated (e.g. FGD pre-treatment water) and the in-stream waste concentration (IWC) for the site. Water quality criteria (WQC) are accessible from the U.S. Environmental Protection Agency (USEPA). In-stream waste concentration (IWC) is calculated based on equation (1).

$$IWC = [(Q_w)/(Q_w + Q_r)] * 100 \quad \text{Equation (1)}$$

Where  $Q_w$  is the design flow of the FGD treatment system and  $Q_r$  is the lowest recorded seven day flow in the past ten years of the receiving system and is referred to as the 7Q10. The RPA is calculated by dividing the WQC or regulatory limit by the fraction of the IWC (i.e. 0.019 for an IWC of 1.9%). If the calculated RPA values (i.e. mass/volume) for a specific constituent are greater than the concentrations measured in the FGD water, the constituent is identified as a COC. This approach for identifying COC is useful for sites with knowledge of their receiving system, but may be limited for sites with undetermined IWC values, or is 100%. For criterion 3, COC in FGD water are identified as constituents having concentrations greater than its WQC values or chronic toxicity values if WQC are not available (e.g. boron). This approach is useful for sites with an IWC of 100%.

Through thorough identification of the COCs in FGD water, a treatment process can be designed to allow for compliance of discharged FGD waters. Current treatment strategies for FGD waters such as activated sludge, reverse osmosis, chemical additives, and holding ponds can have many disadvantages. These include construction, maintenance, and operation costs, disposal and liability of by-products, and production of highly diverse unnatural waste streams (i.e. inefficient or ineffective treatment). A plausible treatment alternative for FGD waters is remediation utilizing constructed wetland treatment systems (CWTS). Successful remediation of various waters has been achieved with this treatment strategy including storm water runoff (Murray-Gulde et al., 2005), nutrient-rich water (Huett et al., 2005), acid mine drainage (Sobolewski, 1996), municipal water (Ansola et al., 2003), agricultural runoff (Moore et al., 2000). CWTS are based upon biogeochemical reactions occurring in natural wetlands that do not occur widely in other aquatic or terrestrial systems. Specifically designed CWTS can alter the physicochemical and biogeochemical characteristics of targeted constituents in waters through transfers and transformations. By manipulation of components within these treatment systems (i.e. environmental conditions), contaminants can be targeted for removal through controlled processes to decrease their solubility and bioavailability to aquatic organisms. Potentially toxic inorganic elements (e.g., Hg, Se, and As) can be transferred to the solid phase (reactions preceded by sedimentation) and transformed into less soluble forms within the treatment systems. Thus, the constructed wetland treatment systems must be poised to make the appropriate reactions possible and likely.

Microbial activity is an important contributor to chemical processes that occur in CWTS, and these organisms help mediate reactions, which are limited by energy (thermodynamics) and time (kinetics) (Lovley, 1997). Therefore, microbial species and ultimately their activity are important components in CWTS for remediation of constituents in FGD waters. Microbial activity can include oxyanion reduction (selenate to selenite to elemental Se), dissimilatory iron and sulfate reduction, nitrification, denitrification, and biodegradation of organic materials (Oremland et al., 1991; Newman et al., 1997; Vester and Ingvorsen, 1998). Electrical potential (Eh), commonly referred to as redox, is characterized as the potential for transfer of electrons and can affect the cycling of elements or compounds in the environment. The cycling of elements such as carbon, sulfur, nitrogen, and selenium are largely influenced by microbial activity (Brune et al., 2000) as well as redox conditions. Inhibitory effects on microbial activity may be caused by exposures to contaminants (e.g. boron, nitrate, chlorides) in some FGD waters and may limit the sequestering and reduction of mercury, selenite (Se IV) and selenate (Se VI). A plausible enhancement for Hg and Se removal is addition of organic carbon to increase the microbial reduction rate of Se (VI) and decrease potential competitive electron acceptors such as nitrate (Zhang et al., 2005). Additions of readily labile organic carbon sources (acetate, lactate, glucose, and trypticase soy agar) have been used to enhance microbial reduction of Se (VI) and Se (IV) to Se<sup>0</sup> from contaminated aqueous wastestreams (Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2003 and 2005).

EPRI (1999) reported that the FGD systems of most coal-fired power plants differ in design and operation and due to these differences, as well as coal source, FGD waters are specific to each production site. Due to the diversity and complexity of FGD waters, a reliable and cost efficient approach such as pilot-scale testing is needed to determine the performance of CWTS for multiple FGD waters. Testable models such as pilot-scale CWTS can be used to 1) measure the performance of these systems for decreasing concentrations of specific constituents in FGD waters, 2) determine the bioavailability of constituents and toxicity of pre- and post-treated waters, 3) determine responses of these systems to operational changes (e.g. hydraulic retention time and water depth) or amendments (e.g. iron, organic carbon, alkalinity sources), 4) determine system operating parameters, 5) provide data regarding compliance and removal rates for scaling of the system, and 6) provide the ability to manipulate reactor designs without potentially comprising existing NPDES permits. Results from pilot-scale CWTS have been scaled successfully to full-scale situations (Murray-Gulde et al., 2008) and are critically important when dealing with waters, such as FGD waters, that contain constituents at concentrations and in forms that can adversely affect the performance of a biological treatment system (i.e. chlorides, cyanide, and boron).

## **1. Research Objectives**

The objectives of this research were to 1) characterize the constituents of concern in flue gas desulfurization (FGD) waters, 2) design and construct pilot-scale constructed

wetland treatment systems to remediate FGD waters, 3) evaluate the performance of pilot-scale constructed wetland treatments to achieve discharge criteria, and 4) enhance the performance of pilot-scale and full-scale CWTS for decreasing selenium concentrations in FGD waters. The rationale of this research is to provide a valid approach for the remediation of constituents of concern in FGD waters. Successful remediation implies that the constituents of concern are decreased to acceptable concentrations and are sequestered and maintained in forms that decrease the risks they may pose to biota.

## **2. Organization of Dissertation**

This dissertation consists of six chapters, including the Introduction (Chapter One), four independent manuscripts (Chapters Two, Three, Four, and Five), and the Summary and Conclusions (Chapter Six). Chapters Two and Three are published in *Environmental Geosciences* and *The Proceedings of the International Waters Conference*, respectively. Chapters Three and Four will be submitted for publication to *Water, Air, and Soil Pollution and Ecological Engineering*, respectively.

Chapters Two and Three present strategies and case studies for remediating four FGD waters using pilot-scale constructed wetland treatment systems (CWTS). In these studies, constituents of concern in FGD waters and designed the pilot-scale CWTS were determined using biogeochemical models and literature reviews to transform and transfer these constituents into less soluble and non-bioavailable forms. For Chapter Two, our specific research objectives were to 1) configure a pilot-scale constructed wetland

treatment system for FGD water, and 2) evaluate treatment effectiveness and performance of this system. For Chapter Three, the specific objectives of this study were to 1) characterize FGD waters in terms of chemical composition and constituents of concern; 2) design constructed wetland treatment systems for remediation of constituents of concern in FGD waters; and 3) measure the performance of constructed wetland treatment systems for formulated and actual FGD waters based on discharge criteria established by the USEPA and regulated by NPDES permits.

Chapter Four presents a strategy for enhancing the removal of selenium (Se) and mercury (Hg) using organic carbon additions to pilot-scale CWTS. For this research we measured and compared the concentrations of total Se and Hg in outflow samples of a control pilot-scale CWTS, sucrose amended pilot-scale CWTS, yeast culture amended pilot-scale CWTS, and hybrid pilot-scale CWTS. The specific objectives of this study were to 1) determine the site performance goals for Se and Hg in FGD water through reasonable potential analysis (RPA), 2) compare and contrast removal rates and extents of removal for selenium and mercury in a FGD water using sucrose amended pilot-scale CWTS, yeast culture amended pilot-scale CWTS, hybrid pilot-scale CWTS, and control pilot-scale CWTS, and 3) determine the compliance of treated FGD waters with RPA values for Se and Hg using data from amended and un-amended pilot-scale CWTS.

For Chapter Five, we conducted laboratory experiments to determine the removal of Se in FGD water receiving four organic carbon sources. Based on these results, we designed an additional study to measure the differences in Se removal between a full-scale CWTS series receiving soluble organic carbon concentrations and an untreated

control full-scale CWTS series. FGD water treated using these full-scale CWTS series were also measured for pH values, biochemical oxygen demand (BOD<sub>5</sub>), nitrate, dissolved oxygen (DO), chloride, sulfate, total suspended solids (TSS), total dissolved solids (TDS), and boron concentrations to determine their relationship to measured Se removals from the amended and control CWTS series. The specific objectives of this study were to 1) measure the change in total Se concentrations from bench-scale experiments receiving different organic carbon types and concentrations in comparison to controls; 2) measure the removal (percent and extent of removal) of total Se in FGD water from an organic carbon amended and control CWTS series; and 3) measure and compare outflow samples from the amended and control CWTS series to estimated performance goals at this site.

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## CHAPTER TWO

### PERFORMANCE OF PILOT-SCALE CONSTRUCTED WETLAND TREATMENT SYSTEMS FOR FLUE GAS DESULFURIZATION (FGD) WATERS

#### **Abstract**

Effective and reliable treatment systems are needed to mitigate the risks of contaminants in flue gas desulfurization (FGD) waters to achieve discharge limitations established under the Clean Water Act (CWA) through the National Pollutant Discharge Elimination System (NPDES). FGD waters are produced as a byproduct when coal-fired power plants utilize dry or wet scrubbers to remove sulfur dioxide from flue gases prior to exhaust. Pilot-scale constructed wetland treatment systems were designed and constructed at Clemson University to evaluate removal of arsenic (As), mercury (Hg), nitrogen (N), selenium (Se), and other constituents from FGD water. From this study, initial research objectives were to: (1) configure a pilot constructed wetland treatment system for FGD water, and (2) evaluate treatment effectiveness and performance of this system. Aqueous samples were collected from the equalization basin, inflows to the constructed wetland treatment system, and outflows from each wetland reactor. To determine rates and extents of removal, parameters measured from these sampling locations included analysis of As, B, Hg, N (nitrite, nitrate, ammonia, and total nitrogen) and Se as well as water chemistry parameters including biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), sulfates, chlorides, conductivity, dissolved oxygen, pH, alkalinity, hardness, and temperature. Percent removals ranged from 40.1% to 77.7% for As, 77.6%

to 97.8% for Hg, 43.9% to 88.8% for N, and no removal to 84.6% for Se. Results from this pilot-scale study indicate that specially designed constructed wetland treatment systems can decrease potential constituents of concern (i.e. As, Hg, N, and Se) in FGD water and that the performance can increase with system maturation.

## **1. Introduction**

In order to comply with the Clean Air Act, coal-fired power plants are required to decrease sulfur dioxide emissions by transforming this gas species into an alternative form, such as a solid or aqueous species. To accomplish this, flue gas desulfurization (FGD) processes were developed and include various designs such as fluid bed reactors (dry scrubbing) and wet lime or limestone scrubbing (Rubin *et al.*, 2004). Of these designs, wet scrubbing processes are the most common treatment approach (87% of all FGD scrubber designs in 2000) with high efficiency (95-99%) for removing gaseous sulfur dioxide emissions from smoke stacks (Jones 1999 and Berland *et al.*, 2003). Wet scrubbing is conducted by contacting flue gases with a water slurry typically composed of calcium carbonate and additives (e.g. dispersants and pH buffers) in a spray tower (Soud, 1994). The resulting water can be recycled for a short period; however, its reuse is limited by the amount of total dissolved solids present in the FGD water. Once the water is near-saturation for the scrubber design or has achieved the limits of the operating or treatment system, the water must be discharged from the system. Additional treatment processes can be conducted pre- and post-wet scrubbing to enhance the total removal of sulfur gases. Electrostatic precipitators (ESP) are used for removal of gas phase particulates, namely oxidized and un-oxidized coal components (fly ash) before the wet-

scrub process. Clarification processes are conducted on the blowdown FGD water to limit the amount of total suspended solids (TSS) and commonly utilize inorganic coagulants and/or high molecular weight polymers. The chemical composition of FGD waters varies due to several factors including coal type, burner design and operation, scrubber design and operation, chemical composition of the additives, and source of water used in wet scrubbing (Mierzejewski, 1991). Despite variations in chemical components and their respective concentrations in FGD waters, certain contaminants are likely to be present in this complex aqueous matrix. Elevated concentrations of contaminants in FGD waters, with respect to continental United States (U.S.) freshwaters, include transition metals (cadmium, copper, chromium, lead, manganese, mercury, and zinc), metalloids (arsenic, boron, and selenium), non-metals (chloride, sulfur, nitrogen, and phosphorous), and organics (fly ash, dibasic acids, and polymers). Undiluted FGD waters are produced in large volumes (0.756 to 1.89 million L/d) and contain constituents in concentrations and forms that are toxic to receiving aquatic system biota if not sufficiently treated.

In order to efficiently implement FGD units at these fossil-fuel fired power plants, an effective and reliable wastewater treatment system is needed. A wastewater stream will be produced from the FGD process, and it must be treated to eliminate contaminants in order to achieve discharge limitations established under the NPDES and CWA. The treatment system must be reliable and performance must be continuously achieved throughout all seasons of the year. Elements such as arsenic, boron, chlorides, mercury, nitrogen, and selenium are generally of concern in these wastewaters. Generic parameters such as 5-day biochemical oxygen demand ( $BOD_5$ ) and chemical oxygen demand (COD)

may also be targeted for treatment, if their concentrations exceed 30 mg/L. Since FGD waters vary from site to site, the constituents requiring treatment in each FGD water will vary and should be characterized individually.

Successful remediation of problematic constituents in various waters has been achieved using specifically designed constructed wetland treatment systems including storm water runoff (Muarry-Gulde et al., 2005), nutrient impacted waters (Huett et al. 2005), acid mine drainage (Sobolewskiv 1996), municipal waters (Ansola et al., 2003), and agricultural runoff (Moore et al., 2000). Wetlands possess unique reactions not occurring in either strictly aquatic or terrestrial systems. Constructed wetlands can be poised or buffered to ensure that desired reactions (transfers and transformations) affecting the targeted constituents proceed at predictable rates and over long periods of time. In order to develop confidence in the ability of a constructed wetland treatment system to treat specific FGD waters, pilot studies may be performed. Pilot studies utilize scaled models that decrease spatial area or other system factors in order to improve cost-efficiency, decrease the study duration (e.g. time for construction and system maturation), and allow for testing of factors that affect the performance of these treatment systems. Pilot studies for CWTS can provide confirm design features for the proposed full-scale constructed wetland treatment systems, proof-of-concept data and convincing information to assist with regulatory permitting of the full-scale facility. Alternatives to treatment with a constructed wetland system are not attractive due to high capital costs and continuing high costs associated with operation and maintenance.

The objectives of this research project were to 1) design and assemble a pilot-scale constructed wetland treatment system to treat constituents of concern in a FGD water produced by a wet-scrubbing FGD unit, and 2) determine the performance of the pilot-scale CWTS by measuring the removal rates and extents of constituents of concern.

## **2. Materials and Methods**

### *2.1 Characterization of Flue Gas Desulfurization (FGD) Water*

FGD water was shipped in a storage tanker (~3000 gallons) from a southeastern U.S. coal-fired power plant to Clemson University, Clemson, SC. Immediately upon arrival, the FGD water was analyzed for elemental composition using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS; EPA Method 200.8) and chloride concentrations according to *Standard Methods for the Examination of Water and Wastewater* (APHA 1998). Constituents in this FGD water requiring treatment (i.e. removal or decreasing the constituents' bioavailability) were identified by determining a risk quotient. Risk quotients were determined by Eq. (1). Constituents with a risk quotient >1 were classified as constituents of concern (COC).

$$\text{Risk quotient} = [\text{constituent}] / \text{NPDES permit limits or WQC} \quad (1)$$

Maximum discharge limits for operating FGD scrubber coal-fired power plants and WQC data for each constituent were obtained from the U.S. EPA's database.

### *2.2 Design of Pilot-Scale CWTS for FGD Water*

For this research, pilot-scale constructed wetland treatment systems were designed based on analyses of biogeochemical cycling of constituents of concern in FGD

waters (Eggert et al., 2008), published literature on removal pathways for these constituents, and previous research with constructed wetland treatment systems.

### 2.3. Assembly and Acclimation of the Pilot-Scale CWTS

Two pilot-scale constructed wetland treatment system designs were used in this study. Each CWTS design included two replicated treatment reactor series (n=2) of either five (CWTS A) or six (CWTS B) reactors per system (Figure 1a and 1b). For CWTS A, the first, second, and third wetland reactors contained approximately 30-cm of river sand hydrosol, 24-hr hydraulic retention time (HRT), were planted with *Schoenoplectus californicus* C. A. Meyer, and are operationally defined as reducing wetland reactors. For CWTS B, an additional wetland reactor was incorporated; however, the only physical difference was the size of the reactor cells. HRT for these systems were 24-hr. For both CWTS, the first oxidizing reactors contained a rock cascade constructed using granite cobble (Fowler Corporation; Seneca, SC) in the first-half of each reactor and were planted with *Typha angustifolia* L. The last wetland reactor in each pilot-scale CWTS contained approximately 30-cm of river sand hydrosol and was planted with *T. angustifolia*. FGD water was transferred from the equalization basin to the pilot systems using Fluid Metering, Inc. (FMI)® piston pumps calibrated to deliver a flow rate to achieve the targeted HRT. FGD water supplying the pilot-scale CWTS was renewed at the beginning of each treatment period. Since constructed wetland treatment systems are biological systems, time required for these systems to mature and develop important physical and chemical characteristics such as plant growth (roots and shoots), acid volatile sulfides (AVS), and detritus (natural organic matter sources). Acclimation of the

pilot-scale CWTS was conducted by loading two simulated FGD waters into these systems for two months prior to loadings of actual FGD waters.

#### *2.4 Sampling and Performance of Pilot-Scale CWTS*

Aqueous samples were collected for physical and chemical analyses and included the equalization basin, inflows to each pilot-scale CWTS, and the outflows of each wetland reactor. To ensure samples of FGD water were treated based on the theoretical designs; all sampling was conducted at the end of each HRT. Elemental analyses (i.e. Hg, Se, As, and B) were measured according to EPA Method 200.8 (USEPA, 1994) using a Sciex Elan 9000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Perkin-Elmer, Norwalk, CT). Nitrogen as total nitrogen, nitrate, and nitrite were determined by the persulfate digestion method (HACH 10071 Method), cadmium reduction method (HACH 8039 Method), and the ferrous sulfate method (HACH 8153 Method), respectively. Ammonia was determined using an Orion ion selective electrode (EPA Method 350.3) Dissolved oxygen and pH were measured using YSI® (model 85) and Orion® (model 410A+) field instruments, respectively. Additional constituents and properties including alkalinity, hardness, conductivity, chloride and sulfate concentrations, chemical oxygen demand, biological oxygen demand, organic carbon, and total and suspended solids were determined according to Standard Methods (APHA 1998). To assess the performance of the pilot-scale CWTS, outflow concentrations of monitored COC were compared to NPDES permits for FGD waters and WQC limits as well as percent removals (%) and removal rates ( $d^{-1}$ ). The percent removal was calculated based on equation 2.

$$\text{Percent Removal} = (1 - ([A]_t / [A]_0)) * 100 \quad \text{Equation (2)}$$

Where  $[A]_t$  is the concentration of the constituent in the equalization basin (pre-treatment),  $[A]_0$  is the concentration of the constituent in the outflow sample of reactor four (post-treatment). Removal rates for mercury and selenium were calculated using a first-order rate equation (3).

$$\text{Removal Rate} = \ln([A]_t / [A]_0) = kt \quad \text{Equation (3)}$$

Where  $[A]_t$  and  $[A]_0$  are the same as described for percent removal,  $t$  is the total time of treatment, and  $k$  is the first-order rate coefficient. General performance of the systems was determined by comparing inflow to outflow concentrations relative to HRT, providing information on removal efficiency for these constituents. HRT was determined by measuring overlying water volume in each wetland cell coupled with accurate and precise measurement of inflow volume (ml/min) using 20-L graduated containers (wetland cells) and 250-ml graduated cylinders (flow rate). HRT (hr) was calculated by the ratio of the overlying water volume to the flow rate. Flow rates were calibrated at the initiation of each treatment week and the total HRT of each system was 120-hr. Oxidation-reduction (redox) potentials of wetland hydrosol were monitored monthly using platinum-tipped electrodes and a handheld voltmeter with an Accumet® calomel reference electrode (Faulkner et al., 1989).

### **3. Results and Discussion**

#### *3.1 Initial Flue Gas Desulfurization (FGD) Water Characterization*

Three aqueous samples of the FGD water were taken from the shipping tanker that included the top water column in the tanker (0 to 3 cm in depth), the first purge

(initial 5 gal), and second purge (50 to 100 gal after the initial purge). From these results, the constituents of concern in this FGD water were identified as cadmium, chlorides, nickel, mercury, and selenium (Table 1). Other potentially problematic constituents in this FGD water are boron and nitrogen species. Boron concentrations (37.6 mg/L) in these waters exceed the lowest observable effect concentration (LOEC) for *Ceriodaphnia dubia* Richard (18.0 mg/L; Hickey, 1989), a species used to test the toxicity of effluent waters under most NPDES permits. Nitrogen species (nitrite, nitrate, and ammonia) can negatively affect invertebrate and vertebrate species in aquatic receiving systems as well as enabling potent eutrophication of these systems, and was targeted for treatment in this water due to an aqueous concentration of 12.88 mg/L.

### 3.2 Design of Pilot-Scale Constructed Wetland Treatment Systems

Pilot-scale constructed wetland treatment systems were assembled with three main treatment components: (1) an equalization basin (2) reducing wetland reactors, and (3) oxidizing wetland reactors (Figure 1). Equalization basins (EQ basin) were designed as the initial component in each experimental system to decrease total suspended solids and homogenize concentrations of contaminants before introduction into the treatment system. Treatment reactors were designed to promote environments that are favorable for either reductive or oxidative transformation of constituents of concern by decreasing its aqueous concentration or bioavailability. For this study, two treatment reactor types were utilized and are operationally defined as reducing and oxidizing reactors.

Reducing reactors were designed to have redox conditions of -250 to -50 mV and pH values between 5 and 7 standard units in the bulk hydrosol. The hydrosol component

was planted with giant bulrush (*Schoenoplectus californicus* C. A. Meyer); a wetland plant that has little radial oxygen loss, helping to maintain low redox conditions (Murray-Gulde et al., 2005b). Organic matter as 10% (v/v) double chip pine mulch was used as the electron donor for microbial activity (e.g. dissimilatory sulfate reduction) and regulation of dissolved oxygen within sediments. Zero-valent iron ( $\text{Fe}^0$ ) was applied to these systems at a rate of 200 lbs per acre to retain sulfides within the hydrosol and serves as a reactant in co-precipitation reactions. These systems were designed based on studies that indicated the mobility of arsenic, cadmium, copper, mercury, and zinc under low dissolved oxygen concentrations (sub-oxic to anaerobic) can be decreased by reactions with sulfide in which sulfide-bearing minerals are formed (Moore et al., 1988; Kirk 2004; Murray-Gulde et al., 2005a). In these reducing reactors, dissimilatory sulfate reduction provides sulfides and mineral-bearing sulfides for removing many constituents of concern from FGD waters. Reduced selenium species are typically less mobile and reduction of Se (VI) to Se (IV) and further reduction of selenite to insoluble  $\text{Se}^0$  has been documented within reducing aqueous environments (Zhang et al., 2003). Based on studies by Masscheleyn and Patrick (1993) and Johnson and Bullen (2003) selenium species can be transformed into elemental species under reducing conditions, such as the reducing reactors described in this paper.

Oxidizing reactors were designed to establish an oxidizing wetland environment with bulk sediment redox potentials of -50 to +200 mV. This was accomplished by selecting a porous hydrosol with low organic carbon and wetland plants with a high rate of radial oxygen loss (*T. angustifolia*). These design characteristics were chosen based on

studies by Kirk (2004) and biogeochemical modeling (Brookens, 1988) that indicate under high dissolved oxygen concentrations, dissolved iron species can be transformed into solid forms (oxyhydroxides) that enable co-precipitation with arsenic and selenium oxyanions. Oxidizing reactors can aid in the re-oxygenation of the treatment water and can decrease nutrient concentrations, thus limiting the environmental risks these waters pose to aquatic receiving systems.

Based on the measured redox potential for either the reducing or oxidizing wetland reactors, the design of these systems was sufficient to maintain the desired redox conditions. Reducing wetland reactors averaged  $-175 \pm 27$  mV (CWTS A) and  $-173 \pm 43$  mV (CWTS B) and the oxidizing wetland reactors averaged  $-8 \pm 20$  mV (CWTS A) and  $13 \pm 19$  mV (CWTS B). Measured redox potentials within in these systems are presented in Figure 2.

### *3.3 Performance of Pilot-Scale CWTS*

FGD waters that were transferred into the first treatment component, the equalization basins, were consistent in their chemical composition throughout this study. The measured elements and parameters averaged  $7.3 \pm 0.14$  (mean and standard deviation) as pH,  $8.85 \pm 0.73$  mg/L as dissolved oxygen (DO),  $56.8 \pm 3.6$  mg/L as alkalinity ( $\text{CaCO}_3$ ),  $4.19 \pm 0.7$  mS/cm as conductivity,  $1550 \pm 140$  mg/L as chlorides,  $1718 \pm 179$  mg/L as sulfate,  $9.66 \pm 8.29$  mg/L as TSS,  $12.49 \pm 0.92$  mg/L as total nitrogen,  $0.00171 \pm 0.00107$  mg/L as mercury,  $0.0513 \pm 0.005$  mg/L as selenium,  $0.0015 \pm 0.0002$  mg/L as arsenic, and  $33.75 \pm 1.70$  mg/L as boron.

Inflow FGD waters averaged  $7.59 \pm 0.23$  as pH,  $9.96 \pm 1.74$  mg/L as dissolved oxygen (DO),  $56.9 \pm 7.8$  mg/L as alkalinity ( $\text{CaCO}_3$ ),  $4.14 \pm 0.07$  mS/cm as conductivity,  $1541 \pm 178$  mg/L as chlorides,  $1786 \pm 183$  mg/L as sulfate,  $4.79 \pm 2.96$  mg/L as TSS,  $11.83 \pm 1.39$  mg/L as total nitrogen,  $0.00168 \pm 0.001205$  mg/L as mercury,  $0.050 \pm 0.006$  mg/L as selenium,  $0.0017 \pm 0.001$  mg/L as arsenic, and  $32.82 \pm 1.59$  mg/L as boron. In comparison to the equalization basin, TSS were decreased by 49.5%; however, the extent of removal in this study is lower than expected at a full-scale site due to the potential differences in the concentration of TSS in FGD waters that would be introduced into the equalization basin.

For CWTS A, the extent and rate of removal for mercury, selenium, arsenic, boron, and nitrogen ranged from 77.6 to 97.8% and  $0.250$  to  $0.652 \text{ d}^{-1}$ , no removal to 35.9% and no removal to  $0.089 \text{ d}^{-1}$ , 15.0 to 77.7% and  $0.032$  to  $0.233 \text{ d}^{-1}$ , 29.1 to 41.5% and  $0.068$  to  $0.107 \text{ d}^{-1}$ , and 51.1 to 89.2% and  $0.145$  to  $0.456 \text{ d}^{-1}$ , respectively. For CWTS B, the extent and rate of removal for mercury, selenium, arsenic, boron, and nitrogen ranged from 89.3 to 96.8% and  $0.373$  to  $0.594 \text{ d}^{-1}$ , 65.7 to 84.6% and  $0.178$  to  $0.319 \text{ d}^{-1}$ , 43.9 to 66.8% and  $0.100$  to  $0.184 \text{ d}^{-1}$ , 31.9 to 61.1% and  $0.085$  to  $0.189 \text{ d}^{-1}$ , and 50.4 to 81.3% and  $0.117$  to  $0.284 \text{ d}^{-1}$ , respectively. Mercury removal dominantly occurred in the reducing wetland reactors accounting for 65.0 and 66.2% of the total removal in CWTS A and B, respectively during this study. Based on the sediment redox potentials for reducing wetland reactors and published literature on mercury biogeochemistry in aqueous environments, mercury removal was likely due to formation of sulfide minerals (dissimilatory sulfate reduction) or bound to organic matter within these systems. The

removal of selenium increased with each sequential loading of this FGD water for either CWTS with no initial removal to a maximum removal extent of 84.6% (Table 2).

Selenium removal for CWTS A was likely altered by previous loadings of simulated FGD that contained a higher selenium concentration (4.5 mg/L as Se) than the actual FGD water (0.04 to 0.05 mg/L as Se) used in this study. For the first four weeks of loading actual FGD water into CWTS A, selenium concentrations were greater in the outflow versus inflow water samples, indicating a leaching of selenium from these systems. Leaching of selenium from this system was likely due to the large difference between the inflow selenium concentrations of these two waters and the potential dissolution of initial insoluble selenium species formed under these high selenium concentrations. Selenium removal increased after this period to a removal extent of 29 and 35.9% for the last two sampling periods. CWTS B was not loaded with simulated FGD water and selenium removal was maintained at an extent  $\geq 65.7\%$  with a maximum removal extent of 84.6% or a mean outflow concentration of 0.0066 mg/L (n=2). Arsenic removal dominantly occurred in the oxidizing wetland reactors accounting for 67.4 and 70.7% of the total removal. Arsenic species (oxyanions) were targeted through a co-precipitation reaction with iron under oxidizing conditions and may have occurred in this study based on the removal extent observed in these wetland reactors. Total nitrogen removal was consistent throughout this study with five of the eight outflow samples receiving  $> 80\%$  removal for this problematic constituent. Removal of total nitrogen dominantly occurred in the reducing wetland reactors accounting for 76.3 and 96% of the total removal in CWTS A and B, respectively. Removal of nitrogen was likely

accomplished by establishing these systems to favor denitrification via microorganisms and phytoconcentration. Based on the speciation of nitrogen in this FGD water, nitrate accounted for 90% of the total nitrogen, followed by nitrite and ammonia (<1%).

Based on the results of this study, the measured constituents of concern were decreased using pilot-scale CWTS. Mercury concentrations in the outflow samples were decreased below a NPDES permit limit of  $\leq 0.63 \mu\text{g/L}$  and the chronic freshwater WQC of  $0.012 \mu\text{g/L}$  for every outflow sample collected in this study. The mean outflow mercury concentration was  $0.094 \mu\text{g/L}$  ( $n=16$ ). Selenium concentrations in all outflow samples of CWTS B met the NPDES permit limit of  $\leq 0.026 \text{ mg/L}$  as Se and averaged  $0.0135 \pm 0.006 \text{ mg/L}$ . The lowest measured selenium concentration in the outflow of CWTS B was  $0.00484 \text{ mg/L}$ , which is less than the WQC for selenium ( $0.005 \text{ mg/L}$ ). Based on the decreasing selenium concentrations in outflow samples of CWTS A with each sequential loading of this FGD water, similar removal extents and rates should occur between the pilot-scale CWTS. Arsenic concentrations in this FGD water were below the WQC of  $0.150 \text{ mg/L}$  and the concentrations of this element were decreased in outflow samples using these pilot-scale CWTS. Acceptable nitrogen (total) concentrations in effluents are commonly listed as monitor and report for NPDES permits and the suggested WQC is defined by eco-regions within the U.S. ranging from  $0.2$  to  $1.2 \text{ mg/L}$ . Based on the upper WQC limit of  $1.2 \text{ mg/L}$  as total nitrogen, two outflow samples were lower or equal to this criterion. The mean outflow concentration of total nitrogen from these systems was  $1.88 \pm 0.609 \text{ mg/L}$  for all sampling periods except for the 4<sup>th</sup> (CWTS A) and 1<sup>st</sup> (CWTS B) loading periods which averaged  $6.17 \pm 1.08 \text{ mg/L}$ . Aqueous boron

concentrations were decreased by both CWTS, but removal extents and rates decreased with sequential loadings of FGD water. Removal of boron was most likely an affect of phytoconcentration by the wetland plant species and this conclusion was supported by visual boron phytotoxicity symptoms of tip necrosis and chlorosis (e.g. yellowing of leaves by *T. angustifolia*) of the shoots and leaves. Boron concentrations in the outflow samples were, however, decreased to concentrations less than the LOEC for *C. dubia* survival (Hickey *et al.*, 1989). Consistent removal of boron in FGD waters using CWTS may not occur during seasonal periods of limited plant growth (late-fall and winter). Additional research efforts regarding the design of CWTS for FGD waters containing boron concentrations > 18.0 mg/L should be addressed due to the potential phytotoxicity of boron in receiving systems and the current difficulty in treating boron impacted waters such as FGD waters. Chloride concentrations were not altered by the pilot-scale CWTS and co-management of the outflow water from these systems should be conducted to decrease its aqueous concentration and remediate its toxicity affects to organisms within a receiving system.

#### **4. Conclusions**

Based on the data obtained from this research, constructed wetland treatment systems can decrease the measured constituents of concern in this FGD water to meet NPDES permits and some WQC standards. The design of pilot-scale CWTS was sufficient to remove mercury, selenium, and nitrogen from FGD waters and possible system alterations may further enhance the removal and long-term sequestering of these potential toxic constituents. By collecting data on removal rates for each measured

constituent of concern, it is possible to design full-scale CWTS for power plants producing FGD waters based on their site-specific conditions and NPDES permit. Full-scale CWTS have been designed for long-term use (> 30 years), large wastestreams (> 1 MGD), and typically require low maintenance and operational costs in comparison to other treatment systems.

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Table 2.1 Analyses (mg/L) of FGD water from the shipping tanker, NPDES permits for FGD discharges, freshwater WQC, risk quotient values, and identified COC.

Parameter	Top Water Column	1st Purge	2nd Purge	NPDES <sup>1</sup>	WQC <sup>2</sup>	Risk Quotient	COC
B	40.5	38.5	37.6	NA	NA	NA	Yes <sup>3</sup>
Na	17.7	15.3	16.1	NA	NA	NA	No
Mg	171.2	151.9	161.9	NA	NA	NA	No
Al	0.841	0.143	0.112	MR	0.087	1.29	No <sup>4</sup>
Si	4.7	4.3	4.8	NA	NA	NA	No
P	0.006	0.003	0.003	MR	0.003-0.17	1.00	No
K	30.5	26.9	27.5	NA	NA	NA	No
Ca	228.6	210.6	207.4	NA	NA	NA	No
Cr	0.009	0.005	0.005	MR	0.011	0.47	No
Mn	1.444	1.179	1.254	MR	NA	NA	No
Fe	5.510	0.452	0.269	NA	1.00	0.27	No
Co	0.021	0.015	0.015	NA	NA	NA	No
Ni	0.131	0.095	0.099	MR	0.052	1.91	Yes
Cu	0.010	0.006	0.008	MR	0.009	0.87	No
Zn	0.185	0.112	0.108	MR	0.12	0.90	No
As	0.010	0.011	0.011	MR	0.150	0.07	No
Se	0.049	0.058	0.046	0.026	0.005	9.23	Yes
Br	1.48	1.43	1.57	NA	NA	NA	No
Mo	0.912	0.912	0.974	NA	NA	NA	No
Ag	BD	BD	BD	MR	NA	NA	No
Cd	0.018	0.017	0.017	MR	0.0003	68.54	Yes
Ba	0.157	0.144	0.004	NA	NA	NA	No
Hg	0.00324	0.00325	0.02854	0.00063	0.000012	2378	Yes
Pb	0.004	0.002	0.002	MR	0.0025	0.81	No
Chlorides	NA	NA	1475	MR	230	6.41	Yes
Total Nitrogen	NA	NA	12.88	MR	0.1-1.44	128.8-8.9	Yes
BOD <sub>5</sub>	NA	NA	1.04	30	NA	0.03	No
TSS	NA	NA	11.8	30	NA	0.39	No
pH (SU)	NA	NA	7.52	6 to 9	6 to 9	--	No

<sup>1</sup> NPDES permits collected from U.S. EPA

<sup>2</sup> Freshwater Criterion Continuous Concentration (CCC)

<sup>3</sup> Boron defined as a COC based on toxicity literature (Hickey, 1981)

<sup>4</sup> Not defined as a COC based on water-effects ratio for hardness

NA: Not available

MR: Monitor and Report

Table 2.2 Removal percentages and rates of measured COC in FGD water treated with CWTS A and B.

Loading	% Removal					Removal Rate (d <sup>-1</sup> )				
	Mercury	Selenium	Nitrogen	Arsenic	Boron	Mercury	Selenium	Nitrogen	Arsenic	Boron
<b>CWTS A</b>										
Week 1	91.2	NR	90.5	72.2	32.4	0.4851	NR	0.4712	0.2558	0.0784
Week 2	96.7	NR	86.6	77.7	29.1	0.5750	NR	0.4027	0.2510	0.0687
Week 3	77.6	NR	88.8	40.1	41.5	0.2500	NR	0.4374	0.0860	0.1071
Week 4	86.9	NR	56.0	76.4	36.7	0.3394	NR	0.1641	0.2409	0.0915
Week 5	97.8	28.9	81.3	69.2	30.2	0.6515	0.0722	0.3350	0.1970	0.0718
Week 6	NM	35.9	89.7	14.9	NM	NM	0.0743	0.3784	0.0270	NM
<b>CWTS B</b>										
Week 1	89.2	70.8	52.7	43.9	61.1	0.3730	0.2081	0.1247	0.0999	0.1576
Week 2	96.8	65.7	71.4	66.8	31.9	0.5941	0.1783	0.2085	0.1838	0.0642
Week 3	NM	84.6	81.5	62.9	NM	NM	0.3187	0.2837	0.1725	NM

NR: No removal

NM: Not measured

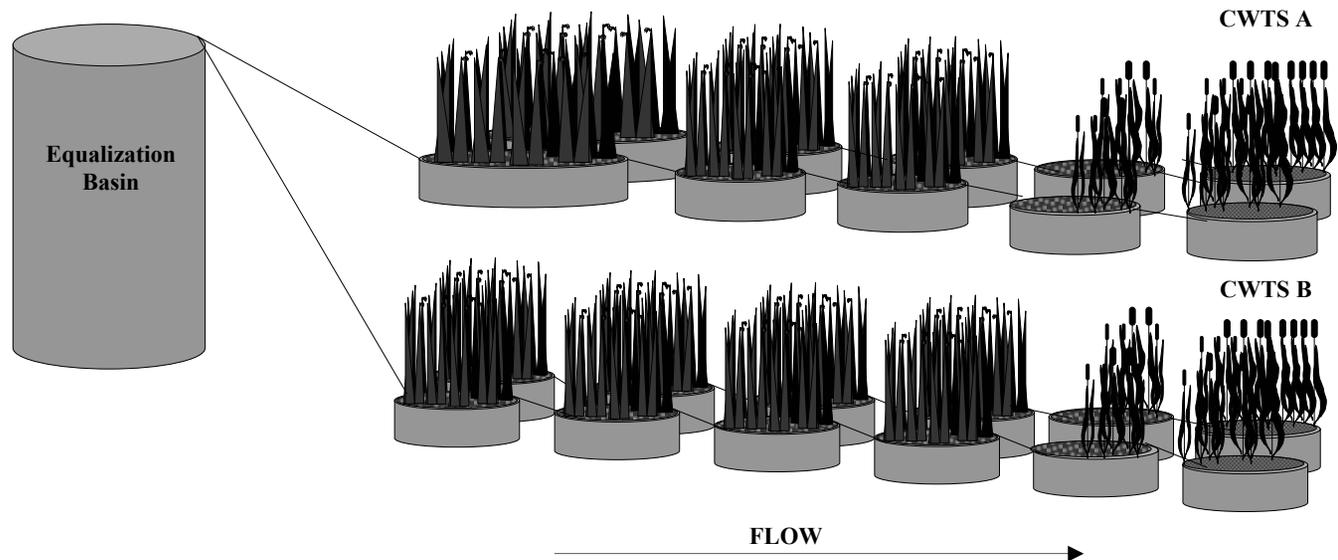


Figure 2.1 Schematic diagram of the pilot-scale constructed wetland treatment systems A and B. For CWTS A, the first three reactors in series are reducing and the last two in series are oxidizing. For CWTS B, the first four in series are reducing and the last two in series are oxidizing.

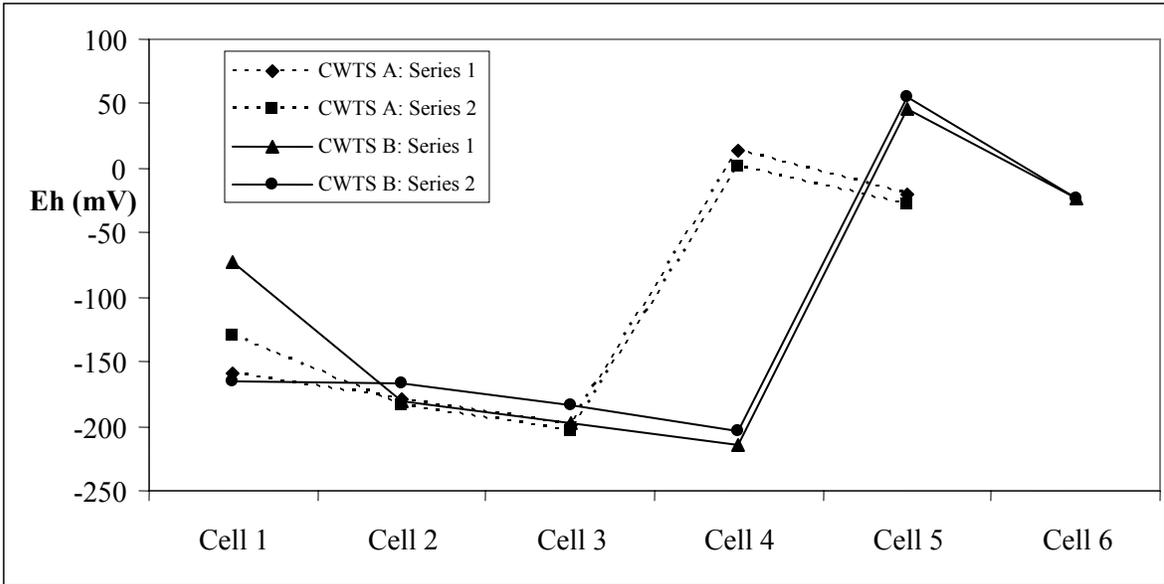


Figure 2.2 Sediment oxidation-reduction (Redox) potential for CWTS A and B.

## CHAPTER THREE

### REMEDICATION OF SIMULATED AND ACTUAL FLUE GAS DESULFURIZATION (FGD) WATERS USING PILOT-SCALE CONSTRUCTED WETLAND TREATMENT SYSTEMS

#### Abstract

Federal laws regarding ambient air quality require industries to reduce emissions of sulfur dioxides. Coal-fired power plants have therefore begun implementing flue gas desulfurization (FGD) scrubbers that utilize highly oxygenated calcium carbonate saturated water to transform sulfur gases into soluble anion species (e.g. sulfite and sulfate). Chemical compositions of FGD waters are dependent on the FGD scrubber design, coal types burned, chemical additives, and scrubbing solution source. FGD waters contain potentially toxic elements including arsenic, cadmium, chemical oxygen demand, copper, mercury, selenium, chloride, sulfates, and zinc. Therefore, these waters must be treated before discharge into a receiving system due to constituents that can elicit toxicity. The specific objectives of this research were to: 1) characterize FGD waters in terms of chemical composition and constituents of concern; 2) design constructed wetland treatment systems for remediation of constituents of concern in FGD waters; and 3) measure the performance of constructed wetland treatment systems for formulated and actual FGD waters based on discharge criteria established by the USEPA and regulated by NPDES permits. FGD waters are characteristically high in total dissolved solids (i.e. calcium, chloride, magnesium, and sulfate), are circumneutral in pH, contain high concentrations of total suspended solids, and contain several potentially toxic constituents. Constituents of concern were identified as cadmium, chemical oxygen demand (COD), chloride, copper, mercury, selenium, and zinc. Pilot-scale constructed

wetland treatment systems (CWTS) were designed based on biogeochemical data and each system contained an equalization basin, two reducing and two oxidizing wetland reactors in series. Three FGD waters were introduced in the pilot-scale CWTS and performance was assessed by measuring targeted constituents of concern (i.e. mercury and selenium) and the toxicity of pre- and post-treatment waters. Results from these studies indicate that mercury and selenium concentrations in FGD waters can be decreased using constructed wetland treatment systems, and with appropriate co-management of low-ionic strength water for chloride concentrations, toxicity of post-treatment samples is decreased to acceptable discharge limits.

## **1. Introduction**

Coal-burning power plants are significantly decreasing air emissions of sulfur dioxides (SO<sub>2</sub>) by installing flue gas desulfurization (FGD) scrubbers (USDOE 2000). As the demand for electrical energy increases, there is concomitant increased production of FGD scrubber waters. According to the U.S. Department of Energy (USDOE), the U.S. burned 1,039 million short tons of coal (Freme, 2005) and the amount of this by-product water can exceed 0.378 million L/d at large facilities (>1,000 Mega Watts). The most commonly used FGD scrubber is referred to as a “wet scrubber.” Wet scrubbers use lime or limestone (calcium carbonate) saturated water to solubilize gaseous SO<sub>2</sub>, and oxidize and precipitate sulfur compounds as calcium sulfite (CaSO<sub>3</sub>) or calcium sulfate (CaSO<sub>4</sub>). This scrubbing process occurs by directly contacting flue gas that remains after oxidization of coal with the scrubbing water and is oxygenated by forced air injection in the collection basin. The resulting by-product water is typically referred to as FGD water. At each coal-fired power plant, the composition of FGD water is a function of several

chemical and physical variables that include the coal source and composition, burner/FGD scrubber design and operation, post-scrubber treatment processes, and initial constituents in the local water supply (Mierzejewski, 1991). Since coals can differ drastically in chemical composition (Gluskoter et al., 1977; PECH 1980; DeVito et al., 1994; Yudovich and Ketris, 2005a and 2005b), FGD waters can be influenced by the type of coal burned as well as the burner capacity and environment (i.e. oxygen content and heat). FGD scrubber design and operation can influence the composition of FGD waters due to physical mechanisms (e.g. area of the gas/water interface, salinity capacity of the reactor, and loss of water vapor) and chemical additives such as pH buffers (i.e. organic dibasic acids). Post-scrubber treatment processes typically target removal of suspended solids and reclamation of FGD water by using gravitational settling basins (e.g. clarifier), hydrocyclones, and dewatering devices (e.g. sludge belt press). Some coal-fired power plants also employ charge neutralizing and chelating compounds (e.g. iron salts, flocculants, and metal precipitants) for removal of solids and specific contaminants.

FGD waters pose several environmental challenges. FGD waters are produced in large volumes, can vary widely in chemical composition, and may contain constituents in concentrations and forms that are toxic to receiving aquatic system biota. Constituents of environmental concern in FGD waters can include arsenic, chemical and biological oxygen demand, boron, cadmium, chromium, copper, chloride, lead, mercury, nitrate, selenium, sulfate, and zinc (Mierzejewski, 1991). FGD waters are typically not suitable for reuse within power plants as make-up or cooling water due to corrosion, scaling, and biofouling effects of these waters. Therefore, treatment and discharge of these waters is required and releases to aquatic systems are regulated by the United States Environmental

Protection Agency (USEPA) under the Clean Water Act through National Pollutant Discharge Elimination System (NPDES) permits. Treatment criteria for FGD waters are site-specific and can include limits for contaminant concentrations (i.e. maximum daily discharge limit), speciation of contaminants (e.g. selenite/selenate) and whole effluent toxicity tests (e.g. 7d static/renewal toxicity experiments with *Ceriodaphnia dubia*). *C. dubia* is a sentinel aquatic invertebrate species widely used for toxicity testing in NPDES programs (Spehar and Fiandt, 1986; Mount et al., 1997; Brix et al., 2001).

To develop innovative and viable approaches for treating FGD waters, a thorough understanding of their composition is essential. Chemical characterization data for FGD waters can provide information to identify constituents of concern for treatment and can offer insight regarding chemical processes that must occur to transform or transfer the constituent to stable or less toxic forms. The physicochemical state, speciation, and concentration of constituents in FGD waters may influence the effectiveness of a treatment system by limiting the reactivity of the targeted constituents or may induce toxicity effects to microbial communities within these systems (e.g. biological treatment systems). Since FGD water may vary from site to site, pilot-scale FGD scrubber units can be operated at specific locations to produce representative FGD water samples. Chemical analyses from pilot-scale FGD scrubber waters as well as actual FGD waters can be used to characterize the constituents of concern, or more specifically toxicants that must be removed or transformed in order to meet regulation criteria for reuse or discharge.

One potential remediation strategy for FGD waters is constructed wetland treatment systems (CWTS). By understanding and manipulating the biogeochemical cycles of constituents of concern, constructed wetlands can be designed to transform or

transfer targeted constituents to stable chemical forms thereby decreasing their mobility, bioavailability, and re-distribution (i.e. dissolution). Successful remediation of diverse waters has been achieved with this treatment strategy including storm water runoff (Murray-Gulde et al., 2005), nutrient-enriched waters (Huett et al., 2005), acid mine drainage (Sobolewskiv 1996), municipal waters (Ansola et al., 2003), and agricultural runoff (Moore et al., 2000). These systems have been used extensively for risk mitigation of many elements or compounds present in FGD waters; however, no studies have been published to date on the performance of CWTS to remediate FGD waters.

This study was initiated to evaluate the potential for CWTS to mitigate risks of constituents of concern in FGD waters. Each identified constituent of concern in FGD waters was investigated for chemical reaction pathways that provided adequate transformation and transfer mechanisms (i.e. stable chemical forms) in aquatic environments (i.e. wetland reactors). After pilot-scale CWTS were designed to treat constituents of concern in FGD waters, we measured the ability of these systems to decrease the targeted constituents of concern. To thoroughly evaluate the ability of CWTS to mitigate risks in diverse FGD waters, formulated FGD water, actual FGD waters, and pilot-scale scrubber FGD waters were used in this study. Formulated FGD waters were used to initially assess the potential treatment and design of constructed wetland treatment systems for synthesized FGD waters, whereas actual FGD waters were used to assess the performance and design of constructed wetland treatment systems for FGD waters that varied in chemical composition. Pilot scrubber FGD waters were actual FGD waters produced in small volumes (operated for one week) at a coal-fired power plant to assess the influence of four coal types on the chemical composition of FGD

waters and measure the treatment performance of pilot-scale CWTS. Specific objectives of this research were to: 1) characterize FGD waters in terms of chemical composition and constituents of concern; 2) design pilot-scale CWTS for remediation of constituents of concern in FGD waters; and 3) measure the performance of pilot-scale CWTS for formulated and actual FGD waters based on discharge criteria established by the USEPA and regulated by NPDES permits.

## **2. Materials and Methods**

### *2.1 Characterization of Flue Gas Desulfurization (FGD) Waters*

Four actual FGD waters were collected from operating scrubber systems, shipped on ice, and measured for inorganics and water chemistry parameters. For inorganic measurements of each water, a 100-ml aliquot of FGD water was preserved with trace metal nitric acid (10% v/v; Fisher Scientific Inc.) and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS; EPA Method 200.8). Total mercury analyses were conducted by cold vapor hydride generation atomic absorption (Perkin Elmer FIMS-400, EPA Method 245.1). Water chemistry parameters were analyzed according to Standard Methods (APHA 1998). Constituents of concern were identified based on comparisons between criteria in NPDES permits and mean concentrations of each constituent in four actual FGD waters. NPDES permit criteria included the maximum discharge limit (MDL) and toxicity reference values. Maximum discharge limits for each constituent were obtained from the USEPA's NPDES permit database for operating FGD scrubber coal-fired power plants. Toxicity reference values were obtained from EPA's toxicity database (ECOTOX Release 4.0) and included the lowest observable effect concentration (LOEC) or lethal mean concentration values, if LOEC values could not be obtained from this

database or literature reviews. When the concentration of a constituent in FGD waters exceeded the MDL or the toxicity reference value, the constituent was classified as a constituent of concern.

## 2.2 Design Pilot-Scale Constructed Wetland Treatment Systems (CWTS)

After characterization of FGD waters, pilot-scale CWTS were designed to remediate constituents of concern by evaluating their biogeochemical cycling (i.e. fate and transport) in aquatic systems and analogous research on treatment strategies from published literature. Using this information, constructed wetland treatment systems were assembled based on sequential ordering of desired reactions and potential for effective remediation of constituents of concern.

### 2.2.1 *Assembly of Constructed Wetland Treatment Systems*

An equalization basin (EQ) was the initial component of the constructed wetland treatment system and consisted of a polypropylene cylindrical container ranging in volume from 3,780 to 6,800 L. Inflow FGD waters were loaded into the treatment systems using piston-driven pumps (Fluid Metering Inc.) calibrated at flow rates (ml/min) to establish a specific hydraulic retention time (HRT) in each system component. Sequential flow through these systems was established using gravity.

To evaluate the performance of pilot-scale CWTS, three replicated series of reactors were used to evaluate the consistency of performance between systems (Figure 1a). Each system consisted of four treatment reactors in series that included two reducing reactors, a rock basin, and an oxidizing reactor. Each reactor was contained in a 378-L Rubbermaid® utility tank. Reducing reactors contained approximately 30-cm of river sand as hydrosol (3-5% organic matter by volume, 1% gypsum by volume, 200lb/ac of

zero-valent iron) and were planted with *Schoenoplectus californicus* C. A. Meyer. The rock basin was 50-cm of pea-gravel (Fowler Corporation; Seneca, SC), and the oxidizing reactor contained approximately 30-cm of river sand hydrosoil planted with *Typha angustifolia* L.

To evaluate the treatment performance of pilot-scale CWTS for pilot-scrubber FGD waters, the experimental pilot-scale CWTS consisted of two treatment systems each with two replicates (Figure 1b). Treatment systems were defined as Ash CWTS and No-Ash CWTS. Both treatment systems were established with four reactors in series that included two reducing reactors, a modified rock basin, and an oxidizing reactor. Each reactor was contained in a 265-L Rubbermaid<sup>®</sup> utility tank. All reducing reactors contained approximately 30-cm of river sand hydrosoil (3-5% organic matter by volume, 1% gypsum by volume) and were planted with *S. californicus*. The modified rock basin was equally divided with the inflow-half consisting of 12.7-cm to 17.8-cm granite cobble and the latter half consisting of 30-cm of hydrosoil and *T. angustifolia*. Oxidizing reactors contained approximately 30-cm of hydrosoil, and were planted with *T. angustifolia*. The hydrosoil in the oxidizing reactors of the Ash CWTS was bottom ash collected from a coal-fired power plant; where as the hydrosoil in the oxidizing reactors of the Non-Ash CWTS was river sand. Total hydraulic retention time (HRT) for the CWTS was 168 hr or 36 hr per reducing reactor plus 48 hr each for the modified rock basin and oxidizing reactor.

### *2.3 Performance Measurement of CWTS for FGD Waters*

#### *2.3.1 Flue Gas Desulfurization Waters*

To understand the remediation potential of constructed wetland treatment systems for constituents of concern in FGD waters, three different FGD waters were selected for this study as described below. These waters were used to assess the removal of constituents of concern from formulated and actual FGD waters that range widely in chemical composition. Due to the phytotoxicity of chlorides, FGD waters were decreased to <5,000 mg as Cl/L through co-management with low ionic strength water (i.e. municipal water, Clemson, SC) for these studies.

Formulated FGD water was synthesized based on data from chemical analyses of four actual FGD waters. This formulation process included amending municipal water with 1) high-purity salts (Fisher Scientific Inc.) for the targeted constituents of concern (Hg, Se, and As); 2) technical grade salts for chloride and sulfate; 3) fly ash at 1000 mg/L; and 4) dibasic acid at an equivalent COD concentration of 250 mg/L. For this initial research, additional constituents such as nitrate, boron, copper, chromium, zinc, and other elements or compounds were not amended. Formulated FGD waters were loaded into the pilot-scale CWTS for twenty weeks (June to November) and samples were collected and analyzed bi-monthly (n=10) to determine the performance of pilot-scale CWTS. Since formulated FGD waters omit some constituents that may influence performance, actual FGD waters were also evaluated in this study.

Actual FGD water from an operating coal-fired facility was transported to Clemson University in an 18,900 L tanker. Due to low concentrations of selenium and mercury measured in this FGD water after dilution for chlorides, amendments were initiated so removal rates and removal percentages of these constituents could be discerned. Selenium was amended using sodium selenate and sodium selenite (2:1,

respectively) to achieve a total selenium concentration of ~2 mg/L. Mercuric nitrate was added to achieve a total mercury concentration of ~0.2 mg/L.

Four pilot scrubber FGD waters were produced using a pilot-scale scrubber (URS Pilot-Scale FGD Scrubber; URS Corp., Austin, TX) in conjunction with a full-scale coal-fired burner. These FGD waters were transported to Clemson University via two 18,900-L tankers. Pilot scrubber FGD waters were used to test the treatment efficiency of pilot-scale CWTS for four distinct FGD waters originating from four different coal sources. FGD waters were diluted to approximately 4,000 mg/L as chloride using the site water from the coal-fired power plant before loading into the pilot-scale CWTS.

#### *2.4 Analytical Procedures*

For each experiment conducted in this study, aqueous samples were collected from the equalization basin, inflows to the pilot-scale constructed wetland treatment system, and outflows from each reactor in series. Aqueous samples were collected in 1000-mL Nalgene<sup>®</sup> containers, preserved, and analyzed as previously described. Percent removal for each constituent of concern was calculated based on equation 1.

$$\text{Percent Removal} = (1 - ([A]_t / [A]_0)) * 100 \quad \text{Equation (1)}$$

Where  $[A]_t$  is the concentration of the constituent in the equalization basin (pre-treatment),  $[A]_0$  is the concentration of the constituent in the outflow sample of reactor four (post-treatment). Removal rates for mercury and selenium were calculated using a first-order rate equation.

$$\text{Removal Rate} = \ln([A]_t / [A]_0) = kt \quad \text{Equation (2)}$$

Where  $[A]_t$  and  $[A]_0$  are the same as described for percent removal,  $t$  is the total time of treatment, and  $k$  is the first-order rate coefficient. Oxidation-reduction (redox) potentials

of wetland hydrosols were measured using a milli-volt meter connected to *in situ* platinum-tipped electrodes and an Accumet® calomel reference electrode (Faulkner et al., 1989). All measurements were adjusted based on hydrogen ion potential of +244 mV.

### 2.5 Toxicity Evaluations

Toxicity evaluations were performed on pre- and post-treatment samples diluted to  $\leq 500$  mg/L as chloride, in order to remove toxicity solely due to chloride concentrations (reproductive NOEC = 640 mg/L as Cl<sup>-</sup>; unpublished data). These evaluations were conducted with *C. dubia* following the U.S. EPA protocol for measuring chronic toxicity of effluents and receiving waters to freshwater organisms (Lewis et al., 1994). Toxicity measurements were evaluated by comparing responses of *C. dubia*, in terms of survival and reproduction, exposed to pre- and post-treatment samples of FGD and control water (moderately hard water). Survival data were statistically compared using chi-square analysis (PROC FREQ; SAS, 1989) and reproduction data were compared using a one-way analysis of variance with Dunnett's tests as the mean separator (PROC GLM; SAS, 1989). All alpha levels were set at 0.05. Statistical methods and alpha limits were based on EPA's whole effluent toxicity test (WET) guidelines (Lewis et al., 1994). Water quality parameters including hardness, alkalinity, pH, dissolved oxygen, conductivity, and water temperature were measured initially (day 0) and daily throughout the duration of the toxicity experiment (days 1-7) according to Standard Methods (APHA, 1998).

## 3. Results and Discussion

### 3.1. Characterization of Flue Gas Desulfurization (FGD) Waters

Four actual FGD waters were analyzed for water chemistry parameters and total inorganic analyses (Table 1). Constituents of concern were identified as cadmium, chemical oxygen demand (COD), chloride, copper, mercury, selenium, and zinc (Table 2). All constituents of concern were identified based on toxicity values, except COD, which was identified as a potential constituent of concern due high concentrations measured in FGD waters ( $1339.3 \pm 377.3$  mg/L) and the relationship of COD to 5-d biochemical oxygen demand (BOD<sub>5</sub>) (maximum daily limit of 30 mg/L as BOD<sub>5</sub>). Boron was not assessed for potential toxicity effects since elemental analyses were not conducted, but may be identified as a constituent of concern, if total concentrations exceed 18 mg/L in effluent samples (Hickey, 1989). Currently available NPDES permits for discharge of FGD waters analyzed in this study have maximum daily limits for copper ( $\leq 1$  mg/L), iron ( $\leq 1$  mg/L), mercury ( $\leq 0.63$   $\mu$ g/L), total suspended solids ( $\leq 65$  mg/L), BOD<sub>5</sub> ( $\leq 45$  mg/L), oil and grease ( $\leq 12$  mg/L), pH (6 to 9 su), and toxicity evaluations using 7d static/renewal experiments with *C. dubia* for exposures of  $\geq 1.9\%$  as FGD water. Based upon review of available information, all other NPDES permits require “monitoring and reporting” for constituents in FGD water other than the listed constituents above. Based on a literature review of NPDES permits, only one discharge site is currently required to meet a maximum daily limit for selenium ( $\leq 26$   $\mu$ g/L as Se). Some NPDES permits also require tissue monitoring for fish species in the receiving system (i.e. mercury and selenium concentrations), speciation of selenium in the effluent samples, and toxicity evaluations using *Pimephales promelas*, but these criteria on NPDES permits were not common and therefore not used as performance criteria in this study.

### 3.2 Design Constructed Wetland Treatment Systems for FGD Waters

For this study, pilot-scale systems were chosen to evaluate treatment performance of constructed wetland treatment systems to minimize cost and space requirements, to enable adjustments, and to efficiently obtain data to assess the remediation potential of these systems for FGD waters. Each component of these systems was designed to target the treatment of specific constituents of concern as follows:

Equalization basins (EQ basin) were designed as the initial component in each experimental system to remove suspended solids. Scale and dimensions of this component were simulated based on full-scale equalization basins.

Reducing reactors were designed to have redox conditions of -250 to -100 mV and pH values between 5 and 7 standard units in the bulk hydrosol. Hydrosol was planted with giant bulrush (*Schoenoplectus californicus* C. A. Meyer); a plant that has little radial oxygen loss that aids in maintaining low redox conditions (Murray-Gulde et al., 2005b). Organic matter as 5% (v/v) double chip pine mulch was used as the electron donor for microbial activity (e.g. dissimilatory sulfate reduction) and regulation of dissolved oxygen concentrations within sediments. These systems were designed based on studies that indicated the mobility of arsenic, cadmium, copper, mercury, and zinc under low dissolved oxygen concentrations (suboxic to anaerobic) can be decreased by co-precipitation reactions with sulfide-bearing minerals (Moore et al., 1988; Kirk 2004; Murray-Gulde et al., 2005a). In these reducing reactors, dissimilatory sulfate reduction provides sulfides and mineral-bearing sulfides for removing many constituents of concern from FGD waters. Based on studies by Masscheleyn and Patrick (1993) and Johnson and Bullen (2003) elemental selenium and metal selenides can form from both chemical and

microbial reduction processes. Reduced selenium species are typically less mobile and reduction of Se (VI) and Se (IV) to insoluble Se<sup>0</sup> has been documented within reducing aqueous environments (Zhang et al., 2003).

Oxidizing reactors were designed to establish an oxidizing wetland environment with bulk sediment redox potentials of -50 to +200 mV. This was accomplished by selecting a porous hydrosol with a low organic carbon content and wetland plants with a high rate of radial oxygen loss (*T. angustifolia*). These design characteristics were chosen based on studies by Kirk (2004) and biogeochemical modeling (Brookens, 1988) that indicate under high dissolved oxygen concentrations, dissolved iron species can be transformed into solid forms (oxyhydroxides) that enable co-precipitation with arsenic and selenium oxyanions. Oxidizing reactors enable re-oxygenation of the ambient water and can decrease nutrient concentrations, thus limiting the environmental risks these waters pose to aquatic receiving systems.

### *3.3 Flue Gas Desulfurization Waters: Chemical Composition*

Chemical compositions of FGD waters are listed in Table 1. For formulated FGD waters, targeted constituents of concern (Hg and Se) were amended as the mean concentrations found in undiluted actual FGD waters and arsenic concentrations were amended at concentrations of 0.17 mg/L rather than the mean of undiluted actual FGD waters due to the effect of one FGD water with evaluated As concentrations (4.10 mg/L as As). Mean chemical oxygen demand concentrations were greater for actual FGD waters due to amendments of organic acids used in the scrubbing process.

Actual-amended FGD waters (n=2) were similar in composition to actual FGD waters after amendments for the targeted constituents of concern (As, Hg, and Se). The

second actual-amended FGD water received less dilution water than the first actual-amended FGD water and resulted in increased in chloride concentrations (5200 vs. 4150mg/L) between sampling periods. Non-amended constituents in the actual FGD waters may have differ by approximately 13%, but selenium and mercury concentrations had no measurable deviation (Table 1).

For comparison of pilot-scrubber FGD waters, targeted constituents of concern (Hg, Se, and As) were variable between FGD waters and ranged in concentrations from 0.00039 to 0.0432 mg/L, 0.610 to 2.97 mg/L, and 0.004 to 0.101 mg/L, respectively. Identified selenium species in pilot-scrubber FGD waters were primarily the selenate oxyanions; however, this analysis (IC-ICP-MS) does not provide information regarding some organic or neutral selenium species. Boron concentrations ranged from 32 to 110 mg/L before dilution for chlorides or 29 to 103 mg/L after dilution. These data indicate that coal-source influences the chemical composition of FGD waters, especially potentially toxic contaminants such as mercury, selenium, arsenic, and boron. Data on other elements (cadmium, chromium, copper, lead, and zinc) in FGD waters also follow these trends (data not shown). Water chemistry parameters differed slightly for chemical oxygen demand (81 to 208 mg/L) sulfate (1245 to 1611 mg/L) and total suspended solid concentrations (5.8 to 356.0 mg/L), but are more consistent when chloride concentrations are standardized between samples.

### *3.4 Performance Measurement of Constructed Wetland Treatment Systems*

Based on NPDES permit criteria identified in this study, the performance of pilot-scale CWTS was determine by monitoring the removal extents and rates of mercury to meet a discharge criteria of  $\leq 0.63 \mu\text{g/L}$  and the pre- and post-treatment toxicity of FGD

waters from the pilot-scale CWTS. No statistical differences were measured for constituent removal extents or rates between ash and no-ash pilot-scale CWTS ( $P < 0.001$ ), and therefore, these data are presented as mean values.

Mean percent removals and rates of mercury from equalization basin samples (pre-treatment) to outflow samples (post-treatment) from the pilot-scale CWTS were 93.2 % and  $0.677 \text{ d}^{-1}$  for formulated FGD waters, 96.1 % and  $0.2370 \text{ d}^{-1}$  for actual-amended FGD waters, and 99.0 % and  $0.687 \text{ d}^{-1}$ , 68.7 % and  $0.168 \text{ d}^{-1}$ , no removal, and 98.7 % and  $0.621 \text{ d}^{-1}$  for the first, second, third, and fourth pilot-scrubber FGD waters (Figures 2, 3, and 4). Based on an NPDES permit criterion of  $\leq 0.63 \text{ }\mu\text{g/L}$  of total mercury in effluent samples, 85% of the post-treatment FGD waters (17 of 20) achieved the targeted treatment performance using pilot-scale CWTS. Only the post-treatment samples from pilot-scale CWTS with loading of actual-amended FGD waters ( $6.2 \text{ }\mu\text{g/L}$ ;  $n=2$ ) and one effluent sample from the third pilot-scrubber FGD waters ( $1.2 \text{ }\mu\text{g/L}$ ;  $n=1$ ) exceeded this daily maximum discharge limit. Actual-amended FGD waters contained mercury concentrations of  $160 \text{ }\mu\text{g/L}$  and may not be representative of currently produced actual FGD waters, since the highest concentration measured in actual FGD waters was only  $47 \text{ }\mu\text{g/L}$ . Dissolved concentrations of mercury in FGD waters may increase if air emission criteria for mercury are established, since forms of mercury such as elemental mercury ( $\text{Hg}^0$ ) are relatively insoluble in FGD waters compared to mercuric chloride ( $\text{HgCl}_2$ ) (Díaz-Somoano *et al.*, 2005). Mercury removal ( $> 98\%$ ) was greater for FGD waters, in which inflow concentrations exceeded  $36 \text{ }\mu\text{g/L}$ , but apparently less effective for FGD waters containing  $< 0.9 \text{ }\mu\text{g/L}$  as mercury (no removal to 68.5 %). As constituent concentrations decrease, the formation of insoluble complexes becomes more

thermodynamically unfavorable (Stumm and Morgan, 1995). This concentration-dependent response may explain differences in mercury removal for these experiments; however, effects of prior loading, biological activity, and differences in constituent speciation cannot be eliminated as influencing factors.

Mean percent removals and rates of selenium from equalization basin samples (pre-treatment) to outflow samples (post-treatment) from pilot-scale CWTS were 84.6 % and 0.468 d<sup>-1</sup> for formulated FGD waters, 80.1 % and 0.404 d<sup>-1</sup> for actual amended FGD waters, and 89.7 % and 0.327 d<sup>-1</sup>, 63.6 % and 0.145 d<sup>-1</sup>, 51.2 % and 0.103 d<sup>-1</sup>, and 29.5 % and 0.050 d<sup>-1</sup> for the first, second, third, and fourth pilot-scrubber FGD waters (Figures 2, 3, and 4). To date, available NPDES permits for FGD water discharge do not contain a maximum daily limit for elemental constituent concentrations other than copper, iron, and mercury. The only exception we found was for selenium (< 26 µg/L), but this discharge limit may not be representative of other sites due to the historic Se contamination within this site's receiving system. Due to these findings, performance criteria for pilot-scale CWTS or maximum daily limit were not justified for selenium and therefore must be determined using toxicity evaluations. For the pilot-scrubber FGD water experiments, selenium removal declined with each sequential loading of FGD water (Table 3). This trend indicates that removal mechanisms were possibly inhibited by constituents in these FGD waters, subject to decreasing binding sites or reactants, or was less efficient due to differences in forms of selenium. Based on selenium biogeochemistry and selenium speciation results, it is suggested that microbial activity (i.e. selenium or iron reduction) or products of these reactions (i.e. ferrous ions) were being inhibited since reduction of selenium to elemental forms and complexation

reactions with ferrous iron can decrease the solubility of selenium oxyanions (Francisco et al., 1992; Losi and Frankenberger, 1997; Oremland et al., 1999; Zhang et al., 2005). Based on potential in situ selenate reduction rates within sediments (Steinberg and Oremland 1990; Oremland et al., 1991; Lortie et al., 1992; Herbel et al., 2003) coupled with electron donor concentrations in these pilot-scale CWTS, we suggest that microbial reduction of selenium species to elemental forms does not account for the removal extents and rates measured in these experiments. Reduction reactions of selenium forms in FGD waters with ferrous or zero-valent iron species (Zhang et al., 2005) and co-precipitation with ferrihydrite or goethite (Balistrieri and Chao, 1987, 1990) may have accounted for the relatively high removal extents measured for the first pilot-scrubber FGD water and may have decreased for the latter pilot-scrubber FGD waters due to the decrease of reactive iron species. Zero-valent iron was amended to all pilot-scale CWTS at concentrations of 22-g per reducing reactor and therefore could have served as a reducing and complexing agent for selenium species. Zingaro et al. (1997) suggested that Se (VI) can be reduced to Se (IV) in the presence of ferrous iron and after transformation to Se (IV), rapid complexation with iron oxyhydroxides ( $\text{Fe}_{\text{OH}}$ ) can occur. Zhang et al. (2005) suggested that Se (VI) may directly adsorb to  $\text{Fe}_{\text{OH}}$  and further react to produce an insoluble selenium-iron species. Microbial transformations of selenium species maybe important reaction pathways in these systems and may aid in the sequestering of selenium by further reductive transformations such as Se (IV) to  $\text{Se}^0$  and Se (-II) in the sedimentary environment (Masscheleyn and Patrick, 1993).

Mean percent removals and rates for arsenic were  $64.4 \pm 43.7 \%$  and  $0.258 \pm 0.112 \text{ d}^{-1}$  for formulated FGD waters, but no removal was measured for actual-amended

FGD waters. For the actual-amended FGD waters, the total arsenic concentration in the equalization basin after four weeks of loading was 0.074 mg/L and the mean outflow concentration was  $0.028 \pm 0.383$  mg/L, indicating a removal extent of 61.6 %. However, during the first sampling period the total arsenic concentrations in the outflow samples ( $0.173 \pm 0.06$  mg/L) were approximately 2.5 times greater than the equalization basin (0.073 mg/L). For both sampling periods with the actual-amended FGD water experiments, the total selenium removal was greatest in outflow samples of the rock basins (91.7 %) versus the oxidizing reactors (80.1 %). These data indicate that leaching of arsenic and selenium occurred during these sampling periods. Based on elemental analyses from each treatment reactor, we hypothesize that the final wetland reactor was the site of re-suspension of arsenic and selenium forms and was due to unstable redox conditions within the oxidizing wetland reactors. Arsenic removal did not occur in either pilot-scale CWTS for pilot-scrubber FGD waters receiving inflow concentrations ranging from 0.005 to 0.101 mg/L. Biogeochemical modeling of arsenic in FGD waters indicated that insoluble forms would occur in reducing reactors with an Eh < -200mV and pH of 7 (Brookens, 1988), but was not documented in these experiments.

Toxicity evaluations using *C. dubia* were used to determine treatment performance of pilot-scale CWTS for the three types of FGD waters used in this study. These evaluations are routinely used for NPDES monitoring of discharge effluents and can indicate the treatment efficiency of a system (i.e. transfer or transformation) for constituents of concern. For the actual-amended FGD waters, pre- and post-treatment samples were diluted for chloride toxicity (unpublished data) by 93.75 % or ~260 (1<sup>st</sup> sampling period) and ~330 mg/L (2<sup>nd</sup> sampling period) as chloride. Since blowdown

FGD waters typically contain approximately 16,000 mg/L as chloride, the concentrations used in these experiments are similar to NDPEs permit criteria of  $\geq 1.9\%$  as FGD water or approximately 300 mg/L as Cl<sup>-</sup>. For both post-treatment samples (1<sup>st</sup> and 2<sup>nd</sup> sampling periods) there was a significant decrease in toxicity from inflow to outflow of pilot-scale CWTS. *C. dubia* survival increased from 20 % to 80 % for the first sampling period. Reproduction was statistically greater for post-treated samples in comparison to pre-treated samples and reproduction in post-treated samples did not differ from laboratory organisms (controls;  $p < 0.001$ ). For first and fourth pilot scrubber FGD waters, the survival of *C. dubia* was adversely affected in exposures of all pre-treated samples (both treatment systems); however, no survival differences were observed for post-treated samples (Figure 5). Additionally, for both pilot scrubber FGD waters, no statistical differences in reproduction occurred for post-treated samples of either treatment system; however, both pre-treated samples statistically inhibited reproduction (Figure 6). For the second pilot scrubber FGD water, significant *C. dubia* mortality occurred for the pre-treated samples but no differences were measured for either post-treated sample (Figure 6). A significant increase in *C. dubia* reproduction was measured between the pre- and post-treated samples for both systems. For the third pilot scrubber FGD water, *C. dubia* survival was not affected for any pre- or post-treated samples of either treatment system. Reproduction was not affected in the pre-treated samples for the no-ash or ash systems, but significantly decreased for exposures of the post-treated sample from the no-ash system. This effect is believed to be due to a handling error since the initial introduction of *C. dubia* resulted in complete mortality and re-testing of the sample resulted in complete survival. Lower reproduction may have been a result of inadequate feeding of

the *C. dubia* population used in the re-testing of the sample. These data indicate that pilot-scale CWTS can decrease environmental risks FGD waters may pose to receiving systems thus enabling discharge of post-treated waters in compliance with NPDES permits.

#### **4. Conclusions**

For this study, a risk characterization was conducted by comparing the mean concentration of elements or compounds measured in four actual FGD waters to NPDES permit criteria obtained from USEPA databases. Results of this risk-based characterization indicate that cadmium, COD, chloride, copper, mercury, selenium, and zinc are constituents of concern in these FGD waters that require treatment before discharge. Since FGD waters must meet discharge criteria established by the USEPA through NPDES permits, pilot-scale CWTS were designed to decrease the chemical solubility of targeted constituents and toxicity of FGD waters. This was accomplished by assessing the biogeochemical cycling of constituents of concern through literature reviews and biogeochemical data. Each treatment system contained an equalization basin and two reducing and oxidizing reactor types. Treatment performance of these systems was monitored for three FGD water types (formulated, actual-amended, and pilot scrubber FGD waters) by measuring percent removals and rates of the constituents of concern and toxicity of pre- and post-treated FGD waters. Results from these studies indicated that targeted constituents of concern in FGD waters can be decreased in constructed wetland treatment systems, and with appropriate co-management of low-ionic strength water for chloride concentrations, toxicity is decreased to acceptable discharge limits. These studies indicate that constructed wetland treatment systems can be

a viable treatment strategy for FGD waters, but continued research is needed to thoroughly understand biogeochemical cycling (i.e. fate and transport) of constituents of concern in these systems thereby enhancing the sequestration of these contaminants.

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Table 3.1 Chemical composition of actual, formulated, actual-amended, and pilot-scrubber FGD waters for elemental and water chemistry parameters presented as means and standard deviation values (mean ± standard deviation) in milligrams per liter (mg/L).

Parameter	Actual FGD Waters	Formulated FGD Waters <sup>1</sup>		Actual-amended FGD Waters		Pilot-Scrubber FGD Waters			
		Nominal	Measured	Pre-	Post-Amended	PS1	PS2	PS3	PS4
<sup>2</sup> Mercury, Total	15.2 ± 28.5	2.0	2.57 ± 1.2	< 0.2	160.0	43.2	4.7	0.39	47.0
Selenium, Total	5.10 ± 8.12	4.00	4.22 ± 0.319	0.15	1.80	2.97	0.61	0.649	2.09
<sup>3</sup> Selenite (Se IV)	NM	NM	NM	NM	NM	95.0%	50.2%	34.8%	86.3%
<sup>3</sup> Selenate (Se VI)	NM	NM	NM	NM	NM	< 1.0%	6.0%	3.6%	< 1.0%
Arsenic, Total	1.07 ± 2.02	0.17	0.171 ± 0.023	0.014	0.072 ± 0.001	0.101	0.004	0.035	0.035
<sup>4</sup> Boron, Total	NM	NM	NM	NM	NM	60	32	100	110
Chloride, Total	10310 ± 6433	4000	3678 ± 288	9300	4675 ± 742	3550	3150	4050	4225
Calcium, Total	2308 ± 1103	900	NM	2880	NM	NM	NM	NM	NM
Magnesium, Total	2960 ± 1156	1150	NM	1360	NM	NM	NM	NM	NM
Sodium, Total	708 ± 472	NA	NM	624	NM	NM	NM	NM	NM
Sulfate	2059 ± 793	800	828 ± 181	1645	432 ± 35	1522	1611	1245	1364
pH	6.28 ± 0.23	7.00	7.00 ± 0.26	6.38	6.72 ± 0.23	6.79	6.99	7.11	7.10
Alkalinity as CaCO <sub>3</sub>	390 ± 194	150	103.4 ± 10.5	152	63 ± 7.1	26	46	24	32
Hardness as CaCO <sub>3</sub>	18677 ± 6013	7250	6540 ± 2480	10400	6600 ± 282	9800	4200	6400	6400
Conductivity	28.86 ± 8.31	11.00	9.21 ± 0.60	23.11	11.16 ± 2.44	10.88	10.05	11.65	11.96
Dissolved Oxygen	7.23 ± 1.22	8.00	7.75 ± 1.55	9.03	8.48 ± 0.16	9.09	8.66	8.66	8.96
Chemical Oxygen Demand	1339.9 ± 377.3	250	227.4 ± 44.9	938	238.5 ± 3.5	183	81	155	208
Organic Carbon	81.94 ± 40.29	100	91.96 ± 58.73	64.49	161.3 ± 95.1	NM	NM	NM	NM
Total Suspended Solids	10901 ± 20042	200	207.0 ± 136.6	25	66.4 ± 1.9	5.80	10.35	159.6	356
Total Dissolved Solids	39103 ± 10724	8000	6183 ± 2965	23875	12267 ± 380	11674	10921	13851	19025

<sup>1</sup> Formulated FGD waters were synthesized based on a chloride concentration of ~4000 mg/L.

<sup>2</sup> Reported as micrograms per liter (µg/L).

<sup>3</sup> Analyzed by Ion Chromatography Inductively Coupled Mass Spectrometry (IC-ICP-DRC-MS).

<sup>4</sup> Measured before dilution for chloride concentrations.

NM: Not Measured.

NA: Not Amended

Table 3.2 Identified constituents of concern from four actual FGD waters based on toxicity effects after co-management for chlorides.

Constituent <sup>1</sup>	Species	Experiment	FGD Waters <sup>2</sup> (mg/L)	Toxicity Value <sup>3</sup> (mg/L)	Reference
Cadmium	C.dubia	7d S/R	0.037	0.004	Suedel <i>et al.</i> , 1997
Chloride	C.dubia	7d S/R	4000	<b>1042</b>	DeGraeve <i>et al.</i> , 1992
Copper	C.dubia	7d S/R	0.283	0.032	Carlson <i>et al.</i> , 1986
Mercury	D. magna	48h S	0.0051	<b>0.0044</b>	Barera and Adams 1983
Selenium	D. magna	48h S	1.30	<b>0.55</b>	Maier <i>et al.</i> , 1993
Zinc	C. dubia	7d S/R	1.50	<b>0.149</b>	Carlson <i>et al.</i> , 1986

<sup>1</sup> Amendment source for toxicity tests included: CdCl<sub>2</sub>, NaCl, CuCl<sub>2</sub>, HgCl<sub>2</sub>, Na<sub>2</sub>SeO<sub>3</sub>, and ZnCl<sub>2</sub>.

<sup>2</sup> Estimated mean concentration of constituents in actual FGD waters after dilution to 4000 mg/L.

<sup>3</sup> Toxicity values in “bold” are estimated lethal mean concentration values (LC<sub>50</sub>).

Table 3.3 Total aqueous concentrations of mercury ( $\mu\text{g/L}$ ) and selenium ( $\text{mg/L}$ ) measured in samples from constructed wetland treatment system components by FGD water type.

FGD Water Type	Constituent Concentrations: Pilot-Scale CWTS Components						Overall	
	EQ Basin	Inflow	Outflow Reactor 1	Outflow Reactor 2	Outflow Reactor 3	Outflow Reactor 4	Removal Extent (%)	Removal Rate ( $\text{d}^{-1}$ )
Formulated								
Hg	2.38±1.25	3.63±1.19	1.33±0.45	0.71±0.25	0.28±0.14	0.16±0.08	93.2	0.675
Se	4.27±0.34	4.11±0.28	2.92±0.72	1.44±0.68	0.67±0.42	0.65±0.30	84.6	0.468
Actual-amended (1 <sup>st</sup> )								
Hg	160.0	136.6±5.78	42.6±6.51	27.33±16.01	10.80±4.30	5.03±3.49	96.8	0.864
Se	1.80	1.80	1.16±0.75	0.36±0.196	0.15±0.09	0.19±0.09	89.4	0.562
Actual-amended (2 <sup>nd</sup> )								
Hg	160.0	163.3±5.77	67.3±37.3	23.66±7.23	10.06±1.74	7.33±0.05	95.4	0.770
Se	1.80	1.86±0.57	0.29±0.072	0.29±0.07	0.15±0.05	0.53±0.15	70.5	0.305
Pilot-Scrubber W1								
Hg	43.2	22.14±12.55	6.68	1.10±0.71	0.41	0.43±0.47	99.0	0.658
Se	2.98	2.75±0.062	1.52	0.77±0.23	0.63	0.30±0.07	89.9	0.327
Pilot-Scrubber W2								
Hg	0.89	0.63±0.03	0.78±0.06	0.59±0.09	0.36±0.04	0.28±0.03	68.5	0.165
Se	0.61	0.60±0.01	0.54±0.11	0.37±0.08	0.30±0.06	0.22±0.03	63.9	0.145
Pilot-Scrubber W3								
Hg	0.39	0.48±0.03	1.17±0.14	0.50±0.21	0.86±0.32	0.91±0.64	NR	--
Se	0.64	0.62±0.01	0.64±0.02	0.51±0.07	0.41±0.08	0.31±0.06	51.5	0.103
Pilot-Scrubber W4								
Hg	36.31	43.01±0.38	16.67±1.76	4.83±1.95	0.79±0.16	0.47±0.13	98.7	0.621
Se	2.09	2.20±0.08	2.16±0.16	2.06±0.23	1.79±0.25	1.47±0.27	29.6	0.050

NR: No measured removal; Hg: Total Aqueous Mercury; and Se: Total Aqueous Selenium

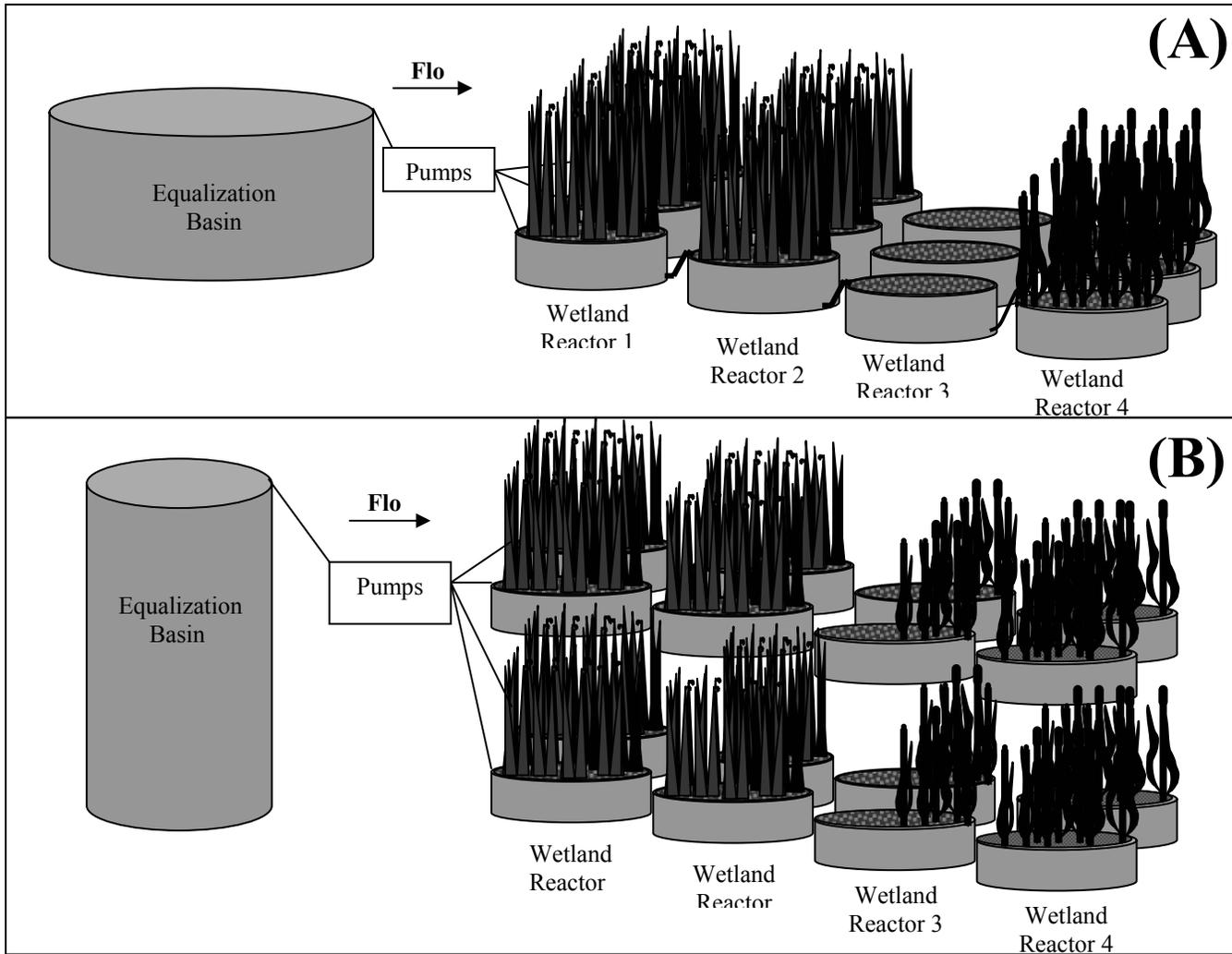


Figure 3.1 Systematic diagram of the pilot-scale constructed wetland treatment systems (CWTS) used to determine performance criteria for (A) formulated and actual-amended FGD waters and (B) pilot-scrubber FGD waters.

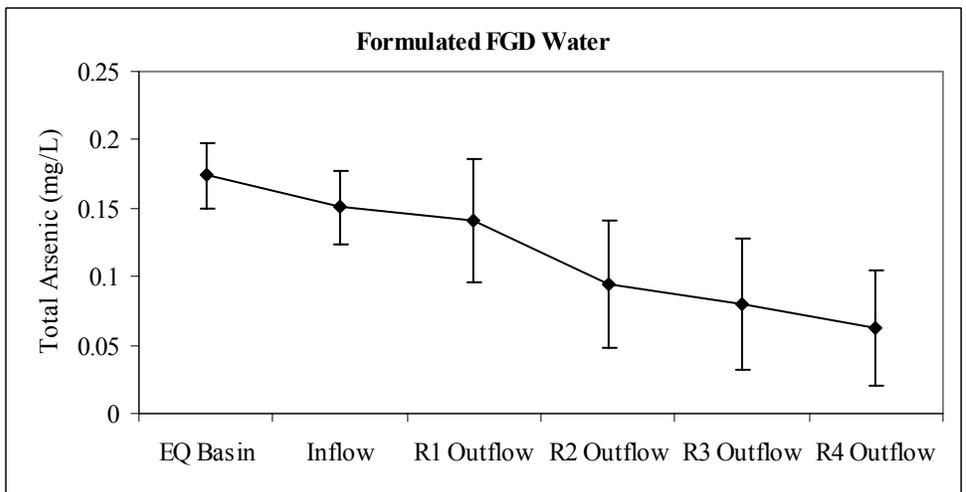
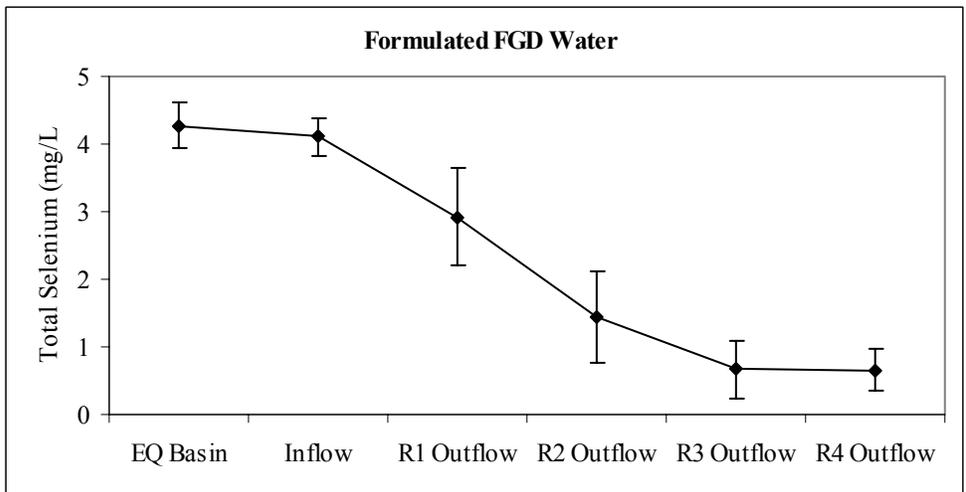
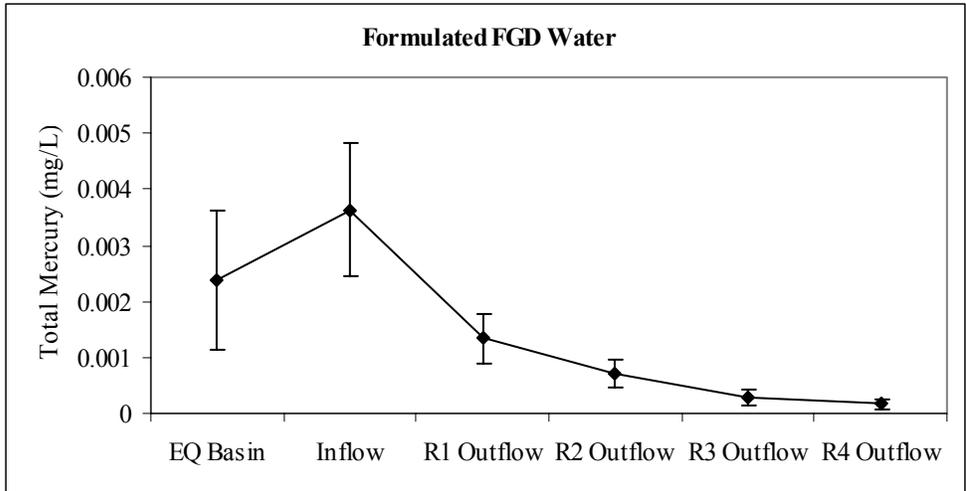


Figure 3.2 Total aqueous concentration of arsenic, selenium, and mercury from the equalization basin and outflow samples each reactor component of the constructed wetland treatment system exposed to formulated FGD waters.

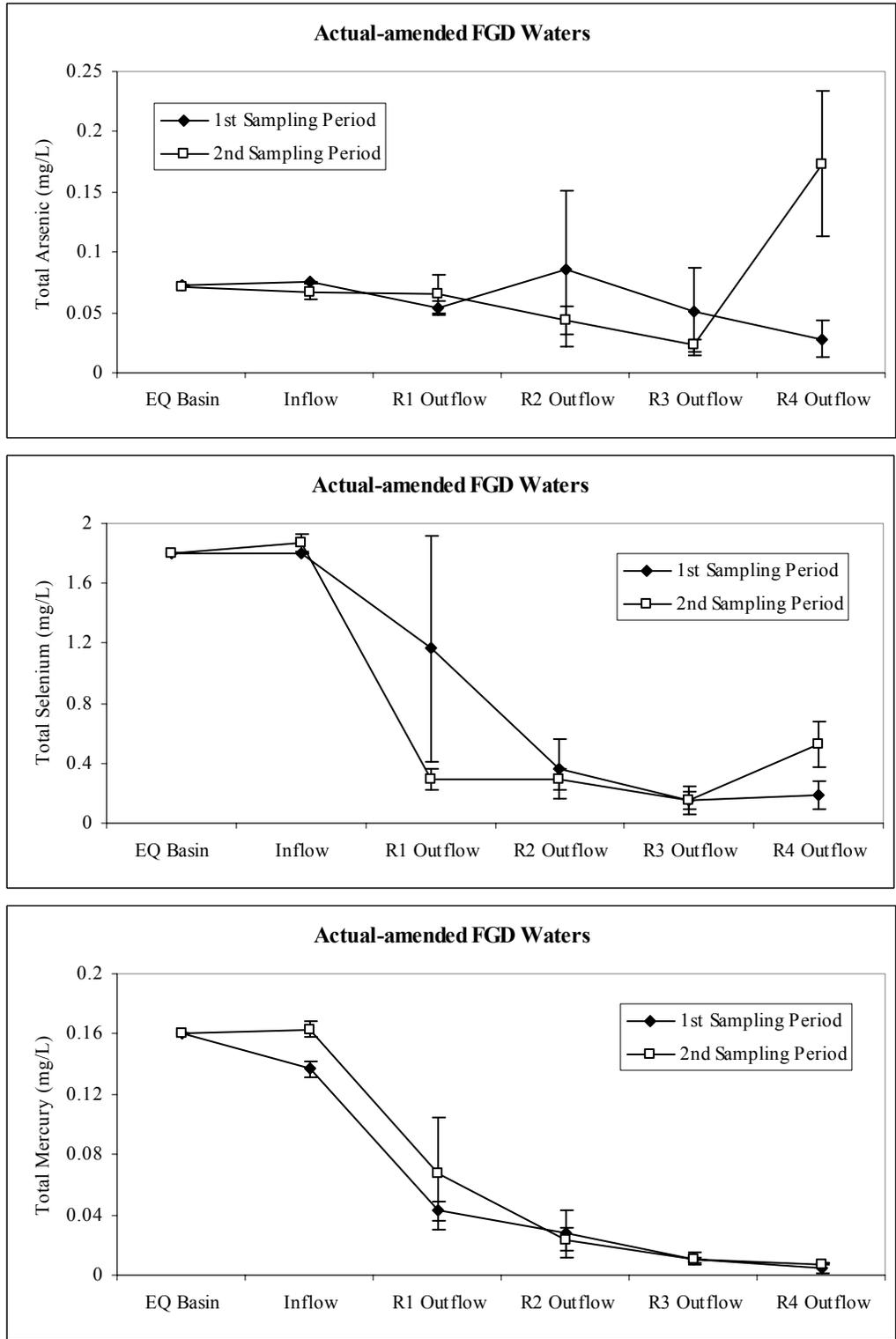


Figure 3.3 Total aqueous concentration of arsenic, selenium, and mercury from the equalization basin and outflow samples each reactor component of the constructed wetland treatment system exposed to actual-amended FGD waters.

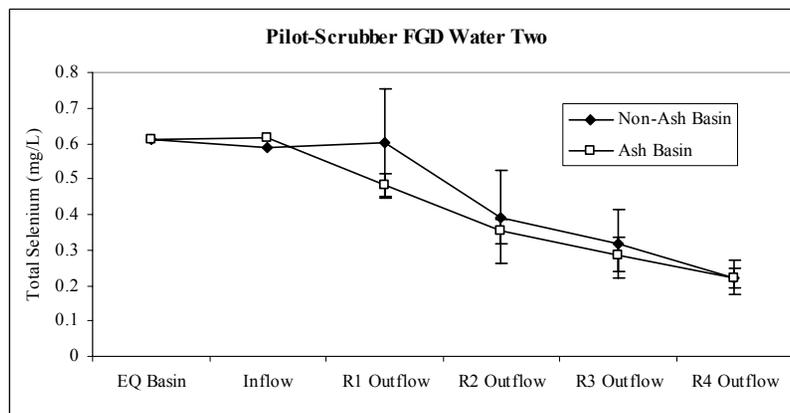
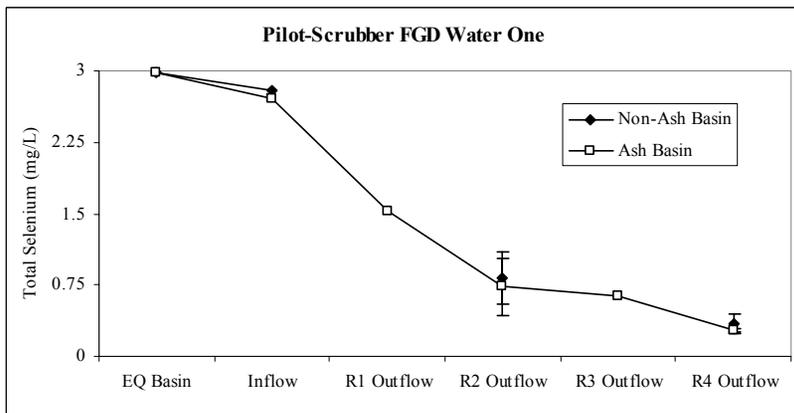
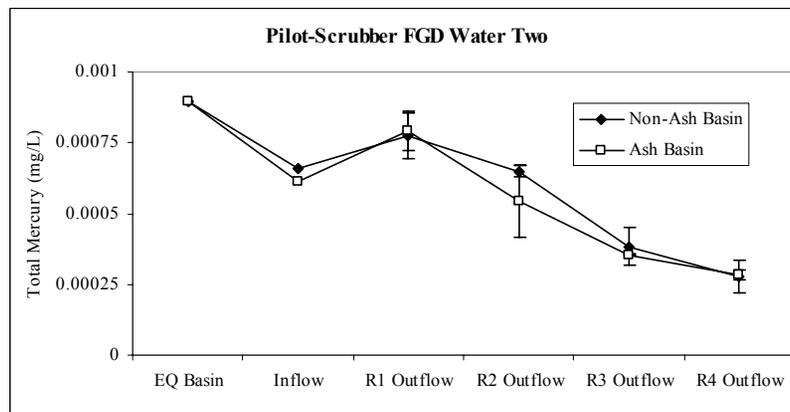
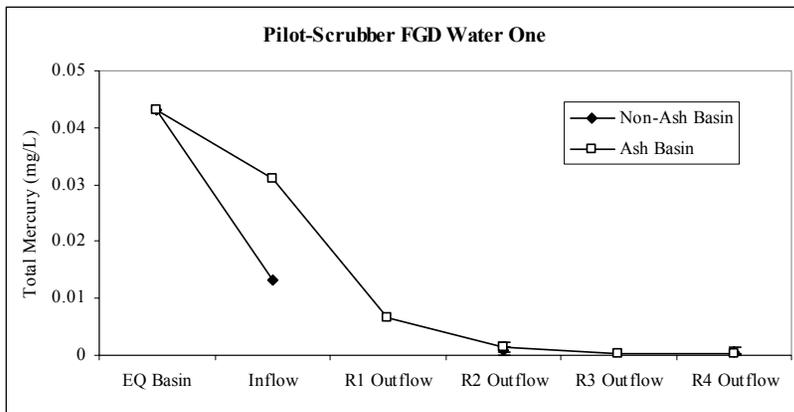


Figure 3.4a Total aqueous concentration of mercury and selenium from the equalization basin and outflow samples each reactor component of the constructed wetland treatment system exposed to pilot-scrubber FGD waters.

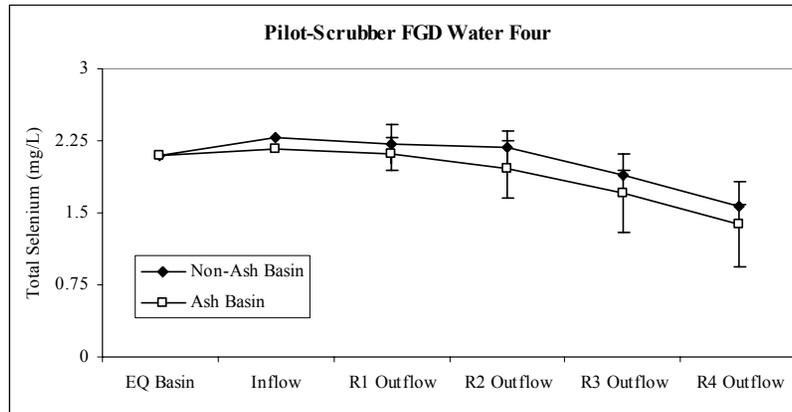
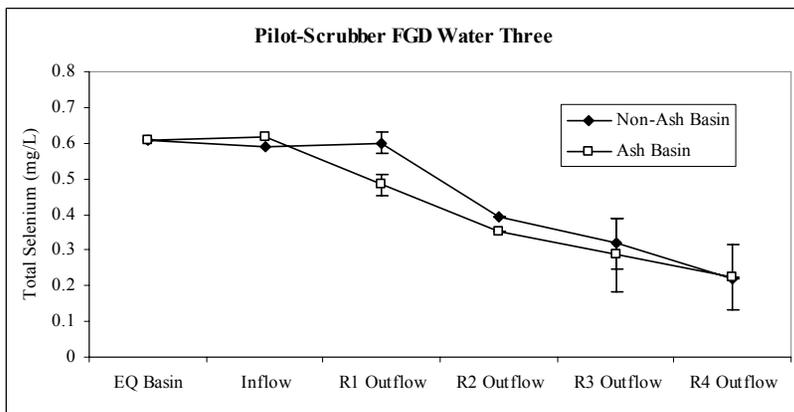
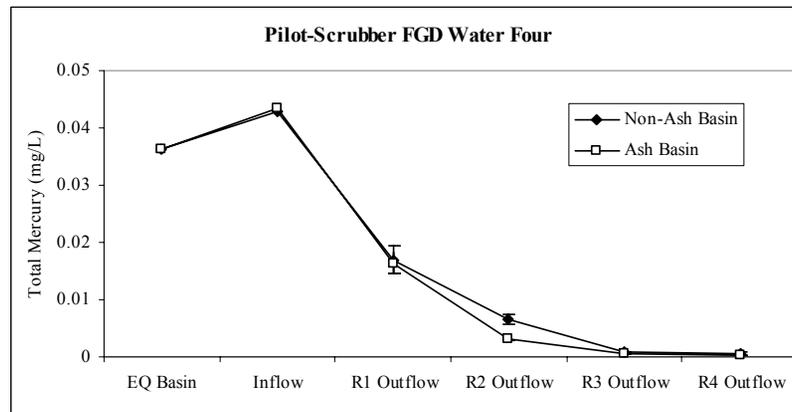
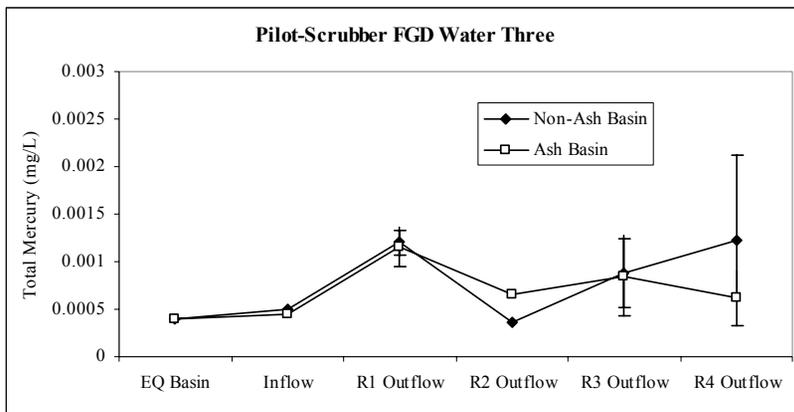


Figure 3.4b Total aqueous concentration of mercury and selenium from the equalization basin and outflow samples each reactor component of the constructed wetland treatment system exposed to pilot-scrubber FGD waters.

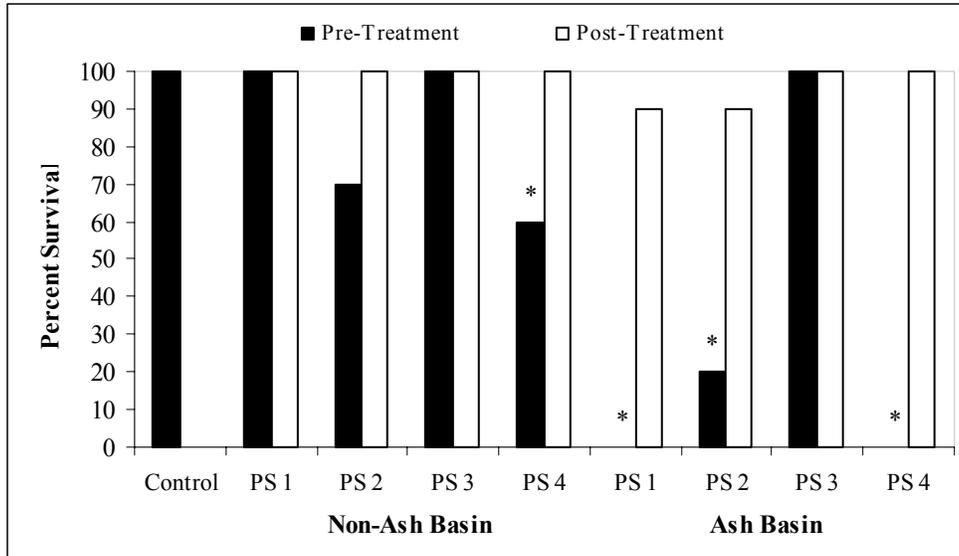


Figure 3.5 Percent survival of *Ceriodaphnia dubia* exposed to pre- and post-treatment samples of four pilot scrubber FGD waters treated by no-ash and ash pilot-scale constructed wetland treatment systems. Significant differences between controls and treatments are identified by asterisk (\*).

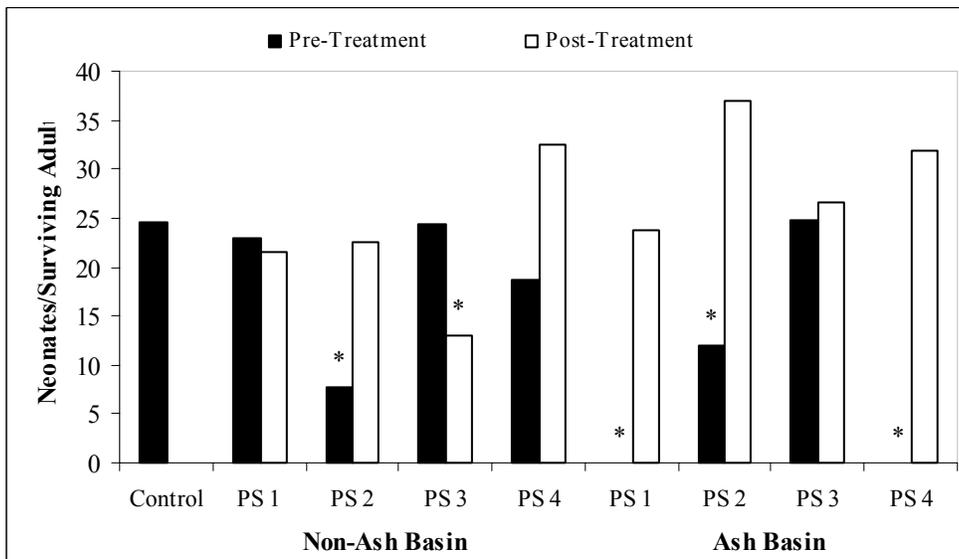


Figure 3.6 Reproduction of *Ceriodaphnia dubia* exposed to pre- and post-treatment samples of four pilot scrubber FGD waters treated by no-ash and ash pilot-scale constructed wetland treatment systems. Significant differences between controls and treatments are identified by asterisk (\*).

## CHAPTER FOUR

### ENHANCING TOTAL SELENIUM AND MERCURY REMOVAL IN FLUE GAS DESULFURIZATION WATER USING ORGANIC CARBON ADDITIONS TO A PILOT-SCALE CONSTRUCTED WETLAND TREATMENT SYSTEM

#### **Abstract**

Due to legislation such as the Clean Air Act (CAA, 1990), coal-fired power plants are decreasing hazardous air pollutants by transforming and transferring these constituents into the water phase. This process is referred to as flue gas desulfurization (FGD). The targeted air pollutant for a FGD system is sulfur dioxide, but during the wet-FGD scrubbing process, contaminants such as mercury (Hg) and selenium (Se) are also transferred into the scrubbing slurry water (i.e. FGD water). Since FGD water is typically discharged due to large volumes produced daily and is incompatible for reuse, treatment of problematic constituents is required to meet National Pollutant and Discharge Elimination System (NPDES) permits under the Clean Water Act. Treatment systems, therefore, are commonly designed and constructed before a site FGD water is characterized as to its chemical composition, constituents requiring treatment, and knowledge of the performance criteria needed to achieve discharge limits. This limitation may require improvement to the performance of existing treatment systems. Additions of organic carbon have been successful for decreasing Se concentrations in low ionic strength waters and this approach may be suitable for enhancing the performance of systems such as constructed wetland treatment systems (CWTS). Testable models such as pilot-scale systems are useful for evaluating the response of CWTS to additions such as organic carbon. To evaluate this approach we established three research objectives: 1)

determine performance goals for Se and Hg in FGD water through reasonable potential analysis (RPA), 2) compare and contrast removal rates and extents of removal for selenium and mercury in a FGD water using sucrose amended pilot-scale CWTS, yeast culture amended pilot-scale CWTS, hybrid pilot-scale CWTS, and a control pilot-scale CWTS, and 3) determine the compliance of treated FGD waters with RPA values for Se and Hg using data from sucrose amended pilot-scale CWTS, yeast culture amended pilot-scale CWTS, hybrid pilot-scale CWTS, and a control pilot-scale CWTS. The calculated RPA values for Hg and Se are 630 ng/L and 263 µg/L, respectively, and were selected as the performance criteria for this study. For post-treated samples, removal rates and extents of removal for Se were greater ( $p < 0.05$ ) for the sucrose and yeast amended pilot-scale CWTS versus the hybrid and control pilot-scale CWTS for all months tested (August, September, October, and November), except the initial month due to acclimation of these systems. Of the four pilot-scale CWTS, only the sucrose-amended pilot-scale CWTS decreased Se concentrations below the RPA estimated discharge limit of 263µg/L in all post-treated samples. Throughout this study, Hg removal rates and extents were greater for sucrose-amended, yeast culture amended, and hybrid pilot-scale CWTS in comparison to untreated control pilot-scale CWTS. These three pilot-scale systems achieved the RPA discharge limit ( $< 630$  ng/L) for all outflow samples, but this criterion was only achieved for 73.7% (14 of 19 samples) of outflow samples from the control pilot-scale CWTS. This research provides an approach to enhance Hg and Se removal rates and extents from FGD waters using CWTS and these data verify that site discharge limits may be achieved with organic carbon amendments to pilot-scale CWTS.

## **1. Introduction**

Elements such as mercury (Hg) and selenium (Se) can pose risks for receiving system biota from flue gas desulfurization (FGD) waters discharged from coal-fired power plants (EPRI, 2009). Mercury and selenium have attracted considerable regulatory interest due to their potential to bioaccumulate in aquatic organisms (Lemly, 1985; Eisler, 1987; Ohlendorf, 1989; Dobbs et al., 1996) and cause toxic effects at relatively low concentrations ( $\leq 10 \mu\text{g/L}$ ) (Boening, 2000; Lemly, 2002). Typically, FGD waters contain concentrations of Hg and Se that are orders of magnitude greater than the chronic water quality criteria (WQC) of 12 ng/L and 5  $\mu\text{g/L}$ , respectively, for these elements (USEPA, 1984; USEPA, 2002; USEPA, 2004). Consequently, effective treatment is required to achieve discharge concentrations under the Clean Water Act (1972) and National Pollutant Discharge and Elimination System (NPDES).

In FGD waters, Se is typically present as the oxyanions, selenite (IV) and selenate (VI), but has been also measured as selenocyanide ( $\text{SeCN}^-$ ), organoselenium species, and unidentified species (EPRI, 2006). Hg is typically present in FGD waters as divalent Hg (II) and is strongly complexed to halogens such as chloride ( $\text{HgCl}^+$ ,  $\text{HgCl}_2$ ,  $\text{HgCl}_3^-$ , and  $\text{HgCl}_4^{2-}$ ) (Gale et al., 2007). Since these forms are highly (mg/L) soluble in this aqueous matrix, treatment through chemical, physical, and biological processes is required to transform or transfer these elements into forms or phases that are insoluble (EPRI, 2009). The efficiency of these treatment processes is affected by the forms of Hg and Se in FGD waters as well as other elements or compounds present in these water that may interfere with or decrease removal processes. Since the forms and concentrations of elements or compounds in FGD waters can vary temporally at each production site (Chapter Five), a

robust treatment system that incorporates multiple treatment processes such as a constructed wetland treatment system may be required.

Constructed wetland treatment systems (CWTS) are an innovative approach for treating a variety of constituents in wastewaters (Kent, 1994; Kadlec and Knight, 1996) including problematic constituents contained in FGD waters (Eggert et al., 2008). CWTS can be designed to incorporate crucial chemical (co-precipitation and complexation reactions), physical (sorption, settling, and volatilization), and biological (oxidation-reduction reactions, biotransformation, and biodegradation) processes to achieve removal of the desired constituent(s) during periods of normal operation or in cases of fluctuations in the composition of pre-treated waters (Rodgers and Castle, 2008). The integration of these treatment processes in CWTS is accomplished through data from biogeochemical cycling, thermodynamic models (e.g. MINTEQ2A and  $E_h$ -pH diagrams), published research, and testing of physical models (pilot-scale CWTS) to confirm the suitability and sustainability of these processes (Rodgers and Castle, 2008).

Selenium's biogeochemical cycle is analogous to sulfur and has four oxidation states including (-II), elemental, (IV), and (VI) (Kadlec and Wallace, 2009). Of these oxidation states, the selenide (-II) and elemental selenium ( $Se^0$ ) forms are less soluble than Se (IV) and Se (VI) due to reactivity with divalent metals (forming inorganic selenides), volatilization potential (organic selenides), and non-polarity ( $Se^0$ ) (Morita et al., 2007). Inorganic selenides ( $Se^{2-}$ ) can form strong mineral complexes with ferrous ions ( $Fe^{2+}$ ) as achavalite ( $FeSe$ ) and ferroselite ( $FeSe_2$ ) in strongly reducing environments (Masscheleyn et al., 1990; Masscheleyn and Patrick, 1993) and may replace a sulfur atom in iron pyrites ( $FeS_2$ ) to form  $FeSSe$  under similar environmental conditions. Reduction

of Se forms to  $\text{Se}^0$  can occur through both abiotic and biotic processes; however, this treatment pathway may be limited to microbial transformations due to the instability, costs, and efficiency of chemical reductants and insufficient removal by other biotic species (Johnson et al., 2004). Of the Se oxyanions, Se (IV) can form stronger insoluble complexes with iron oxyhydroxides and some divalent metals in comparison to Se (VI), but the extent of removal for these processes may not be solely adequate for discharge of the treated water (Zhang et al., 2005b).

The biogeochemical cycle of Hg is complex. Hg has three oxidation states including elemental ( $\text{Hg}^0$ ), mercurous (Hg I), and mercuric (Hg II) with solubility generally increasing with oxidation (Kaplan et al., 2002). Hg can exist in the gas phase as inorganic ( $\text{Hg}^0$ ) and organic forms [e.g.  $\text{CH}_3\text{Hg}$  and  $(\text{CH}_3)_2\text{Hg}$ ] (Robinson and Tuovinen, 1984). Hg undergoes biotic and abiotic transformations (Winfrey and Rudd, 1990), can biomagnify in food chains (Barbosa, 2003), and can interact with other biogeochemical cycles such as carbon and sulfur (King et al., 2000; Ravichandran, 2004). Due to physical and chemical characteristics, Hg has a tendency to be mobile through gas, liquid, and solid phases, but can also form relatively stable complexes such as meta-cinnabar or cinnabar ( $\text{HgS}$ ) (Kosolapov et al., 2004). Environments that favor production of  $\text{HgS}$  contain soluble sulfides from microbial degradation of organic carbon (e.g. dissimilatory sulfate reduction) and permit complexation reactions between Hg and  $\text{S}^{2-}$  to proceed before microbial reduction of Hg (II) can occur (Kadlec and Wallace, 2009). Formation of mercuric polysulfides can also occur in low  $E_h$  environments ( $< -100$  mV) and is a result of high concentrations of reactive sulfide (Paquette and Helz, 1995).

Based on the biogeochemical cycles of Se and Hg, published literature on treatment of these constituents, and pilot-scale testing of FGD waters (Eggert et al., 2008), a full-scale CWTS was designed and built at an Eastern NC coal-fired power plant. This full-scale CWTS was designed to provide multiple treatment pathways for mercury sequestration in the hydrosols through sulfide complexation reactions, sorption to organic matter and microbial biofilms, and cation exchange reactions with the hydrosol. Se sequestering within this system was targeted through microbial reduction of Se (IV) and Se (VI), co-precipitation reactions with reduced and oxidized species of iron, and anion exchange with hydrosol constituents. This full-scale CWTS has consistently decreased Hg concentrations to discharge limits for this site FGD water, but Se removal ( $8.4 \pm 12.6\%$ ) may require further enhancements. Based on monitoring data, Se (VI) species are the dominant form of selenium in pre- ( $89.8 \pm 10.3\%$ ) and post-treated ( $90.8 \pm 7.6\%$ ) FGD waters and these forms are highly mobile due to their limited ability to form insoluble complexes (Antonioli et al., 2007). A plausible enhancement for Se removal is addition of soluble organic carbon to increase the microbial reduction rate of Se (VI) and decrease potential competitive electron acceptors such as nitrate (Zhang et al., 2005a). Additions of readily labile organic carbon sources (acetate, lactate, glucose, and trypticase soy agar) have been used to enhance microbial reduction of Se (VI) and Se (IV) to  $\text{Se}^0$  from contaminated aqueous wastestreams (Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2003, 2005a).

Crucial for determining the efficiency of a treatment system is selection or calculation of the performance goals. One approach for establishing treatment

performance goals is reasonable potential analysis (RPA). The RPA method has been used by regulatory agencies to determine NPDES permit limits (USEPA, 1985). This method uses site criteria, such as flow data from the receiving system and the treatment system to provide constituent specific discharge limits that ensure concentrations of targeted constituents in receiving systems will not exceed WQC standards or chronic toxicity values when WQC are not available.

Testing of actual FGD water for experimental purposes is critical for determining the efficiency of the treatment system. Composition of FGD waters at sites can be heterogeneous and due to this diversity, no one treatment process may be applied to all FGD waters. The diversity and complexity of FGD waters arise from many factors within a coal-fired power plant including the coal source, burner, burner load, air pollution control system (e.g. selective catalytic reactor, electrostatic precipitator, mist eliminator, and heat exchangers), wet scrubber, and pre-treatment processes (e.g. clarifier, coagulants, flocculants, chelating agents, and metal co-precipitators)(Mierzejewski, 1991). EPRI (2006) reported that most coal-fired power plants differ in design and operation of their FGD system and due to these differences as well as coal source, FGD waters are specific to each production site.

A reliable and cost efficient approach such as pilot-scale testing is warranted. Testable models such as pilot-scale CWTS can be used to 1) measure the performance of these systems for decreasing concentrations of specific constituents in FGD waters, 2) determine the bioavailability of constituents and toxicity of pre- and post-treated waters, 3) determine responses of these systems to operational changes (e.g. hydraulic retention time and water depth) or amendments (e.g. iron, organic carbon, alkalinity sources), 4)

determine system operating parameters, 5) provide data regarding compliance and removal rates for scaling of the system, and 6) provide the ability to manipulate reactor designs without potentially comprising existing NPDES permits. Results from pilot-scale CWTS have been scaled successfully to full-scale situations (Murray-Gulde et al., 2008) and are critically important when dealing with waters, such as FGD waters, that contain constituents at concentrations and in forms that can adversely affect the performance of a biological treatment systems (i.e. chlorides, cyanide, and boron).

The overall goal of this research was to determine if organic carbon amendments to pilot-scale CWTS could decrease Se and Hg concentrations in FGD water to acceptable discharge limits. In order to accomplish this overall objective, we developed three specific objectives for this research: 1) determine the site performance goals for Se and Hg in FGD water through reasonable potential analysis (RPA), 2) compare and contrast removal rates and extents of removal for selenium and mercury in a FGD water using amended and un-amended pilot-scale CWTS, and 3) determine the compliance of treated FGD waters with RPA values for Se and Hg using data from amended and un-amended pilot-scale CWTS.

## **2. Materials and Methods**

### *2.1 Reasonable Potential Analysis (RPA)*

Potential discharge limits for industrial effluents such as FGD waters can be estimated using reasonable potential analysis (RPA). This calculation requires knowledge of the water quality criteria or regulatory limits (e.g. chronic toxicity values) for constituents in a wastestream to be treated (e.g. FGD pre-treatment water) and the in-stream waste concentration (IWC) for the site. Water quality criteria are accessible from

the U.S. Environmental Protection Agency (USEPA). In-stream waste concentration (IWC) is calculated based on equation (1).

$$IWC = [(Q_w)/(Q_w + Q_r)] * 100 \quad \text{Equation (1)}$$

Where  $Q_w$  is the design flow of the FGD treatment system and  $Q_r$  is the lowest recorded seven day flow in the past ten years of the receiving system and is referred to as the 7Q10. The RPA is calculated by dividing the WQC or regulatory limit by the fraction of the IWC (i.e. 0.019 for an IWC of 1.9%).

## 2.2 Site FGD Water

The FGD water used in this study was collected from a coal-fired power plant in eastern North Carolina. FGD waters were pre-treated on site for total suspended solids using a clarifier in conjunction with a high molecular weight anionic flocculant polymer (GE Betz, AE1125) and for metals, specifically targeting Hg, using an organothiol compound (GE Betz, MetClear). Pre-treated FGD waters were transferred into 550-gallon high-density polyethylene (HDPE) tanks using an industrial grade trash pump, and were transported to the testing facility at Clemson University, Clemson, SC. Since FGD water at this site is co-managed for chlorides (1 part pre-treated FGD water and 5 parts low ionic strength water [surface water < 300  $\mu\text{S}/\text{cm}$ ]), all FGD waters used in this pilot-scale study were co-managed at this ratio with low ionic strength water (Clemson City water, Clemson, SC). Due to the low alkalinity of this water (<6 mg as  $\text{CaCO}_3/\text{L}$ ), 25g of sodium bicarbonate ( $\text{NaHCO}_3$ ) per 100-gallons of co-managed FGD water was added to a holding tank (i.e. equalization basin) and mixed with a submersible pump for 2-hrs. These waters were allowed to settle for 24-hr before loading into the pilot-scale CWTS.

## 2.3 Pilot-Scale CWTS

Pilot-scale CWTS were designed based on previous research (Eggert et al., 2008) and were assembled to mimic the existing full-scale CWTS for FGD waters. The full-scale CWTS design included two treatment series (A and B) each with an equalization basin (EQ), and two reactors operationally defined as “reducing” (1<sup>st</sup> and 2<sup>nd</sup> reactors), a rock-cascade (3<sup>rd</sup> reactor), and an “oxidizing” wetland reactor (4<sup>th</sup> reactor) (Figure 1). The equalization basin was designed to decrease the temperature of the influent FGD water to < 35 °C and was constructed of high-density concrete. Reducing wetland reactors were constructed using site hydrosol amended with 735 kg/ha of hay and 36.7 kg/ha of zero-valent iron and were planted with *Schoenoplectus californicus* C.A. Meyer (California bulrush). Rock-cascades were constructed with cobble-size granite rocks (Fowler Corporation; Seneca, SC) to a vertical depth of approximately 15.3 cm. Oxidizing wetland reactors were constructed using site hydrosol and were planted with *Typha latifolia* L. (broadleaf cattail).

Three of the four pilot-scale CWTS used for this study were built and assembled to mimic the full-scale CWTS. Wetland reactors were contained in 378-L Rubbermaid tanks (77.5 x 122 x 63.5 cm) and were assembled with the same hydrosol, hydroperiod, and macrophytes as the full-scale CWTS. To test a more porous hydrosol, the fourth pilot-scale series was designed with a river sand hydrosol (>92% as coarse river sand) and *T. latifolia* as the sole macrophyte in all wetland reactors. To mimic the rock cascade of the full-scale CWTS, 10 to 20-cm granite cobbles were placed in the first-half of the first oxidizing wetland reactor in all pilot-scale CWTS. The hydraulic retention time (HRT) was 24 h per wetland reactor for all systems and water depths were maintained at 45.7cm and 30.5 cm for the reducing and oxidizing wetland reactors, respectively.

To determine if soluble organic carbon sources can enhance Se and Hg removal in pilot-scale CWTS, we selected two sources, sucrose and yeast culture. These carbon sources were metered into the pilot-scale CWTS to achieve a constant inflow concentration of 0.2 g /L for the four months (July to October) and 0.3g/L for the last month of this study (November). Delivery of FGD waters and organic carbon sources (yeast and sucrose) was accomplished using Fluid Metering pumps (FMI). Sucrose and yeast culture were delivered to the pilot-scale CWTS as a liquid solution and were <1% of the total volume of inflow FGD waters. Stock solutions of sucrose and yeast culture were prepared every three days. The four pilot-scale CWTS included: 1) control pilot-scale CWTS (un-amended to mimic the untreated full-scale CWTS), 2) sucrose-amended pilot-scale CWTS, 3) yeast-culture amended pilot-scale CWTS, and 4) hybrid pilot-scale CWTS (coarse sand hydrosoil and *T. latifolia*).

#### 2.4 Sampling and Analyses

To determine the performance of the pilot-scale CWTS, aqueous samples were collected from five sampling locations within each pilot-scale CWTS including inflows and outflows of each of the four wetland reactors in series. Each sampling period (i.e. n = 19 for this study) consisted of loading FGD water for 7-10 days before sampling and analyses. This study was initiated in mid-July and conducted during the last week of November. Aqueous samples collected from these sampling locations were analyzed for total Hg and Se concentrations and water chemistry parameters. Samples for Hg determination were collected in acid-cleaned 60-ml borosilicate glass bottles and preserved with 0.2N BrCl (2% v/v). Samples for Se determination were collected in acid-cleaned 125-ml HDPE bottles and preserved with concentrated trace metal-grade nitric

acid (1% v/v). Total Hg concentrations were determined using a cold-vapor atomic absorption spectrometer (CV-AAS; EPA Method 245.1) with a gold amalgamation system. Total Se concentrations were determined using a hydride generation atomic absorption spectrometer (HG-AAS; modified EPA Method 7741A). Water chemistry parameters included measurements of chlorides, pH, conductivity, alkalinity, dissolved oxygen, chemical oxygen demand, and biochemical oxygen demand according to Standard Methods (APHA, 1998). Oxidation-reduction (redox) potentials of wetland hydrosols were measured using a milli-volt (mV) meter, Accumet® calomel reference electrode, and *in situ* platinum-tipped electrodes (Faulkner et al., 1989). All measurements were adjusted based on the hydrogen ion potential (+244 mV).

#### 2.4.1 Selenium and Mercury Removal Rates and Extents

The percent removal for Se and Hg was calculated using the equation (2).

$$\text{Percent removal} = (1 - ([A]_t / [A]_0)) * 100 \quad \text{Equation (2)}$$

Where  $[A]_t$  is the concentration of Se and Hg in the equalization basin (pre-treatment),  $[A]_0$  is the concentration of Se and Hg in the outflow sample of reactor four (i.e. post-treatment). Removal rates for Se and Hg were calculated using a first-order rate equation (3).

$$\text{Removal Rate} = \ln([A]_0 / [A]_t) = kt \quad \text{Equation (3)}$$

Where  $[A]_t$  and  $[A]_0$  are the same as described for extent of removal,  $t$  is the total time of treatment, and  $k$  is the first-order rate coefficient. Removal extents for Se and Hg concentrations in final outflow samples of each pilot-scale CWTS were compared to RPA limits to determine if these systems could achieve discharge limits.

#### 2.4.2. Statistical Analyses

Significant differences in removal extents and removal rates of Se and Hg were determined between outflow samples of the four pilot-scale CWTS using analysis of variance (ANVOA) with the Tukey's test as the mean separation if data were normally distributed based on Sharipo-Wilk's test. For non-normally distributed data sets, a Wilcoxon rank test was performed with the Tukey's test as the mean separator. Alpha levels were 0.05 for all statistical tests. All analyses were performed using Statistical Analysis System (SAS, Institute Inc., Cary, NC).

### **3. Results**

#### *3.1 Reasonable Potential Analysis (RPA)*

RPA and IWC calculations used for this study were accomplished using flow design criteria for the existing full-scale treatment system and 7Q10 data from the receiving system at this site. The calculated IWC was 1.9% and WQC standards of 12 ng/L for mercury and 5 µg/L for selenium (USEPA, 1984; USEPA, 2004). In this case, the calculated RPA values for Hg and Se are 630 ng/L and 263 µg/L, respectively, and these concentrations were used as the performance criteria for this study.

#### *3.2 Selenium (Se)*

##### *3.2.1 Removal rates and Extents*

Mean Se concentration in the inflow FGD waters was  $537 \pm 126$  µg/L and ranged from 345 to 810 µg/L during this study (Table 1). For post-treated samples, removal rates and extents of removal for Se were greater for amended versus un-amended pilot-scale CWTS during the months of August, September, October, and November ( $p < 0.05$ ), but no measurable differences occurred during the first month of this study (July). Se concentrations from the first reactors of the amended pilot-scale CWTS were statistically

lower in comparison to un-amended pilot-scale CWTS for all months except July. Between amended pilot-scale CWTS, significantly higher removal rates and extents of Se were measured in post-treated samples of the sucrose amended than yeast culture amended pilot-scale CWTS during October ( $p = 0.0057$  and  $p = 0.0073$ , respectively) and a higher removal extent of Se during November ( $p = 0.0393$ ). No differences in removal rates or extents were measured between the sucrose and yeast culture amended pilot-scale CWTS during July ( $p = 0.6702$  and  $p = 0.6702$ , respectively), August ( $p = 0.0554$  and  $p = 0.0723$ , respectively), and September ( $p = 0.7388$  and  $p = 0.7673$ , respectively).

### *3.2.2 Comparisons to RPA Limits*

Of the four pilot-scale CWTS, only the sucrose-amended pilot-scale CWTS decreased Se concentrations below the RPA estimated discharge limit of  $263\mu\text{g/L}$  in all post-treated samples ( $p < 0.05$ ). Se concentrations in the post-treated samples from the sucrose amended pilot-scale CWTS averaged  $88 \pm 78 \mu\text{g/L}$  with a range of 12 to  $224 \mu\text{g/L}$ . Mean percent removal and removal rate for the sucrose amended pilot-scale CWTS were  $84.0 \pm 14.6\%$  and  $-0.5518 \pm -0.2246 \text{ d}^{-1}$ , respectively. Yeast culture amended pilot-scale CWTS decreased selenium concentrations to  $< 263\mu\text{g/L}$  in all post-treated samples with the sole exception of the last sampling period in November (i.e. outflow  $[\text{Se}] = 264 \mu\text{g/L}$ ). Se concentrations in the post-treated samples of the yeast culture amended pilot-scale CWTS averaged  $123 \pm 98 \mu\text{g/L}$  with a range of 8 to  $265 \mu\text{g/L}$ . Mean percent removal and removal rate for the yeast culture amended pilot-scale CWTS were  $78.3 \pm 17.1\%$  and  $-0.5056 \pm -0.2968 \text{ d}^{-1}$ , respectively. Neither the control nor hybrid pilot-scale CWTS consistently decreased Se concentrations to  $< 263 \mu\text{g/L}$  during this study. The control pilot-scale CWTS initially removed  $31.5 \pm 11.2\%$  of the total Se from inflow

samples, but after the first sampling period in August, total Se removal averaged  $1.1 \pm 1.9\%$ . A similar decline in Se removal was measured for the hybrid pilot-scale CWTS, in which percent removals were higher for the first eight sampling periods ( $42.0 \pm 15.5\%$ ) in comparison to the last eleven sampling periods ( $3.3 \pm 3.0\%$ ). Based on these data neither the control nor hybrid pilot-scale CWTS would be sufficient for decreasing Se to less than the calculated RPA discharge limit of  $263 \mu\text{g/L}$ .

### *3.3 Mercury (Hg)*

#### *3.3.1 Removal Rates and Extents*

The mean Hg concentration in the inflow FGD waters was  $4,218 \pm 3,392 \text{ ng/L}$  and ranged from 1,104 to 11,090 ng/L during this study (Table 2). Removal rates for Hg in post-treated samples were greatest for the hybrid pilot-scale CWTS for all months (Table 2). For the first three months of this study, differences in removal rates were measured between pilot-scale CWTS. During the months of July, August, and September, removal rates of Hg were greater for the hybrid and yeast culture amended pilot-scale CWTS than control pilot-scale CWTS ( $p = 0.0079$  and  $p = 0.0158$ ;  $p < 0.001$  and  $p = 0.0004$ ; and  $p = 0.0053$  and  $p = 0.0157$ , respectively). Removal rates for the sucrose amended pilot-scale CWTS were greater than control pilot-scale CWTS only the month of August ( $p = 0.0176$ ) and were lower than the hybrid pilot-scale CWTS during July ( $p = 0.0352$ ) and August ( $p = 0.0040$ ). Similar to Hg removal rates, post-treated samples from hybrid pilot-scale CWTS had greater removal extents for Hg than the sucrose amended pilot-scale CWTS during July ( $p = 0.0352$ ) and August ( $p < 0.001$ ), yeast culture amended during August ( $p = 0.0441$ ), and control pilot-scale CWTS during July ( $p = 0.0079$ ), August ( $p < 0.001$ ), and September ( $p = 0.0031$ ). No differences in removal

rates or extents of Hg were measured between pilot-scale CWTS during the months of October and November.

### *3.3.2 Comparisons to RPA Limits*

Total Hg concentrations in all post-treated samples from the sucrose amended, yeast culture amended, and hybrid pilot-scale CWTS were decreased below the RPA discharge limit of 630 ng/L. The control pilot-scale CWTS decreased Hg concentrations to <630 ng/L for fourteen of the nineteen sampling periods with a mean percent removal and removal rate of  $417 \pm 231$  ng/L and  $-0.5552 \pm 1679$  d<sup>-1</sup>, respectively. The highest mean percent removal and removal rate of Hg in post-treated samples were measured from the hybrid pilot-scale CWTS ( $95.9 \pm 2.3\%$  and  $0.8349 \pm 0.1324$  d<sup>-1</sup>), followed by the yeast culture amended pilot-scale CWTS ( $94.1 \pm 3.3\%$  and  $0.7540 \pm 0.1849$  d<sup>-1</sup>), and the sucrose amended pilot-scale CWTS ( $93.2 \pm 3.9\%$  and  $0.7169 \pm 0.1585$  d<sup>-1</sup>).

### *3.4 Water Chemistry Parameters*

Biological oxygen demand (BOD) and chemical oxygen demand (COD) measurements of post-treated samples from the sucrose amended and yeast culture amended pilot-scale CWTS increased with time from the study initiation in July to November (Table 3). Mean BOD and COD measurements of post-treated samples from the sucrose amended and yeast culture amended pilot-scale CWTS were greatest for the month of November and included measurements of  $41.7 \pm 8.5$  and  $46.9 \pm 10.3$  mg as O<sub>2</sub>/L and  $26.5 \pm 10.9$  and  $32.5 \pm 5.4$  mg as O<sub>2</sub>/L, respectively. Post-treated samples using the hybrid and control pilot-scale CWTS averaged < 4 mg as O<sub>2</sub>/L for BOD and < 25 mg as O<sub>2</sub>/L for COD throughout this study. Monthly dissolved oxygen (DO) concentrations (mg as O<sub>2</sub>/L) were similar between inflow samples and all wetland reactor samples of the

control pilot-scale CWTS (Table 4a-e). DO concentrations in outflow samples of the hybrid pilot-scale CWTS were consistently less than 5.0 mg/L for the final wetland reactor during the months of July and August, but were similar to inflow DO concentrations during the last three months of this study. In contrast to the un-amended pilot-scale CWTS, significantly lower DO concentrations were measured in outflow samples of the first wetland reactors of the sucrose and yeast culture amended pilot-scale CWTS for all monthly comparisons. Other water chemistry parameters including pH, conductivity, and chlorides did not differ between any of the pilot-scale CWTS tested in this study. Hydrosol redox measurements from the sucrose-amended, yeast culture-amended, and control pilot-scale CWTS confirm the theoretical design of lower mV potentials within the reducing wetland reactors (1<sup>st</sup> and 2<sup>nd</sup> reactors) and higher mV potentials within the oxidizing wetland reactors (3<sup>rd</sup> and 4<sup>th</sup> reactors) (Table 5). Redox measurements from hydrosols within the hybrid pilot-scale CWTS were greater for the reducing wetland reactors than the oxidizing wetland reactors.

#### **4. Discussion**

The risk mitigation approach used for this study was to 1) determine anticipated discharge limits of a site FGD water through RPA calculations, 2) compare and contrast removal rates and extents of removal for Hg and Se using amended and un-amended pilot-scale CWTS, and 3) determine if RPA limits for Hg and Se can be achieved using amended or un-amended pilot-scale CWTS.

RPA discharge limits were used to determine the performance of pilot-scale CWTS due to the ability of this method to account for site specific factors that could influence the risks that each constituent may pose to receiving system biota. Site specific

factors can include the composition of these FGD waters, volumes of FGD water produced per day (million L/d), and receiving system type (e.g. lentic and lotic system), and flow (million L/d). WQC or chronic toxicity values for Hg or Se (e.g. no observable effects concentration; NOEC) do not vary based on receiving system characteristics and therefore were not selected as the performance criteria. The calculated RPA limit for mercury (0.63 µg/L) was used by the USEPA as the NPDES permit limit for this site and indicates the utility of this method for estimating future discharge limits of constituents in FGD waters at specific locations.

Enhancing Se and Hg removal from FGD water was accomplished with amendments of sucrose and yeast culture to pilot-scale CWTS in comparison to untreated control systems. Increased removal of Se and Hg is likely due to the availability and form of the electron donors within these systems, increased microbial activity, and environmental conditions favoring Se (IV), Se (VI), and sulfate reduction (Kadlec and Wallace, 2009). The theoretical design of the CWTS in this case involves transfer of electrons to specific constituents (i.e. S and Se species) in order to transform these forms into insoluble states which require sufficient electron donors. Organic carbon is an electron rich source that can be added to CWTS, and while sufficient quantities of these forms are required, the ability of microbes to transfer these electrons to selenium species is crucial to the performance of these systems. Organic carbon in the forms of sucrose and yeast culture have greater degradation rates than other organic sources such as hay or bulrush and cattail detritus in un-amended pilot-scale CWTS. These degradation rates were confirmed based on differences in dissolved oxygen concentrations in un-amended and amended pilot-scale CWTS. Increasing the cycling of organic carbon within

amended pilot-scale CWTS likely resulted in microbial reduction of Se (VI) to Se (IV) and Se<sup>0</sup> and since these species are less mobile in aqueous systems, higher Se removals were measured for systems receiving organic carbon additions.

Bacterial reduction of Se (VI) has been enhanced through additions of molasses and trypticase soy broth (TSB) to selenium-contaminated drainage waters (Zhang et al., 2008). These authors reported rate coefficients for Se (VI) and total Se removal were dependent on molasses concentrations and bacterium tested with rate constants for removal of total Se ranging from 0.016 to 0.333 d<sup>-1</sup> for Se amended drainage waters receiving 0.2% molasses. These removal rates for total Se are less in comparison to Se removal rates from amended pilot-scale CWTS reported in this study which suggests that the environmental components (e.g. hydrosol, hydroperiod, macrophytes) comprising CWTS along with sucrose and yeast culture additions may additively enhance Se removal. Other factors that may contribute to differences in the removal of total Se in results reported by Zhang et al., (2008) and this study include composition of source waters (Se amended drainage water versus FGD water), character of organic carbon additions, and the bacteria in each system.

An important factor that may have also contributed to the observed differences in removal rates and extents measured between un-amended and amended pilot-scale CWTS is the ratio of electron availability to competitive or inhibitory electron acceptors within this site FGD water. FGD waters typically contain mg/L concentrations of competitive electron acceptors including sulfate, nitrate, iron, and manganese as well µg/L concentrations of oxyanions (e.g. chromium and arsenic). It was hypothesized that amended pilot-scale CWTS contain more readily accessible electrons from sucrose and

yeast culture amendments than un-amended pilot-scale CWTS and a greater extent of electron transfer to Se (VI) may have occurred through decreasing the inhibitory effects caused by competitive electron acceptors as a result of altering their forms or concentrations in amended systems. In laboratory and field conditions, elevated nitrate concentrations can inhibit or decrease microbial reduction of Se (VI) (Oremland et al., 1989; Steinburg and Oremland, 1990; Steinburg et al., 1992), but after sufficient denitrification of these waters, Se (VI) reduction can occur. Inhibition of microbial reduction of Se (VI) by nitrate however, does not occur for all microbial species or strains and these respiratory processes can take place simultaneously (Oremland et al., 1999). For this study, it is unclear if nitrate concentrations significantly affected Se (VI) reduction or total Se removal, but denitrification rates were likely higher in amended pilot-scale CWTS due to organic carbon additions (Wang et al., 2007).

The removal rates and extents of Se increased initially from July to August and remained constant until the months of October and November for sucrose and yeast culture amended pilot-scale CWTS. Decline in the removal of Se may have been a result of higher Se inflow concentrations during these periods, but other factors such as water temperature may have affected the removal processes within the amended pilot-scale CWTS. Under laboratory conditions, selenite and selenate reduction rates by a *Pseudomonas stutzeri* isolate were significantly affected by temperature with mean rates ranging from  $87.72 \pm 2.15$  to  $93.67 \pm 2.53$  nmol Se/ml/h for 25°C to 30°C, and no reduction to  $44.68 \pm 0.63$  nmol Se/ml/h for 10°C to 20°C (Lortie et al., 1992). Based on monthly BOD measurements from the amended pilot-scale CWTS, microbial activity decreased during the months of cooler water temperatures (October and November) and

this may have influenced the rates of microbial Se (VI) and Se (IV) reduction or altered other Se removal processes within the pilot-scale CWTS.

Removal of total Se dominantly occurred within the 1<sup>st</sup> and 2<sup>nd</sup> wetland reactors in series of the amended pilot-scale CWTS and presumably as a result of greater microbial activity. These reducing wetland reactors were constantly lower in DO concentrations and are potentially more favorable environments for the reduction and sequestering of Se species. Based on  $E_h$ -pH diagrams, Se occurring in environments with  $E_h$  potentials of -200 mV to 0 mV is predicted to dominate as  $Se^0$  (Masscheleyn et al., 1990). Under these low  $E_h$  conditions, other reduced species such as ferrous iron ( $Fe^{2+}$ ) may bind with Se to form insoluble complexes (Masscheleyn and Patrick, 1993). The oxidizing wetland reactors (3<sup>rd</sup> and 4<sup>th</sup> wetland reactors in series) contributed to the overall Se removal in amended pilot-scale CWTS, but lower removals were likely due to higher DO and redox measurements than reducing wetland reactors. Se removal in the hybrid pilot-scale CWTS also occurred in wetland reactors with the lowest DO concentrations which suggests that this is an important environmental parameter for decreasing total Se concentrations in FGD waters using pilot-scale CWTS. Phytoconcentration of Se within the wetland species used in this study was not measured, but based on removal rates and extents from untreated control pilot-scale CWTS, this pathway did not contribute significantly to the overall removal of Se.

Throughout this study, Hg removal rates and extents were higher for sucrose-amended, yeast culture amended, and hybrid pilot-scale CWTS in comparison to untreated control pilot-scale CWTS. A potential reason for increased Hg removal from the amended pilot-scale CWTS would include higher microbial activity, specifically

dissimilatory sulfate reduction, that allows for formation of mercuric sulfide. Enhanced Hg removal in the hybrid pilot-scale CWTS may be due to the electrochemical attraction of divalent Hg species and sand particles with negativity charged surfaces (Eisler, 2000). Sorption of Hg species to sand particles may have resulted in the initial removal of Hg from the water column and saturation of these sorbent sites may have been limited if further reactions and displacement of these Hg species is occurring at sufficient rates. Dominantly, the highest removal rates and extents of Hg occurred in the 1<sup>st</sup> wetland reactor of all pilot-scale CWTS and suggest that similar removal pathways are invoked in these systems, such as sulfides complexation or sorption to minerals and organic carbon components. Unlike Se removal, removal rates and extents of Hg did not significantly decrease during the latter months of this study probably be due to the differences in reactivity between Se (VI) and mercury species within pilot-scale CWTS.

## **5. Conclusions**

This research provides an approach to enhance Hg and Se removal rates and extents from FGD waters using CWTS and these data verify that site discharge limits may be achieved with organic carbon amendments to existing CWTS. An organic carbon source such as sucrose is a relatively inexpensive (2009 price ~\$0.66 to 0.88/kg) and can be incorporated into an existing system with minimal capitals costs for a delivery system. Operation and maintenance costs for organic carbon additions will be minimal since this material can be metered into a full-scale CWTS as a liquid solution using gravity flow or small metering pumps. Since sucrose additions can be applied constantly to a full-scale CWTS, saturation of the removal pathway is unlikely and will allow for continuous removal of problematic constituents in FGD waters such as Hg and Se.

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Table 4.1 Monthly mean removal extents, percent removals, and removal rates of Se from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported in parentheses.

<b>Pilot-scale CWTS</b>	<b>Parameter</b>	<b>July</b>	<b>August</b>	<b>September</b>	<b>October</b>	<b>November</b>
Inflow (EQ Basin)	Inflow (Se µg/L)	381 (50)	432 (29)	474 (59)	604 (8)	701 (101)
Control	Post-treated (Se µg/L)	256 (46)	402 (70)	474 (33)	611 (9)	696 (96)
	Percent Removal (%)	32.8 (3.3)	6.9 (14.9)	0 (6.4)	NR	0.7 (1.6)
	Removal Rate (d-1)	0.0995 (0.0122)	0.0178 (0.0433)	0.0001 (0.0159)	NR	0.0017 (0.0039)
Sucrose-amended	Post-treated (Se µg/L)	150 (69)	26 (6)	24 (18)	68 (25)	209 (12)
	Percent Removal (%)	60.7 (23.5)	94.0 (1.6)	95.0 (3.1)	88.7 (4.2)	70.2 (5.8)
	Removal Rate (d-1)	0.2337 (0.1529)	0.7035 (0.0686)	0.7499 (0.1469)	0.5445 (0.0908)	0.3028 (0.0484)
Yeast-cultured amended	Post-treated (Se µg/L)	179 (32)	17 (10)	29 (24)	161 (49)	250 (19)
	Percent Removal (%)	53.0 (14.5)	96.2 (2.4)	93.8 (4.4)	73.4 (8.5)	64.3 (4.8)
	Removal Rate (d-1)	0.1886 (0.0769)	0.8167 (0.1366)	0.6967 (0.2234)	0.3309 (0.0836)	0.2578 (0.0322)
Hybrid	Post-treated (Se µg/L)	217 (85)	270 (47)	307 (161)	601 (10)	664 (96)
	Percent Removal (%)	43.1 (14.9)	37.5 (14.4)	35.3 (26.4)	0.6 (2.0)	5.2 (1.4)
	Removal Rate (d-1)	0.1410 (0.0675)	0.1175 (0.0635)	0.1090 (0.1085)	0.0015 (0.0052)	0.0134 (0.0038)

Table 4.2 Monthly mean removal extents, percent removals, and removal rates of Hg from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported in parenthesis.

<b>Pilot-scale CWTS</b>	<b>Parameter</b>	<b>July</b>	<b>August</b>	<b>September</b>	<b>October</b>	<b>November</b>
Inflow (EQ Basin)	Inflow (Hg µg/L)	3490 (1304)	2360 (805)	2654 (1554)	7519 (4024)	3877 (4157)
Control	Post-treated (Hg µg/L)	667 (79)	449 (188)	319 (268)	371 (216)	416 (299)
	Percent Removal (%)	80.9 (10.1)	81.0 (5.9)	88.0 (7.7)	95.1 (2.0)	89.3 (4.6)
	Removal Rate (d-1)	0.4139 (0.1252)	0.4148 (0.0816)	0.5298 (0.1662)	0.7521 (0.0988)	0.5579 (0.0898)
Sucrose-amended	Post-treated (Hg µg/L)	317 (8)	191 (6)	114 (49)	225 (129)	226 (63)
	Percent Removal (%)	90.9 (3.9)	91.9 (2.7)	95.7 (2.0)	97.0 (1.3)	94.2 (5.2)
	Removal Rate (d-1)	0.6001 (0.1018)	0.6288 (0.0840)	0.7862 (0.1240)	0.8773 (0.0975)	0.7103 (0.1841)
Yeast culture-amended	Post-treated (Hg µg/L)	181(118)	132 (32)	70 (48)	335 (168)	269 (131)
	Percent Removal (%)	94.8 (1.5)	94.4 (2.5)	97.4 (3.6)	95.5 (1.4)	93.1 (3.9)
	Removal Rate (d-1)	0.7398 (0.0795)	0.7202 (0.0884)	0.9095 (0.3092)	0.7776 (0.0768)	0.6670 (0.1220)
Hybrid	Post-treated (Hg µg/L)	133 (79)	91 (46)	62 (35)	243 (168)	194 (110)
	Percent Removal (%)	96.2 (0.9)	96.1 (1.3)	97.7 (1.3)	96.8 (1.1)	95.0 (3.5)
	Removal Rate (d-1)	0.8178 (0.0621)	0.8142 (0.1019)	0.9405 (0.1462)	0.8576 (0.0912)	0.7494 (0.1350)

Table 4.3 Monthly mean biochemical oxygen demands (BOD) and chemical oxygen demand (COD) measurements (mg/L) from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported in parenthesis.

Pilot-scale CWTS	Sampling Point	July		August		September		October		November	
		BOD	COD	BOD	COD	BOD	COD	BOD	COD	BOD	COD
Inflow	EQ Basin	0.4 (0.1)	6.3 (1.8)	0.4 (0.2)	6.9 (1.3)	0.3 (0.2)	10.0 (5.0)	1.5 (0.6)	12.5 (3.1)	1.2 (0.6)	14.4 (1.3)
Control	Reactor 1	0.4 (0.2)	10.0 (0)	0.9 (0.3)	8.8 (2.5)	1.0 (0.7)	22.5 (15.9)	2.1 (1.2)	19.0 (3.8)	2.3 (0.1)	21.3 (3.2)
	Reactor 2	0.9 (0.3)	12.5 (0)	0.7 (0.2)	8.8 (3.2)	1.2 (0.1)	16.9 (6.3)	2.1 (1.0)	17.0 (3.7)	2.1 (0.5)	23.1 (4.3)
	Reactor 3	1.1 (0.3)	12.5 (0)	1.3 (0.6)	13.1 (1.3)	1.0 (0.3)	17.5 (9.4)	2.4 (1.7)	23.5 (16.5)	2.3 (0.8)	20.6 (2.4)
	Reactor 4	1.1 (0)	12.5 (3.5)	1.2 (0.1)	12.5 (2.0)	1.1 (0.4)	15.0 (10.6)	2.9 (1.9)	19.0 (2.9)	1.8 (0.4)	20.0 (5.4)
Sucrose amended	Reactor 1	93.9 (9.0)	111.3 (1.8)	97.7 (13.3)	120.0 (10.2)	109.1 (13.3)	170.0 (60.1)	117.5 (20.2)	190.5 (27.1)	235.9 (68.5)	309.4 (72.2)
	Reactor 2	52.5 (10.4)	51.3 (5.3)	46.3 (5.0)	50.6 (8.3)	53.1 (5.7)	86.9 (38.3)	50.1 (14.2)	106.0 (42.2)	90.5 (23.0)	134.4 (15.9)
	Reactor 3	28.1 (2.2)	32.5 (0)	25.0 (4.7)	30.0 (2.9)	19.1 (6.4)	43.8 (29.9)	35.3 (10.3)	60.0 (27.6)	50.5 (8.4)	56.3 (4.8)
	Reactor 4	16.6 (2.8)	20.0 (0)	15.8 (2.9)	21.3 (1.4)	11.5 (4.8)	23.1 (8.5)	24.5 (6.9)	43.5 (26.1)	41.7 (8.5)	46.9 (10.3)
Yeast culture amended	Reactor 1	29.4 (5.4)	47.5 (0)	44.4 (5.7)	53.8 (1.4)	32.9 (10.8)	59.4 (9.4)	39.6 (16.6)	63.5 (29.1)	61.4 (23.6)	76.3 (24.4)
	Reactor 2	18.8 (1.2)	30.0 (3.5)	21.0 (5.3)	30.0 (2.0)	17.0 (5.8)	38.8 (10.9)	28.0 (17.4)	43.5 (27.5)	35.4 (14.7)	41.3 (13.0)
	Reactor 3	16.5 (5.4)	25.0 (3.5)	12.4 (2.8)	21.9 (2.4)	11.0 (7.3)	28.1 (5.9)	19.0 (9.7)	32.0 (12.5)	27.1 (7.5)	32.5 (6.8)
	Reactor 4	7.7 (0.8)	17.5 (0)	7.7 (2.8)	18.1 (1.3)	6.5 (3.5)	25.0 (6.1)	13.1 (5.3)	29.0 (13.8)	26.5 (10.9)	32.5 (5.4)
Hybrid	Reactor 1	0.2 (0.1)	6.3 (1.8)	0.5 (0.4)	11.3 (4.3)	0.9 (0.6)	17.5 (11.9)	2.3 (1.0)	16.5 (2.9)	2.3 (0.1)	18.1 (1.3)
	Reactor 2	0.5 (0.3)	8.8 (1.8)	0.7 (0.5)	12.5 (2.0)	0.9 (0.5)	18.1 (9.4)	2.2 (1.3)	17.5 (3.5)	2.2 (0.3)	19.4 (2.4)
	Reactor 3	1.4 (0.5)	12.5 (0)	1.1 (0.5)	13.1 (1.3)	1.2 (0.4)	15.6 (3.8)	2.2 (1.8)	18.5 (6.0)	1.8 (0.2)	21.3 (1.4)
	Reactor 4	1.8 (0.8)	11.3 (1.8)	1.2 (0.1)	13.1 (2.4)	1.3 (0.6)	15.0 (2.9)	2.2 (1.9)	19.0 (5.2)	2.2 (0.3)	20.6 (3.1)

Table 4.4a Mean water chemistry parameters measured during July from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported within parenthesis.

<b>PS-CWTS</b>	<b>July</b>	<b>pH</b>	<b>Conductivity (mS/cm)</b>	<b>Chlorides (mg/L)</b>	<b>DO (mg/L)</b>
Inflow	EQ Basin	6.28 (0.07)	3.71 (0.23)	1587 (53)	7.66 (0.45)
Control	Reactor 1	5.73 (1.00)	3.77 (0.16)	1613 (53)	4.85 (0.70)
	Reactor 2	5.67 (0.97)	3.83 (0.12)		
	Reactor 3	5.54 (1.22)	3.94 (0.12)		
	Reactor 4	5.52 (1.14)	4.06 (0.06)	1675 (35)	6.83 (0.57)
Sucrose amended	Reactor 1	5.82 (0.86)	3.74 (0.14)	1600 (70)	4.27 (0.71)
	Reactor 2	5.75 (0.87)	3.85 (0.12)		
	Reactor 3	5.68 (0.99)	3.96 (0.26)		
	Reactor 4	5.42 (1.17)	4.17 (0.07)	1700 (0)	6.98 (0.83)
Yeast culture amended	Reactor 1	6.61 (0.69)	3.86 (0.06)	16123 (18)	6.50 (0.55)
	Reactor 2	6.56 (0.70)	3.96 (0.18)		
	Reactor 3	6.47 (0.83)	3.99 (0.08)		
	Reactor 4	6.47 (0.69)	4.10 (0.16)	1675 (35)	6.29 (1.34)
Hybrid	Reactor 1	6.52 (0.53)	3.83 (0.23)	1588 (53)	7.00 (0.80)
	Reactor 2	6.46 (0.95)	3.91 (0.16)		
	Reactor 3	6.49 (1.07)	3.95 (0.14)		
	Reactor 4	6.56 (0.78)	4.09 (0.09)	1700 (0)	6.65 (0.71)

Table 4.4b Mean water chemistry parameters measured during August from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported within parenthesis.

<b>PS-CWTS</b>	<b>August</b>	<b>pH</b>	<b>Conductivity (mS)</b>	<b>Chlorides (mg/L)</b>	<b>DO (mg/L)</b>
Inflow	EQ Basin	6.38 (0.14)	3.69 (0.21)	1556 (80)	7.67 (0.22)
Control	Reactor 1	6.29 (0.06)	3.81 (0.21)	1562 (95)	3.16 (1.09)
	Reactor 2	6.31 (0.14)	3.93 (0.16)		
	Reactor 3	6.29 (0.17)	4.08 (0.19)		
	Reactor 4	6.35 (0.17)	4.29 (0.17)	1718 (38)	7.43 (1.07)
Sucrose amended	Reactor 1	6.18 (0.09)	3.82 (0.21)	1581 (80)	3.85 (0.28)
	Reactor 2	6.21 (0.16)	3.91 (0.24)		
	Reactor 3	6.32 (0.12)	4.06 (0.17)		
	Reactor 4	6.43 (0.21)	4.36 (0.15)	1712 (52)	6.09 (0.97)
Yeast culture amended	Reactor 1	6.97 (0.14)	3.85 (0.22)	1562 (93)	5.46 (0.80)
	Reactor 2	7.01 (0.10)	3.99 (0.16)		
	Reactor 3	7.04 (0.08)	4.15 (0.17)		
	Reactor 4	7.06 (0.25)	4.35 (0.23)	1731 (24)	5.62 (0.61)
Hybrid	Reactor 1	7.16 (0.15)	3.82 (0.20)	1575 (71)	7.01 (0.40)
	Reactor 2	7.13 (0.24)	4.00 (0.20)		
	Reactor 3	6.92 (0.45)	4.01 (0.43)		
	Reactor 4	6.84 (0.47)	4.38 (0.09)	1706 (32)	7.05 (0.75)

Table 4.4c Mean water chemistry parameters measured during September from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported within parenthesis.

<b>PS-CWTS</b>	<b>September</b>	<b>pH</b>	<b>Conductivity (mS)</b>	<b>Chlorides (mg/L)</b>	<b>DO (mg/L)</b>
Inflow	EQ Basin	7.18 (0.78)	3.74 (0.27)	1643 (181)	8.45 (0.54)
Control	Reactor 1	6.26 (0.47)	3.86 (0.24)	1644 (195)	3.16 (1.06)
	Reactor 2	6.19 (0.52)	3.85 (0.32)		6.24 (0.65)
	Reactor 3	6.23 (0.55)	4.15 (0.18)		8.79 (0.35)
	Reactor 4	6.37 (0.36)	4.29 (0.10)	1825 (188)	8.28 (0.70)
Sucrose amended	Reactor 1	6.10 (0.71)	3.87 (0.26)	1650 (190)	3.82 (1.70)
	Reactor 2	6.12 (0.64)	3.90 (0.23)		5.60 (1.18)
	Reactor 3	6.17 (0.67)	4.04 (0.21)		8.38 (0.13)
	Reactor 4	6.34 (0.60)	4.10 (0.26)	1806 (185)	8.12 (0.82)
Yeast culture amended	Reactor 1	7.12 (0.47)	3.79 (0.22)	1663 (173)	6.43 (1.13)
	Reactor 2	7.11 (0.60)	3.97 (0.11)		7.92 (0.76)
	Reactor 3	7.37 (0.34)	4.07 (0.24)		7.93 (0.84)
	Reactor 4	7.30 (0.39)	4.09 (0.15)	1819 (168)	7.88 (0.54)
Hybrid	Reactor 1	7.24 (0.54)	3.82 (0.27)	1662 (173)	7.49 (0.60)
	Reactor 2	7.43 (0.48)	3.99 (0.17)		8.89 (0.64)
	Reactor 3	7.34 (0.39)	4.09 (0.19)		8.67 (0.62)
	Reactor 4	7.54 (0.53)	4.27 (0.07)	1850 (188)	7.99 (0.85)

Table 4.4d Mean water chemistry parameters measured during October from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported within parenthesis.

<b>PS-CWTS</b>	<b>October</b>	<b>pH</b>	<b>Conductivity (mS)</b>	<b>Chlorides (mg/L)</b>	<b>DO (mg/L)</b>
Inflow	EQ Basin	7.79 (0.13)	4.86 (0.39)	2105 (142)	10.00 (0.86)
Control	Reactor 1	6.67 (0.23)	4.84 (0.37)	2135 (156)	3.75 (0.79)
	Reactor 2	6.59 (0.15)	4.97 (0.40)		6.34 (0.59)
	Reactor 3	6.67 (0.20)	5.06 (0.43)		9.08 (0.58)
	Reactor 4	6.73 (0.27)	5.13 (0.39)	2190 (156)	8.98 (0.65)
Sucrose amended	Reactor 1	6.64 (0.17)	4.83 (0.37)	2090 (146)	3.93 (1.05)
	Reactor 2	6.75 (0.35)	4.94 (0.40)		6.54 (0.83)
	Reactor 3	6.80 (0.29)	5.06 (0.43)		8.17 (0.84)
	Reactor 4	6.67 (0.23)	5.09 (0.39)	2182 (143)	8.28 (0.98)
Yeast culture amended	Reactor 1	7.63 (0.13)	4.92 (0.42)	2120 (145)	8.97 (1.91)
	Reactor 2	7.55 (0.18)	4.97 (0.41)		9.26 (1.33)
	Reactor 3	7.40 (0.19)	5.07 (0.39)		9.37 (1.39)
	Reactor 4	7.51 (0.18)	5.07 (0.36)	2190 (133)	9.33 (1.62)
Hybrid	Reactor 1	7.61 (0.17)	4.89 (0.37)	2100 (122)	9.22 (1.41)
	Reactor 2	7.65 (0.24)	4.95 (0.42)		9.00 (1.43)
	Reactor 3	7.60 (0.15)	5.09 (0.39)		9.01 (1.59)
	Reactor 4	7.57 (0.29)	5.05 (0.41)	2200 (94)	8.90 (1.14)

Table 4.4e Mean water chemistry parameters measured during November from inflow and post-treated samples of control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS. Standard deviations are reported within parenthesis.

<b>PS-CWTS</b>	<b>November</b>	<b>pH</b>	<b>Conductivity (mS)</b>	<b>Chlorides (mg/L)</b>	<b>DO (mg/L)</b>
Inflow	EQ Basin	7.67 (0.10)	5.59 (0.42)	2456 (97)	11.20 (0.89)
Control	Reactor 1	7.76 (0.07)	5.71 (0.53)	2475 (96)	11.46 (0.76)
	Reactor 2	7.64 (0.11)	5.71 (0.45)		11.51 (0.47)
	Reactor 3	7.79 (0.06)	5.74 (0.48)		10.59 (0.55)
	Reactor 4	7.63 (0.26)	5.71 (0.46)	2525 (140)	9.69 (0.79)
Sucrose amended	Reactor 1	6.98 (0.35)	5.63 (0.42)	2481 (114)	4.44 (0.66)
	Reactor 2	6.85 (0.17)	5.60 (0.48)		7.04 (1.97)
	Reactor 3	6.82 (0.06)	5.76 (0.50)	2481 (128)	10.82 (0.34)
	Reactor 4	6.66 (0.30)	5.85 (0.52)		11.07 (0.25)
Yeast culture amended	Reactor 1	6.62 (0.33)	5.66 (0.53)	2450 (114)	6.35 (0.85)
	Reactor 2	6.68 (0.07)	5.67 (0.48)		9.03 (1.68)
	Reactor 3	6.60 (0.14)	5.65 (0.48)	2531 (125)	10.56 (0.69)
	Reactor 4	6.66 (0.29)	5.71 (0.46)		10.96 (0.92)
Hybrid	Reactor 1	7.53 (0.27)	5.60 (0.55)	2513 (120)	10.81 (1.31)
	Reactor 2	7.53 (0.17)	5.70 (0.51)		11.35 (0.53)
	Reactor 3	7.61 (0.08)	5.69 (0.53)	2519 (107)	10.94 (0.42)
	Reactor 4	7.70 (0.10)	5.69 (0.43)		11.24 (0.65)

Table 4.5 Monthly hydrosol oxidation-reduction potential (redox) from control, sucrose-amended, yeast culture-amended, and hybrid pilot-scale CWTS.

<b>Pilot-scale CWTS</b>	<b>Reactor</b>	<b>July mV</b>	<b>August mV</b>	<b>September mV</b>	<b>October mV</b>	<b>November mV</b>
Control	Reactor 1	-181	-208	-216	-205	-179
	Reactor 2	-191	-214	-224	-225	-169
	Reactor 3	-189	-218	-207	-127	-135
	Reactor 4	-155	-221	-173	-211	-177
Sucrose amended	Reactor 1	-181	-168	-174	-245	-434
	Reactor 2	-141	-144	-147	-252	-245
	Reactor 3	-21	-21	1	-220	-232
	Reactor 4	-98	-210	-252	-209	-144
Yeast culture amended	Reactor 1	-106	-141	-120	-194	-290
	Reactor 2	-140	-155	-158	-70	-254
	Reactor 3	-108	-78	-83	-105	-144
	Reactor 4	58	44	84	122	44
Hybrid	Reactor 1	-106	-121	-102	-148	-159
	Reactor 2	-116	-206	-179	-166	-177
	Reactor 3	-120	-221	-210	-198	-209
	Reactor 4	-151	-211	-204	-206	-223

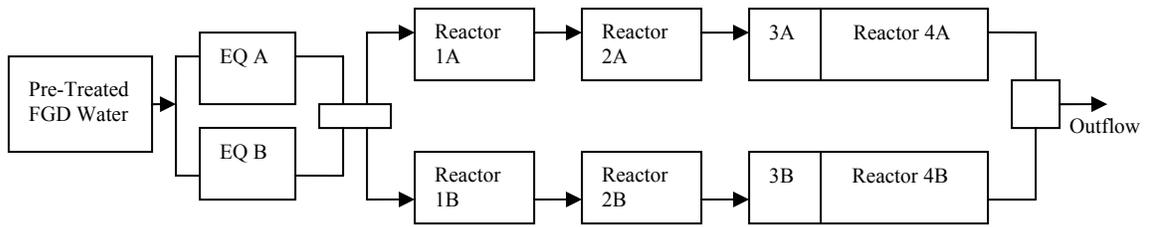


Figure 4.1 Process flow diagram of full-scale CWTS used for remediating FGD waters produced at an eastern North Carolina coal-fired power plant.

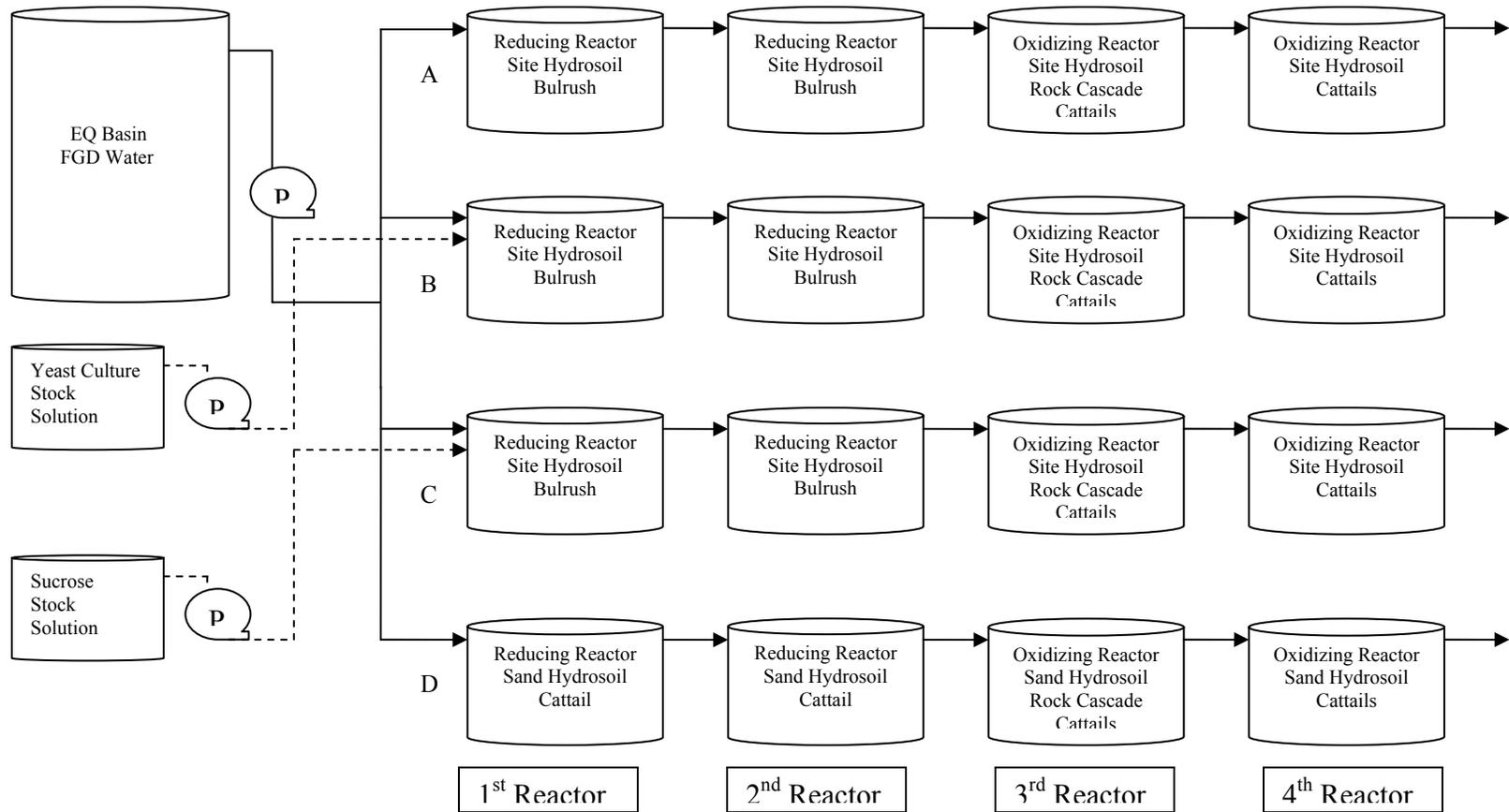


Figure 4.2 Process flow diagram of (A) control, (B) yeast culture amended, (C) sucrose amended, and (D) hybrid pilot-scale CWTS used to determine treatment of selenium and mercury from FGD waters produced at an eastern North Carolina coal-fired power plant. Metering pumps are indicated by (P).

## CHAPTER FIVE

### ENHANCING TOTAL SELENIUM REMOVAL IN FLUE GAS DESULFURIZATION WATER USING ORGANIC CARBON ADDITIONS TO A FULL-SCALE CONSTRUCTED WETLAND TREATMENT SYSTEM

#### **Abstract**

Water used in coal-fired power plants, such as flue gas desulfurization (FGD) waters, is commonly contaminated with selenium (Se) and requires treatment before discharge due to its potential to bioaccumulate and cause toxicity to receiving system biota. One approach to decreasing Se concentrations in FGD water is a constructed wetland treatment system (CWTS). These treatment systems can decrease Se concentrations in FGD waters, but the removal may be limited in these waters due to elevated (> 40 mg/L) concentrations of competing electron acceptors, such as nitrate. Additions of electron donors may be required to enhance the removal of Se in FGD waters with competing electron acceptors and can include organic carbon sources such as sucrose and yeast culture. The objectives of this study were to: 1) measure the change in total Se concentrations from bench-scale experiments receiving different organic carbon types and concentrations in comparison to controls; 2) measure the removal (percent and extent of removal) of total Se in FGD water from an organic carbon amended and control CWTS series; and 3) compare and contrast outflow measurements from the amended and control CWTS series to performance goals at this site. Bench-scale experiments indicated that the organic carbon additions of 0.2 g/L and 0.4 g/L sucrose and 0.2 g/L and 0.4 g/L yeast extract significantly decreased selenium concentrations in FGD water compared to organic carbon additions of 1% and 5% hay, 5% *T. latifolia* detritus, and controls. Based on these data, we evaluated the removal of Se in FGD water using a full-scale CWTS

series receiving organic carbon additions of yeast culture and sucrose and a control CWTS series (e.g. no additions of sucrose or yeast culture). Organic carbon concentrations in the FGD water were increased with time and included five loading periods: 0.015 g yeast culture/L for days 0 to 83, 0.045 g/L (25% as yeast culture and 75% as sucrose) for days 84 to 113, 0.06 g as sucrose/L for days 114 to 148, 0.075 g as sucrose/L for days 149 to 180, and 1.1 g as sucrose/L for days 181 to 224. All additions of organic carbon were made at a splitter box before inflow into the first reactor, except for the last loading period (i.e. days 181 to 224) in which additions were made to inflow water of the second reactor. Organic carbon additions to the amended CWTS series significantly enhanced the removal of selenium from this FGD water. Incremental increases in Se removal from the final outflow samples of the amended CWTS series were measured in response to higher organic carbon concentrations with mean percent removal of 21.5, 40.9, 47.4, 40.6, and 54.9% for loading periods 1-5, respectively. The mean percent removal of total Se in the control CWTS series was 15.0, 13.8, 28.7, 15.0, and 23.6% for loading periods 1-5, respectively. Statistically, percent removals for Se in final outflow samples (i.e. outflows of reactor 4) were greater for the amended CWTS series than the control CWTS series for loading period 2 ( $p=0.0125$ ), loading period 4 ( $p=0.0003$ ), and loading period 5 ( $p=0.0022$ ). A linear fit between the mean differences in Se concentrations among amended and control CWTS series and organic carbon concentration resulted in an  $r^2$  value of 0.9182 and indicates these systems may further decrease Se concentrations in FGD water with higher organic carbon concentrations ( $> 1.1$  g/L). The amended CWTS series achieved the performance goal of  $\leq 200$   $\mu\text{g}$  total Se/L for all final outflow samples except the last sampling event (i.e.  $211 \mu\text{g/L}$ ); however,

the control CWTS series failed to meet the performance goal during seven sampling events during this study. This research provides an approach to enhance the removal of Se in FGD water using CWTS that receive additions of sucrose as an electron donor.

## **1. Introduction**

Combustion of coal for thermoelectric power production has contributed sources of selenium (Se) to aquatic ecosystems that have adversely affected biota (Lemly, 2002). The mass of selenium liberated from coal combustion and recovery of this contaminant from air emissions is increasing due to a greater demand for power and implementation of air pollution control systems used at coal-fired power plants for decreasing sulfur dioxide (SO<sub>2</sub>) (Feeley et al., 2005). The United States Environmental Protection Agency (U.S. EPA) identified SO<sub>2</sub> as a criterion pollutant due to adverse effects on human health and welfare (Rubin et al., 2004). In response to Clean Air Act legislation (Clean Air Act, 1990), coal-fired power plants are decreasing SO<sub>2</sub> emissions using flue gas desulfurization (FGD) scrubbers. FGD scrubbers typically use a wet scrubbing process to contact flue gases with saturated calcium water allowing oxidation of SO<sub>2</sub> gases and formation of calcium sulfite (CaSO<sub>3</sub>) and calcium sulfate (CaSO<sub>4</sub>). Oxidation of SO<sub>2</sub> can be assisted through introduction of force air in scrubbing towers. This scrubbing process produces an aqueous stream referred to as FGD water. In addition to the calcium sulfate salts, FGD waters can contain a multitude of problematic constituents including arsenic, boron, cadmium, chromium, chloride, mercury, selenium, and zinc (Mierzejewski, 1991). Of these constituents, selenium is of primary concern due its concentration in FGD waters and ability to adversely affect aquatic organisms at concentrations measured in these waters. Se is also of concern in these waters since it can be difficult to remove,

especially in high ionic strength waters such as FGD waters. Based on the EPA ambient water quality criteria for Se and peer-reviewed literature, the most sensitive species to exposures of Se from contaminated waters are fish species (Lemly, 1999; USEPA, 2004). Lemly (2002) reported that Se from a coal-fired power plant effluent was accumulated in local fish species and caused adverse affects (i.e. biochemical function, teratogenic deformities, and mortality) when Se concentrations exceeded approximately 10 µg/g or greater in eggs. This publication provides a strong case study on the impacts Se may cause to receiving system biota from a coal-fired power plant effluent; however, data regarding other problematic contaminants (e.g. As, B, Hg, Cd, Cr, Cu, and Zn) associated with ash basin water (Cherry and Guthrie, 1977) and possible antagonistic or synergistic effects were not discussed in this paper. In order mitigate the toxicity of Se to aquatic biota from discharged FGD water, reliable treatment processes are needed in order to decrease its concentration and bioavailability.

Removal of Se from FGD waters can be difficult due to high concentrations (>50 to 20,000mg/L) of potentially interfering constituents (e.g. sulfates, nitrates, chlorides, and carbonates), limited reactivity or binding of selenium forms (e.g. selenate species) to sorptive materials, and cost of intensive treatment systems (i.e. reverse osmosis nanofiltration, and ion exchange resins) (Balistrieri and Chao, 1987; Parida et al., 1997). Se adsorption to ferrihydrite is effective for selenite (Se IV) at pH values < 8, but removal decreases in waters containing elevated concentrations of interfering aqueous species (phosphate, silicate, arsenate, and carbonates) such as FGD waters (EPRI, 1980; Manning and Burau, 1995). Selenate (Se VI) adsorption to ferrihydrite is low (no removal to ~20%), and removal extents are likely insufficient for remediating FGD

waters. Other adsorptive materials, such as alumina have been reported (Trussell et al., 1980; Batista and Young, 1994) to efficiently remove Se (IV) and to a lesser extent Se (VI), but may be limited for full-scale treatment system of FGD waters due to interfering aqueous species, mass of alumina required to treat 0.378 to 1.51 million L/d of FGD waters, and potential toxicity of residual alumina in post-treated waters. Removal of selenium through reduction of Se (VI) using zero-valent iron ( $\text{Fe}^0$ ) and ferrous salts (e.g.  $\text{FeOH}_2$ ,  $\text{FeCl}_2$ , and  $\text{FeSO}_4$ ) is effective for decreasing Se concentrations (Zhang et al., 2005), but costs of pH buffering reagents and handling or disposal of iron sludge can limit the application of these technologies. Microbial remediation of selenium has been successfully applied to agricultural and industrial wastewater (Zhang et al., 2004) and may be useful for treating selenium and other constituents contained in FGD waters.

Microbial remediation of selenium is accomplished through dissimilatory reduction of Se (VI) to Se (IV) and Se (IV) to elemental Se ( $\text{Se}^0$ ) (Steinberg and Oremland, 1990). These oxyanion forms of Se function as the terminal electron acceptor in microbial respiration (Dungan and Frankenberger, 1998). Establishing environmental conditions that favor these microbial transformations may assist in the removal of total Se from the water column due to the low solubility of  $\text{Se}^0$  (Kessi et al., 1999) and its ability to accumulate in sediments (Zhang et al., 2004). Under low oxidation-reduction ( $E_h$ ) environments,  $\text{Se}^0$  can be further reduced to selenide ( $\text{Se}^{2-}$ ) which can complex with ferrous iron to form stable minerals such as achavalite ( $\text{FeSe}$ ) and ferroselite ( $\text{FeSe}_2$ ). Based on the  $K_{sp}$  of metal selenides, transformation of Se into these solid phases provides a useful remediation strategy for sequestering of Se within hydrosols (Masscheleyn et al., 1990). Metal selenides are practically insoluble (Masscheleyn and

Patrick, 1993; Peters et al., 1996) and can be maintained as these forms in low  $E_h$  sediments, such as wetland hydrosols.

Constructed wetland treatment systems (CWTS) have been used to remediate constituents in FGD waters (Eggert et al., 2008). The treatment efficiency of these systems for removal of Se from FGD waters has ranged from <10% to 68% and may require alterations to these systems to enhance microbial reduction of Se (IV) and Se (VI) contained in FGD waters. Previous research (Cantafio et al., 1996; Zhang et al., 2003, 2004) on microbial remediation of Se contaminated waters indicates that additions of electron donors can increase the rate of dissimilatory Se (VI) and Se (IV) reduction in laboratory and pilot-scale experiments. Electron donors such as soluble organic carbon (e.g. molasses, glucose, methanol, tyripcase soy broth, sucrose, and amino acids) can enhance the reduction and removal of Se forms contained in FGD waters (dominantly Se (IV) and Se (VI) (Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2003, 2005). Since Se respiring-bacteria are ubiquitous in aquatic sediments (Narasingarao and Haggblom, 2007), additions of organic carbon to a CWTS should enhance the reduction and removal of Se in FGD waters.

In order to test the hypothesis that organic carbon additions to FGD waters can enhance the removal of total Se, bench-scale laboratory experiments were conducted to determine type and approximate concentration of organic carbon required to decrease total Se concentration in FGD water. Data from these experiments were used to determine the type of organic carbon to amend into an existing CWTS treating approximately 4.54 million L/d (1.2 million gal/d; MGD) of FGD water. Determination

of sufficient organic carbon concentrations in this FGD water was conducted at the full-scale CWTS. The objectives of this study were to: 1) measure the change in total Se concentrations from bench-scale experiments receiving different organic carbon types and concentrations in comparison to controls; 2) measure the removal (percent and extent of removal) of total Se in FGD water from an organic carbon amended and control CWTS series; and 3) compare and contrast outflow measurements from the amended and control CWTS series to performance goals at this site.

## **2. Materials and methods**

### *2.1 Bench-scale Experiments*

Bench-scale experiments were conducted in 500-ml borosilicate glass jars with 100-g of site sediment and 400-ml of FGD water. Organic carbon types included sucrose (0.2 and 0.4 g/L), yeast extract (0.2 and 0.4 g/L), hay (1.0% and 5% w/w) and *Typha latifolia L.* detritus (5% w/w). Controls were not amended with organic carbon. Each treatment was duplicated for replication. To simulate the hydraulic retention time (HRT) of a flow-through CWTS and minimize disturbance of these experiments, 50% of the FGD water was removed every 3-d and replaced with un-treated FGD water. Total selenium concentrations, pH, and dissolved oxygen (DO) concentrations were measured every 3-d. Samples for Se determination were collected in acid-cleaned 50-ml centrifuge tubes and preserved with concentrated trace metal-grade nitric acid (1% v/v). Total selenium measurements were determined using hydride generation atomic absorption spectrometer (HG-AAS) according to EPA method 7741A. DO concentrations and pH values were determined using standard methods (APHA, 1998).

### *2.2 Full-scale CWTS*

### 2.2.1 Study Site

The constructed wetland treatment system (CWTS) used for this study was located in eastern North Carolina at a 2,090 mega watt (MW) coal-fired power plant. The CWTS was designed to treat approximately 4.54 million L/d (1.2 million gal/d; MGD) and included two equalization (EQ) basins and three wetland reactor series (Figure 4). Equalization basins were designed to decrease water temperatures to <35°C and also functioned to decrease total suspended solids (TSS) and regulate flows into the CWTS. Area of each EQ basin was approximately 0.31-ha (0.76-ac) with a hydraulic retention time (HRT) of 24-h. Each CWTS series was designed with two reducing reactors (i.e. 1<sup>st</sup> and 2<sup>nd</sup> reactors) for removal of metals and metalloids and a rock-cascade followed by an oxidizing reactor (i.e. 4<sup>th</sup> reactor) for removal of metalloids by co-precipitation with iron and manganese oxyhydroxides. Oxidizing reactors also functioned to increase dissolved oxygen (DO) concentrations in the FGD water from radial oxygen loss from wetland plants. Hydrosols for the reducing and oxidizing reactors were local soils collected on-site. Reducing reactor hydrosols were amended with pine mulch and hay to achieve 5 to 8% organic matter by weight, gypsum (100 g/m<sup>2</sup>) as a sulfate source, a control-release fertilizer (Osmocote) (300 g/m<sup>2</sup>), and were planted with *Schoenoplectus californicus* C.A. Meyer (giant bulrush). Oxidizing reactor hydrosols were amended with a control-release fertilizer (Osmocote) (300 g/m<sup>2</sup>) and were planted with *Typha latifolia* L. (common cattail). The area and HRT were 0.52-ha (1.28-ac) and 36-h for reducing reactors and 0.91-ha (2.24-ac) and 64-h for oxidizing reactors, respectively. Total HRT for each CWTS series was approximately 136-h (5.67-d).

Construction of the CWTS began in August, 2004, and was completed in April, 2005. Bulrush and cattails were planted in July, 2005 and FGD water was introduced into this system in November, 2006. This study was initiated during July, 2008, approximately 22 months after FGD water was introduced into the CWTS.

### *2.2.2 FGD Water*

Flue gases produced at this site originate from burning eastern bituminous coal (i.e. Eastern and Northern Appalachian coal sources) and are treated using spray towers (i.e. four spray levels) and a limestone slurry as the sorbent in these scrubbers. Fly ash and nitrous oxides (NO<sub>x</sub>) in the flue gas were treated using cold side electrostatic precipitators (ESP) and selective catalytic reactors (SCR) before introduction to the scrubbers. FGD water produced in the scrubbers was transferred to a holding tank and treated for total suspended solids (TSS) using additions of a cationic polymer in an upstream clarifier. The clarified FGD water was co-managed with intake water from the local reservoir (1 part FGD water to 1.2 parts intake water) to decrease chloride and boron concentrations in order to maintain the health of wetland plants. Normal flows of FGD water to the EQ basin were 2948-3024 L/min (780-800 gal/min).

### *2.2.3 Performance Goals*

The performance goal of the CWTS was to decrease total Se concentration to  $\leq 200 \mu\text{g/L}$ . This performance goal was estimated based on anticipated discharge limits and co-management of treated FGD water with ash basin water.

### *2.2.4 Organic Carbon Sources*

To determine the organic carbon source and concentrations required to achieve performance goals at this site, one series of reactors in the CWTS was initially amended

with low organic carbon concentrations (0.015 g/L) and increased with time to discern the contribution of additional organic carbon concentrations (Table 1). Additions of organic carbon were conducted by metering appropriate volumes of a stock organic carbon solution into the amended CWTS series. The stock solution was contained in a 6048-L high density polypropylene (HDPE) conical-bottom tank and mixed using a DC powered submersible pump. Organic carbon sources were added to the amended CWTS series at the outflow of the EQ basin (e.g. splitter box) for all amendment periods. To test if Se removal could be enhanced in the 2<sup>nd</sup> reducing reactor, organic carbon was added to outflow FGD waters of 1<sup>st</sup> wetland reactor during loading period 6 (Figure 1). Additions of organic carbon and concentrations are listed in Table 1 and are referred to as loading periods.

#### *2.2.5 Performance Evaluation*

To determine if Se removal (i.e. percent and extent of removal) can be enhanced with organic carbon additions to CWTS to meet site performance goals, aqueous samples were collected weekly and measured for total Se from the inflows and outflows of the EQ basin and outflows of control wetland reactors and amended wetland reactors. Samples for Se determination were collected in acid-cleaned 125-ml HDPE bottles and preserved with concentrated trace metal-grade nitric acid (1% v/v). Total Se measurements were determined using inductively coupled plasma mass spectroscopy with a collision reaction cell (ICP-CRC-MS) (EPA Method 200.8) and HG-AAS (EPA method 7741A). Percent removal of Se was calculated using the equation (1).

$$\text{Percent removal} = (1 - ([A]_t / [A]_0)) * 100 \quad \text{Equation (1)}$$

Where  $[A]_i$  is the concentration of Se in the equalization basin (pre-treatment),  $[A]_0$  is the concentration of Se in the outflow sample of reactor four (i.e. post-treatment). Extent of Se removal is defined as the total concentration of Se in outflows from the final wetland reactor of the control and amended CWTS series.

### *2.2.6 Monitoring Parameters*

Aqueous monitoring parameters were collected weekly and measured from inflow and outflow samples of the EQ basin and outflow samples of control wetland reactors and amended wetland reactors. Parameters measured on-site included temperature, pH, water column oxidation redox potentials (ORP), and dissolved oxygen (DO) according to Standard Methods (APHA, 1998). Parameters requiring laboratory analyses were placed in high density polypropylene (HPDE) bottles and stored at 4°C until analyzed. These parameters included chloride, sulfate (EPA Method 300.0), nitrate (EPA Method 300.0), total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD). All monitoring parameters were determined using Standard Methods (APHA, 1998) or EPA Methods. Samples for boron determination were collected in HDPE bottles, preserved with trace metal grade nitric acid (1% v/v), and determined using ICP-MS (EPA Method 200.8). Samples for mercury determination were placed in borosilicate glass vials and preserved with bromide chloride solution (2% v/v). Mercury concentrations for inflow FGD waters were determined using pre-concentration techniques (i.e. gold amalgamation traps) coupled to a cold vapor atomic fluorescence spectrometer (CV-AFS) (EPA Method 1631).

### *2.3 Statistical Analyses*

To determine differences in percent removal and extents of removal for Se and nitrate measurements between the amended and control CWTS series, we used Statistical Analysis System (SAS, 2008) to perform normality tests (Shapiro-Wilks, Proc Univariate) and determined differences using a paired t-test with  $\alpha = 0.05$ . Data were paired by loading period. The linear relationship between selenium enhancement and organic carbon additions was performed using Excel to obtain a r-squared value.

### 3. Results

#### 3.1 Bench-scale Experiments

To determine differences in Se removal among treatments, measurements of mean selenium concentrations from treatment samples were consolidated for every three collection dates after experiment initiation and included three testing durations of 0 to 9-d, 12 to 18-d, and 21 to 27-d. For days 0-9, mean Se concentrations were lowest for the 0.2 g/L sucrose treatment ( $43 \pm 16 \mu\text{g/L}$ ) followed by the 0.4 g/L sucrose treatment ( $50 \pm 20 \mu\text{g/L}$ ) (Figure 2). No differences were measured between either yeast extract treatments and the 5% hay and 5% *T. latifolia* detritus treatments ( $p > 0.05$ ). Control and 1% hay treatments were less effective for Se removal than all other treatments. For days 12 to 18, all labile organic carbon treatments (sucrose and yeast extract) had lower mean Se concentrations in comparison to control and the hay and *T. latifolia* detritus treatments (Figure 3). Between soluble organic carbon treatments, the 0.2 g/L yeast extract treatment had the lowest mean Se concentrations ( $24 \pm 6 \mu\text{g/L}$ ) followed by the 0.2 g/L sucrose treatment ( $26 \pm 8 \mu\text{g/L}$ ), the 0.4 g/L sucrose treatment ( $39 \pm 12 \mu\text{g/L}$ ), and the 0.4 g/L yeast extract treatment ( $48 \pm 40 \mu\text{g/L}$ ). Similar to days 12 to 18, all labile organic carbon treatments decreased Se to lower concentrations than control, hay, and *T. latifolia*

detritus treatments during days 21 to 28 (Figure 4). No differences in mean Se concentrations were measured between the 0.2 g/L sucrose treatment and the 0.2 g/L yeast extract treatment ( $p = 0.7182$ ) or the 0.4 g/L yeast extract treatment ( $p = 0.4016$ ). The 0.2g/L sucrose treatment was more efficient for decreasing Se concentrations than the 0.4 g/L sucrose treatment ( $p=0.0181$ ) during days 21 to 28.

Dissolved oxygen (DO) concentrations were lower in the sucrose and yeast extract treatments than the control, 1% hay, and *T. latifolia* detritus treatments and during days 12 to 28 for the 5% hay treatment (Table 2). For these experiments, pH measurements of the treatments were similar to the inflow FGD water, except for the sucrose treatments. The 0.4 g/L and 0.2 g/L sucrose treatments had pH measurements of  $5.48 \pm 0.12$  and  $5.90 \pm 0.32$  for days 12 to 18 and  $5.56 \pm 0.16$  and  $6.10 \pm 0.43$  for days 21 to 28, respectively.

### 3.2 Full-scale CWTS

#### 3.2.1 FGD Water

The FGD water for this study was similar to brackish waters with total dissolved solids (TDS) and chloride ( $\text{Cl}^-$ ) concentrations of  $5,200 \pm 1017$  (mean  $\pm$  standard deviation) mg/L and  $2504 \pm 580$  mg/L, respectively (Table 3). Other unique characteristics of this FGD water include elevated concentrations of sulfate ( $506 \pm 121$  mg/L), COD ( $225 \pm 194$  mg/L), boron ( $47 \pm 9$  mg/L), nitrate ( $55 \pm 14$  mg/L), and mercury ( $87 \pm 122$  ng/L). Throughout this study, total Se concentrations (pre-treated) measured from inflow FGD water samples averaged  $202 \pm 116$   $\mu\text{g/L}$  ( $n=28$ ). Se concentrations increased in the inflow FGD water during this study and averaged  $129 \pm 37$   $\mu\text{g/L}$ ,  $138 \pm 39$   $\mu\text{g/L}$ ,  $222 \pm 92$   $\mu\text{g/L}$ ,  $223 \pm 67$   $\mu\text{g/L}$ , and  $288 \pm 168$   $\mu\text{g/L}$  for loading

periods 1-5, respectively. High variability in Se concentrations from inflow FGD water samples was measured during this study with the greatest variability occurring during the last loading period (i.e. range of Se concentrations from 81 to 490  $\mu\text{g}$  as Se/L).

### 3.2.2 Performance Evaluation

Organic carbon additions to the amended CWTS series significantly enhanced the removal of Se from this FGD water. Incremental increases in Se removal from the final outflow samples of the amended CWTS series were measured in response to higher organic carbon concentrations (Table 1) with mean percent removal of 21.5, 40.9, 47.4, 40.6, and 54.9% for loading periods 1-5, respectively (Figure 7). The mean percent removal of total Se in the control CWTS series was 15.0, 13.8, 28.7, 15.0, and 23.6% for loading periods 1-5, respectively. Statistically, percent removals for Se in final outflow samples (i.e. outflows of reactor 4) were greater for the amended CWTS series than the control CWTS series for loading period 2 ( $p=0.0125$ ), loading period 4 ( $p=0.0003$ ), and loading period 5 ( $p=0.0022$ ).

As selenium removal in the amended CWTS series increased with higher organic carbon concentrations, a larger difference in Se concentrations between the control CWTS series was measured during this study (Figures 5, 6, and 7). Differences in the mean Se concentrations between the amended and control CWTS series ( $[\text{Se}]_{\text{amended}} - [\text{Se}]_{\text{control}}$ ) measured from final outflow samples were  $8.3 \pm 11.7 \mu\text{g/L}$  for loading period 1 ( $p=0.0838$ ),  $37.5 \pm 20.0 \mu\text{g/L}$  for loading periods 2 ( $p=0.0341$ ),  $41.6 \pm 21.0 \mu\text{g/L}$  for loading period 3 ( $p=0.0296$ ),  $54.0 \pm 20.0 \mu\text{g/L}$  for loading period 4 ( $p=0.0001$ ), and  $90.3 \pm 49.0 \mu\text{g/L}$  for loading period 5 ( $p=0.0013$ ). A linear fit between the mean differences in

Se concentrations among amended and control CWTS series and organic carbon concentration resulted in an  $r^2$  value of 0.9182 (Figure 8).

The majority of Se removal in the amended CWTS series occurred in reactor 1 and accounted for 90.2, 68.7, 73.8, 82.3, and 61.9% of the total removal of Se measured during loading periods 1-5, respectively (Figure 9). For the control CWTS series, reactor 1 accounted for 70.0, 0, 59.3, 35.3, and 25.4% of the total removal of Se measured during loading periods 1-5, respectively. The amended CWTS series achieved the performance goal of  $\leq 200 \mu\text{g total Se/L}$  for all final outflow samples (i.e. reactor 4) except the last sampling event (i.e.  $211 \mu\text{g/L}$ ). The control CWTS series failed to meet the performance goal during seven sampling events (Figure 11). The mean Se concentration measured in samples from the control CWTS series not meeting the performance goal was  $277 \pm 50.0 \mu\text{g/L}$  with a range of 220 to  $336 \mu\text{g as Se/L}$ .

### *3.2.3 Monitoring Parameters*

Nitrate removals measured from outflow samples of reactors 1, 2, and 4 of the amended CWTS series were greater in comparison to the control CWTS series during the loading periods 2-5 ( $p < 0.001$ ). Nitrate removal averaged  $65.1 \pm 11.7\%$  for the amended CWTS series where as the control CWTS series averaged  $4.9 \pm 6.8\%$  for sampling events during loading periods 2-5 (Figure 12). Similar to Se removal, no differences for mean nitrate removal were measured between the CWTS series during the loading period 1 ( $p > 0.05$ ). During the first loading period, the average nitrate removal for amended and control CWTS series was  $10.6 \pm 4.8 \%$  and  $3.7 \pm 5.8\%$ , respectively. A strong positive correlation ( $r^2=0.9028$ ) between the monthly mean removals of Se and nitrate was measured for the amended CWTS series (Figure 13), but was lower for the control

CWTS series ( $r^2=0.4104$ , Figure 14). Monthly mean removals were used to determine a linear relationship between Se and nitrate removal, in order to provide a larger sample size ( $n=7$ ) than loading periods ( $n=5$ ) which produced a similar positive linear relationship ( $r^2 = 0.851$ ).

Another water chemistry parameter that may explain the differences in Se removal measured between the amended and control CWTS series was biochemical oxygen demand ( $BOD_5$ ). Organic carbon additions to the amended CWTS series increased  $BOD_5$  measurements in comparison to the control CWTS series for outflow samples of all reactors during loading periods 3-5 (Tables 3, 4, and 5). Mean  $BOD_5$  values for the amended CWTS series during loading periods 3-5 were  $19.1 \pm 12.5$  mg as  $O_2/L$  (reactor 1),  $21.3 \pm 12.8$  mg as  $O_2/L$  (reactor 2), and  $13.5 \pm 8.6$  mg as  $O_2/L$  (reactor 4), whereas mean  $BOD_5$  values for the control CWTS series were  $2.3 \pm 1.9$  mg as  $O_2/L$  (reactor 1),  $2.2 \pm 2.0$  mg as  $O_2/L$  (reactor 2), and  $7.8 \pm 2.4$  mg as  $O_2/L$ , respectively. As expected, mean  $BOD_5$  values for samples from the amended CWTS series increased with each successive loading period and were greater in reactor one outflow samples for all loading periods except loading period 6 (i.e. loading of 0.0375g sucrose/L to the inflow of reactor 2). DO measurements collected on-site support these findings and indicate a higher microbial activity within first and second reactors amended with organic carbon sources (Tables 3 and 4). Increases in the activity of microbial communities likely led to lower ORP measurements in the first and second wetland reactors of the amended CWTS series (Tables 3 and 4). Measurements of TDS, TSS, chlorides, sulfates, boron, pH, and temperature were similar between reactors of the amended and control CWTS series during this study (Tables 3, 4, and 5).

#### 4. Discussion

The overall objective of this study was to enhance the removal of Se from a FGD water using an existing full-scale CWTS. In order to accomplish this objective, we decided to test the hypothesis that organic carbon additions to a CWTS could increase the removal of total Se from a FGD water. Due to the unique composition of this FGD water and large size of these systems (~2 to 60 acres), testing and confirmation of appropriate organic carbon sources and concentrations at a bench-scale were needed to efficiently and effectively augment the full-scale CWTS.

Data from the bench-scale experiments indicated that sucrose and yeast culture additions of 0.2g/L and 0.4g/L were sufficient for decreasing total Se concentrations in this FGD water in comparison to control, hay, and *T. latifolia* detritus treatments. The organic carbon sources of 1% hay and 5% hay and *T. latifolia* detritus did not increase the removal of Se in comparison to controls and was likely due to lower microbial activities within these experimental units. In treatments with higher microbial activities (i.e. DO concentrations < 2 mg as O<sub>2</sub>/L), lower Se concentrations were measured, suggesting microbial reduction of the Se species and/or removal through complexation reactions with cations (e.g. iron and manganese). Masscheleyn and Partrick (1990) reported that in low E<sub>h</sub> environments (-400, -200, and 0 mV), similar to treatments with DO concentrations < 2 mg as O<sub>2</sub>/L, selenium species were dominated by less soluble forms (Se<sup>0</sup> and Se<sup>2-</sup> species) and these biochemical changes likely resulted in the removal of Se measured in the sucrose and yeast extract treatments. An enhancement in the removal of Se was not measured between the treatments receiving 0.2g/L and 0.4g/L sucrose or yeast extract. These results may be due to treatments having similar quantities

of suspended microbial cells with internal and external Se forms and differences were not discerned since Se was measured as total during these experiments. Another reason for these results may include differences in microbial communities between the 0.2 and 0.4g/L treatments. An acclimation period of approximately 9-d after test initial was needed for consistent removal of Se in treatments used in this study and indicates possible sorption of Se to organic carbon surfaces and a time requirement for growth of microorganisms. These experiments confirmed that the organic carbon sources of sucrose and yeast extract can enhance the removal of Se from a FGD water under laboratory conditions and have the potential to increase the removal of Se in an existing CWTS.

Based on the results of the bench-scale experiments, amendments of soluble organic carbon sources to an existing full-scale CWTS were conducted to (1) determine differences in Se concentrations from inflow and reactor outflow FGD water samples using a control CWTS series for comparisons and (2) determine if Se performance goals ( $< 200 \mu\text{g/L}$ ) in final outflow samples could be achieved using this approach. To discern the appropriate concentration of organic carbon needed to achieve these objectives, we chose to amend the CWTS series with low organic carbon concentrations initially and increase these concentrations after approximately 30-d. Monitoring of the amended and control CWTS series was conducted after a 28-d acclimation period to allow for microbial growth and stabilization of the environmental parameters within each reactor (i.e. DO and BOD).

Significant differences in Se concentrations from final outflow samples were measured between the amended and control CWTS series after the first loading period to the conclusion of this study. During these loading periods (2 to 5), we selected sucrose as

an organic carbon source and increased its concentrations in the FGD water from 0.03, 0.06, 0.075, and 0.075 in the first reactor and amended the second reactor with 0.0375 g/L during the last loading period. The incremental increases of sucrose concentrations in the FGD water resulted in greater differences for Se concentrations between samples from the amended and control CWTS series, and are presumably a result of higher microbial activity. As the BOD values within the reactors of amended CWTS series increased, dissolved oxygen concentrations and ORP measurements decreased producing a lower  $E_h$  environment. Transformations of selenium such as the reduction of Se (VI) and Se (IV) to  $Se^0$  are more favorable under low  $E_h$  environments and allow for the growth and activity of many selenite and selenate respiring microorganisms (Viamajala et al., 2006).

Other microbial processes such as denitrification of the FGD waters also increased with sequential loading periods. A strong correlation between the mean nitrate and Se removal from amended CWTS series was measured for loading periods 2 to 5, but it is unclear if nitrate concentrations affected the biochemical reduction and removal of Se species in this FGD water. Decreasing the concentrations of competing electron acceptors such as nitrate could have enabled higher microbial reduction rates of Se, but increasing their activity within the amended CWTS series may have proportionally enhanced the removal of both Se and nitrate. During sampling events in which nitrate removal was low (< 12%) for the amended or control CWTS series, a disproportional removal of Se was measured and resulted in low correlation between these constituents. This non-linear relationship may have occurred due physical treatment of selenium (e.g.

settling of filterable Se forms which averaged approximately  $17 \pm 12\%$  for FGD waters entering the EQ basin), but would not appreciably affect nitrate concentrations.

Through additions of sucrose to the amended CWTS series, Se concentrations decreased below the performance goals for all sampling events except the last sampling event of this study (i.e. loading period 5). In comparison, the control CWTS did not sufficiently decrease Se concentrations less than the performance goals for seven sampling periods. During the last period, inflow Se concentrations increased from an average of  $222 \pm 67 \mu\text{g/L}$  (loading period 4) to  $288 \pm 168 \mu\text{g/L}$  with a range of 81 to 490  $\mu\text{g/L}$ . The mean outflow Se concentrations from the amended and control CWTS series were  $130 \pm 51 \mu\text{g/L}$  and  $221 \pm 94 \mu\text{g/L}$ , respectively, and indicate the robustness of the amended CWTS series to decrease Se concentrations during periods with variable inflow concentrations. Based on the results of this study, increasing the sucrose concentrations above 0.11 g/L in this FGD water should further enhance the removal of Se and could be increased to approximately 0.25 g/L without impacting the oxygen demand of final outflow waters (i.e.  $> 30 \text{ mg as BOD/L}$ ).

## 5. Conclusions

The approach presented in this study provides a solution to decreasing total Se concentrations in FGD waters. Bench-scale experiments provided data that labile organic carbon sources of sucrose and yeast extract can decrease Se concentrations in FGD water and therefore were tested in the field. Sucrose additions to the CWTS improved the treatment of Se in the FGD water and also decreased nitrate concentrations. Increasing the concentrations of sucrose in the FGD water enhanced Se removal and resulted in higher BOD<sub>5</sub> measurements in reactors receiving sucrose additions. Sucrose is relatively

inexpensive as an organic carbon source and may range in costs based on product type (liquid solution or granular), quantities purchased, and delivery to site. The estimated annual cost to treat 3.78 million L/day (1 MGD) of FGD water receiving 0.15g as sucrose/L is approximately \$137,000 to 183,000/year (2009). Other materials such as storage tanks and delivery system could be purchased for less than \$100,000. This research documents that CWTS can be altered to enhance the removal of constituents (i.e. Se and nitrate) in FGD waters.

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Table 5.1 Organic carbon (OC) sources and concentrations used to enhance selenium removal in the amended CWTS series.

<b>Loading Period</b>	<b>Dates</b>	<b>Duration (d)</b>	<b>Amendment Site</b>	<b>OC Source(s)<sup>1</sup></b>	<b>OC Conc. (g/L)</b>
Acclimation <sup>2</sup>	15-Jul to 11-Aug	28	Inlet Reactor 1	YC	0.015
1	12-Aug to 6-Oct	55	Inlet Reactor 1	YC	0.015
2	7-Oct to 6-Nov	30	Inlet Reactor 1	25% YC, 75% Suc	0.045
3	7-Nov to 11-Dec	35	Inlet Reactor 1	Suc	0.06
4	12-Dec to 13-Jan	32	Inlet Reactor 1	Suc	0.075
5	13-Jan to 24-Feb	44	Inlet Reactor 1 and (2) <sup>3</sup>	Suc	0.075 (0.0375)

<sup>1</sup>Organic carbon sources used in this study were yeast culture (YC) and sucrose (Suc).

<sup>2</sup>Acclimation period was used to promote growth of microorganisms and stabilize water chemistry parameters within reactors.

<sup>3</sup>During loading period 5, sucrose was added to the inflow FGD waters of the second reactor of the amended CWTS series to achieve 0.0375g sucrose/L.

Table 5.2 Mean dissolved oxygen concentrations and pH values measured from samples of eight treatments tested in the bench-scale experiments. Standard deviations are italicized below the corresponding mean value.

Treatment	Concentration	0-9d		12-18d		21-28d	
		pH	DO (mg/L)	pH	DO (mg/L)	pH	DO (mg/L)
Yeast Extract	0.4g/L	6.48	0.95	6.72	0.88	7.32	0.87
		<i>0.15</i>	<i>0.09</i>	<i>0.54</i>	<i>0.08</i>	<i>0.14</i>	<i>0.13</i>
	0.2g/L	6.94	1.04	6.91	0.86	7.50	1.23
		<i>0.21</i>	<i>0.30</i>	<i>0.57</i>	<i>0.07</i>	<i>0.26</i>	<i>0.18</i>
Sucrose	0.4g/L	6.52	1.01	5.48	0.93	5.56	0.93
		<i>0.05</i>	<i>0.14</i>	<i>0.12</i>	<i>0.70</i>	<i>0.16</i>	<i>0.78</i>
	0.2g/L	7.37	2.15	5.90	0.96	6.10	1.18
		<i>0.08</i>	<i>0.34</i>	<i>0.32</i>	<i>0.48</i>	<i>0.43</i>	<i>0.56</i>
Hay	5% (w/w)	7.64	1.52	7.25	3.80	7.75	4.73
		<i>0.15</i>	<i>0.53</i>	<i>0.41</i>	<i>1.08</i>	<i>0.23</i>	<i>1.25</i>
Hay	1% (w/w)	7.62	4.22	7.32	5.10	7.49	6.06
		<i>0.04</i>	<i>0.68</i>	<i>0.36</i>	<i>0.73</i>	<i>0.27</i>	<i>0.42</i>
<i>T. latifolia</i>	5% (w/w)	7.49	2.96	7.12	4.80	7.67	5.88
		<i>0.11</i>	<i>1.01</i>	<i>0.38</i>	<i>0.79</i>	<i>0.35</i>	<i>0.39</i>
Control	---	7.65	8.05	7.42	7.08	7.53	7.01
		<i>0.03</i>	<i>0.09</i>	<i>0.17</i>	<i>0.18</i>	<i>0.22</i>	<i>0.30</i>

Table 5.3 Water characteristics of inflow flue gas desulfurization (FGD) water received by the amended and un-amended CWTS series. Aqueous samples were collected at the outflow of the equalization basin (EQ).

Loading Period (LP)	Parameter	Nitrate (mg/L)	Selenium (µg/L)	Mercury (ng/L)	TDS (mg/L)	TSS (mg/L)	Boron (mg/L)	COD (mg/L)	Chloride (mg/L)	Sulfate (mg/L)
LP-1	Mean	76	129	48	6100	4.2	56.6	109	2700	600
	Std	10	37	32	1000	3.0	8.0	51	500	90
	Min, Max	60, 89	65, 181	13, 110	4900, 7800	<sup>1</sup> BRL, 7.2	43.5, 63.9	32, 170	2100, 3300	480, 750
LP-2	Mean	46	138	48	4800	9.3	38.2	128	2200	380
	Std	7	39	23	700	11.2	3.3	17	300	70
	Min, Max	36, 51	98, 177	25, 79	4000, 5600	2.6, 26.0	33.2, 40.1	110, 150	1800, 2400	300, 450
LP-3	Mean	45	222	211	4700	12.0	43.6	316	2200	470
	Std	9	92	274	1500	18.8	11.2	234	800	140
	Min, Max	33, 56	91, 307	34, 620	3100, 6700	<sup>1</sup> BRL, 40.0	29.6, 57.0	65, 630	1300, 3300	320, 640
LP-4	Mean	53	223	84	4300	5.2	42.8	107	2000	460
	Std	6	67	62	500	1.4	4.2	22	400	30
	Min, Max	44, 47	167, 272	23, 170	3800, 4900	3.0, 6.0	38.2, 48.4	89, 140	1700, 2500	430, 490
LP-5	Mean	46	288	132	5600	7.2	43.4	455	3000	520
	Std	6	168	137	1200	4.6	6.8	205	600	130
	Min, Max	39, 55	81, 490	44, 440	3600, 7200	<sup>1</sup> BRL, 14.0	32.2, 50.7	95, 780	2000, 3700	330, 730

<sup>1</sup>BRL: Below reporting limit.

Table 5.4 Mean water chemistry parameters (mg/L) measured from outflow samples of the first reactor for the amended and control CWTS series during loading periods 1 to 5. Standard deviations are italicized below the corresponding mean value.

<b>CWTS Series</b>	<b>Loading Period</b>	<b>TDS</b>	<b>TSS</b>	<b>B</b>	<b>COD</b>	<b>Cl<sup>-</sup></b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>BOD</b>	<b>Temp</b>	<b>pH</b>	<b>ORP</b>	<b>DO</b>
Reactor 1 - Amended	1	5950	7.5	57.0	120	2650	620	3.3	27.3	6.4	507.1	4.6
		<i>809</i>	<i>4.7</i>	<i>7.7</i>	<i>47</i>	<i>450</i>	<i>76</i>	<i>2.4</i>	<i>4.3</i>	<i>0.1</i>	<i>74.1</i>	<i>1.5</i>
Reactor 1 - Amended	2	4850	7.7	39.5	120	2200	400	4.6	19.5	6.5	447.3	5.1
		<i>252</i>	<i>5.8</i>	<i>2.1</i>	<i>22</i>	<i>115</i>	<i>42</i>	<i>1.3</i>	<i>3.3</i>	<i>0.2</i>	<i>117.3</i>	<i>0.9</i>
Reactor 1 - Amended	3	4625	6.5	44.0	285	2375	620	14.8	12.1	6.7	422.6	5.6
		<i>1040</i>	<i>2.9</i>	<i>8.1</i>	<i>77</i>	<i>591</i>	<i>220</i>	<i>13.2</i>	<i>3.5</i>	<i>0.1</i>	<i>45.8</i>	<i>2.3</i>
Reactor 1 - Amended	4	4000	7.2	41.1	119	1950	443	16.8	14.2	6.6	297.4	5.6
		<i>913</i>	<i>1.6</i>	<i>7.3</i>	<i>36</i>	<i>493</i>	<i>64</i>	<i>5.2</i>	<i>4.2</i>	<i>0.1</i>	<i>104.2</i>	<i>1.2</i>
Reactor 1 - Amended	5	5629	8.7	43.0	443	2957	556	22.2	11.3	6.5	390.8	5.6
		<i>1292</i>	<i>3.3</i>	<i>7.3</i>	<i>216</i>	<i>718</i>	<i>186</i>	<i>15.6</i>	<i>1.9</i>	<i>0.3</i>	<i>138.2</i>	<i>2.2</i>
Reactor 1 - Control	1	5875	3.2	56.4	107	2575	607	3.6	26.7	6.6	529.7	7.4
		<i>736</i>	<i>3.9</i>	<i>7.4</i>	<i>36</i>	<i>399</i>	<i>78</i>	<i>2.3</i>	<i>3.3</i>	<i>0.1</i>	<i>59.9</i>	<i>1.3</i>
Reactor 1 - Control	2	4750	2.8	38.7	104	2200	395	0.7	19.7	6.7	601.0	9.3
		<i>342</i>	<i>2.5</i>	<i>3.1</i>	<i>7</i>	<i>183</i>	<i>61</i>	<i>1.3</i>	<i>4.6</i>	<i>0.2</i>	<i>134.0</i>	<i>1.6</i>
Reactor 1 - Control	3	3900	10.1	40.0	114	1875	430	2.6	13.7	6.9	507.1	11.4
		<i>922</i>	<i>3.5</i>	<i>6.1</i>	<i>47</i>	<i>450</i>	<i>175</i>	<i>2.0</i>	<i>4.0</i>	<i>0.2</i>	<i>132.5</i>	<i>1.2</i>
Reactor 1 - Control	4	3900	10.1	40.0	114	1875	430	2.6	13.7	6.9	507.1	11.4
		<i>837</i>	<i>12.0</i>	<i>6.8</i>	<i>56</i>	<i>465</i>	<i>48</i>	<i>1.8</i>	<i>3.9</i>	<i>0.1</i>	<i>128.0</i>	<i>1.2</i>
Reactor 1 - Control	5	5743	5.0	43.3	377	3029	564	2.9	11.4	6.8	546.4	10.0
		<i>1401</i>	<i>2.9</i>	<i>7.0</i>	<i>218</i>	<i>748</i>	<i>190</i>	<i>1.8</i>	<i>2.4</i>	<i>0.2</i>	<i>87.7</i>	<i>3.5</i>

Table 5.5 Mean water chemistry parameters (mg/L) measured from outflow samples of the second reactor for the amended and control CWTS series during loading periods 1 to 5. Standard deviations are italicized below the corresponding mean value.

<b>CWTS Series</b>	<b>Loading Period</b>	<b>TDS</b>	<b>TSS</b>	<b>B</b>	<b>COD</b>	<b>Cl<sup>-</sup></b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>BOD</b>	<b>Temp</b>	<b>pH</b>	<b>ORP</b>	<b>DO</b>
Reactor 2 - Amended	1	6013	9.7	57.6	133	2800	640	2.7	26.1	6.5	525.3	8.7
		<i>1052</i>	<i>5.8</i>	<i>7.4</i>	<i>53</i>	<i>501</i>	<i>82</i>	<i>2.4</i>	<i>3.2</i>	<i>0.2</i>	<i>65.0</i>	<i>1.8</i>
Reactor 2 - Amended	2	5175	21.0	43.2	130	2475	438	3.9	17.3	6.9	611.5	9.4
		<i>310</i>	<i>18.7</i>	<i>3.3</i>	<i>8</i>	<i>250</i>	<i>29</i>	<i>3.1</i>	<i>4.1</i>	<i>0.2</i>	<i>125.9</i>	<i>1.7</i>
Reactor 2 - Amended	3	4300	9.1	41.9	165	2250	538	13.9	9.7	6.9	623.7	8.3
		<i>455</i>	<i>6.3</i>	<i>3.7</i>	<i>25</i>	<i>238</i>	<i>165</i>	<i>11.4</i>	<i>4.4</i>	<i>0.3</i>	<i>134.3</i>	<i>1.8</i>
Reactor 2 - Amended	4	3925	7.8	40.0	105	1925	430	14.4	11.8	6.7	504.6	8.6
		<i>624</i>	<i>2.3</i>	<i>4.1</i>	<i>25</i>	<i>330</i>	<i>57</i>	<i>4.7</i>	<i>4.1</i>	<i>0.1</i>	<i>90.6</i>	<i>1.3</i>
Reactor 2 - Amended	5	5714	10.6	46.5	354	3157	579	29.6	9.2	6.7	524.5	8.3
		<i>1298</i>	<i>3.1</i>	<i>5.4</i>	<i>156</i>	<i>658</i>	<i>161</i>	<i>12.7</i>	<i>2.5</i>	<i>0.2</i>	<i>80.4</i>	<i>3.1</i>
Reactor 2 - Control	1	5988	7.5	58.2	117	2713	641	3.7	26.6	6.5	526.4	7.4
		<i>986</i>	<i>5.2</i>	<i>6.9</i>	<i>46</i>	<i>340</i>	<i>61</i>	<i>2.5</i>	<i>3.5</i>	<i>0.1</i>	<i>55.1</i>	<i>1.5</i>
Reactor 2 - Control	2	5300	7.8	42.4	115	2500	435	1.6	18.8	6.2	610.0	9.5
		<i>141</i>	<i>5.5</i>	<i>2.4</i>	<i>13</i>	<i>141</i>	<i>26</i>	<i>1.9</i>	<i>4.6</i>	<i>0.5</i>	<i>134.3</i>	<i>1.4</i>
Reactor 2 - Control	3	4575	3.4	41.9	148	2350	588	0.9	10.0	7.0	605.2	9.0
		<i>538</i>	<i>3.0</i>	<i>3.4</i>	<i>49</i>	<i>300</i>	<i>179</i>	<i>1.8</i>	<i>3.8</i>	<i>0.3</i>	<i>143.3</i>	<i>2.3</i>
Reactor 2 - Control	4	4050	3.5	40.4	105	1950	423	2.1	12.1	6.9	497.3	11.9
		<i>580</i>	<i>0.4</i>	<i>3.5</i>	<i>18</i>	<i>289</i>	<i>56</i>	<i>1.5</i>	<i>3.4</i>	<i>0.1</i>	<i>102.0</i>	<i>1.3</i>
Reactor 2 - Control	5	5943	5.4	46.7	386	3129	577	2.9	9.7	6.9	567.1	11.6
		<i>1239</i>	<i>3.3</i>	<i>4.2</i>	<i>285</i>	<i>783</i>	<i>127</i>	<i>2.2</i>	<i>2.4</i>	<i>0.2</i>	<i>46.1</i>	<i>3.1</i>

Table 5.6 Mean water chemistry parameters (mg/L) measured from outflow samples of the fourth reactor for the amended and control CWTS series during loading periods 1 to 5. Standard deviations are italicized below the corresponding mean value.

<b>CWTS Series</b>	<b>Loading Period</b>	<b>TDS</b>	<b>TSS</b>	<b>B</b>	<b>COD</b>	<b>Cl<sup>-</sup></b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>BOD</b>	<b>Temp</b>	<b>pH</b>	<b>ORP</b>	<b>DO</b>
Reactor 4 - Amended	1	6025	26.6	56.6	145	2700	623	2.4	25.4	6.6	522.9	7.4
		<i>1144</i>	<i>19.3</i>	<i>6.3</i>	<i>60</i>	<i>421</i>	<i>89</i>	<i>1.7</i>	<i>3.8</i>	<i>0.3</i>	<i>39.4</i>	<i>2.6</i>
Reactor 4 - Amended	2	5025	24.3	42.2	128	2350	443	2.7	17.2	6.9	594.0	9.0
		<i>141</i>	<i>5.5</i>	<i>2.4</i>	<i>13</i>	<i>141</i>	<i>26</i>	<i>1.9</i>	<i>4.6</i>	<i>0.5</i>	<i>134.3</i>	<i>1.4</i>
Reactor 4 - Amended	3	4450	15.5	42.1	180	2350	575	10.1	9.7	7.0	646.4	7.6
		<i>1008</i>	<i>5.4</i>	<i>5.8</i>	<i>93</i>	<i>451</i>	<i>295</i>	<i>11.1</i>	<i>4.5</i>	<i>0.3</i>	<i>127.6</i>	<i>1.8</i>
Reactor 4 - Amended	4	3750	12.5	38.0	167	1900	400	10.8	11.2	6.8	520.9	8.6
		<i>265</i>	<i>4.7</i>	<i>2.2</i>	<i>91</i>	<i>183</i>	<i>56</i>	<i>2.0</i>	<i>3.8</i>	<i>0.1</i>	<i>89.2</i>	<i>2.5</i>
Reactor 4 - Amended	5	5700	13.5	46.7	404	3000	561	17.0	8.9	6.7	546.7	6.7
		<i>1197</i>	<i>3.6</i>	<i>4.7</i>	<i>238</i>	<i>726</i>	<i>89</i>	<i>9.2</i>	<i>3.3</i>	<i>0.1</i>	<i>76.1</i>	<i>2.7</i>
Reactor 4 - Control	1	6250	37.9	58.2	138	2575	519	5.4	24.8	6.4	485.9	6.5
		<i>1260</i>	<i>13.0</i>	<i>6.7</i>	<i>53</i>	<i>396</i>	<i>255</i>	<i>3.6</i>	<i>3.4</i>	<i>0.2</i>	<i>55.0</i>	<i>1.9</i>
Reactor 4 - Control	2	5075	27.5	42.0	153	2325	440	5.9	16.1	6.4	602.3	9.4
		<i>395</i>	<i>13.7</i>	<i>0.8</i>	<i>19</i>	<i>50</i>	<i>27</i>	<i>2.8</i>	<i>4.3</i>	<i>0.2</i>	<i>147.7</i>	<i>2.0</i>
Reactor 4 - Control	3	4475	25.5	41.8	180	2325	578	8.2	9.1	7.0	644.9	9.3
		<i>998</i>	<i>11.8</i>	<i>6.4</i>	<i>110</i>	<i>499</i>	<i>302</i>	<i>4.5</i>	<i>3.6</i>	<i>0.4</i>	<i>111.3</i>	<i>2.4</i>
Reactor 4 - Control	4	3775	13.8	36.5	96	1750	383	6.9	9.9	6.7	528.4	12.1
		<i>486</i>	<i>6.4</i>	<i>3.6</i>	<i>23</i>	<i>252</i>	<i>39</i>	<i>1.3</i>	<i>3.7</i>	<i>0.3</i>	<i>92.9</i>	<i>1.4</i>
Reactor 4 - Control	5	5814	25.0	47.1	363	3100	576	8.2	7.1	6.7	603.1	10.3
		<i>1327</i>	<i>12.5</i>	<i>4.5</i>	<i>185</i>	<i>690</i>	<i>86</i>	<i>1.1</i>	<i>3.3</i>	<i>0.2</i>	<i>53.5</i>	<i>1.3</i>

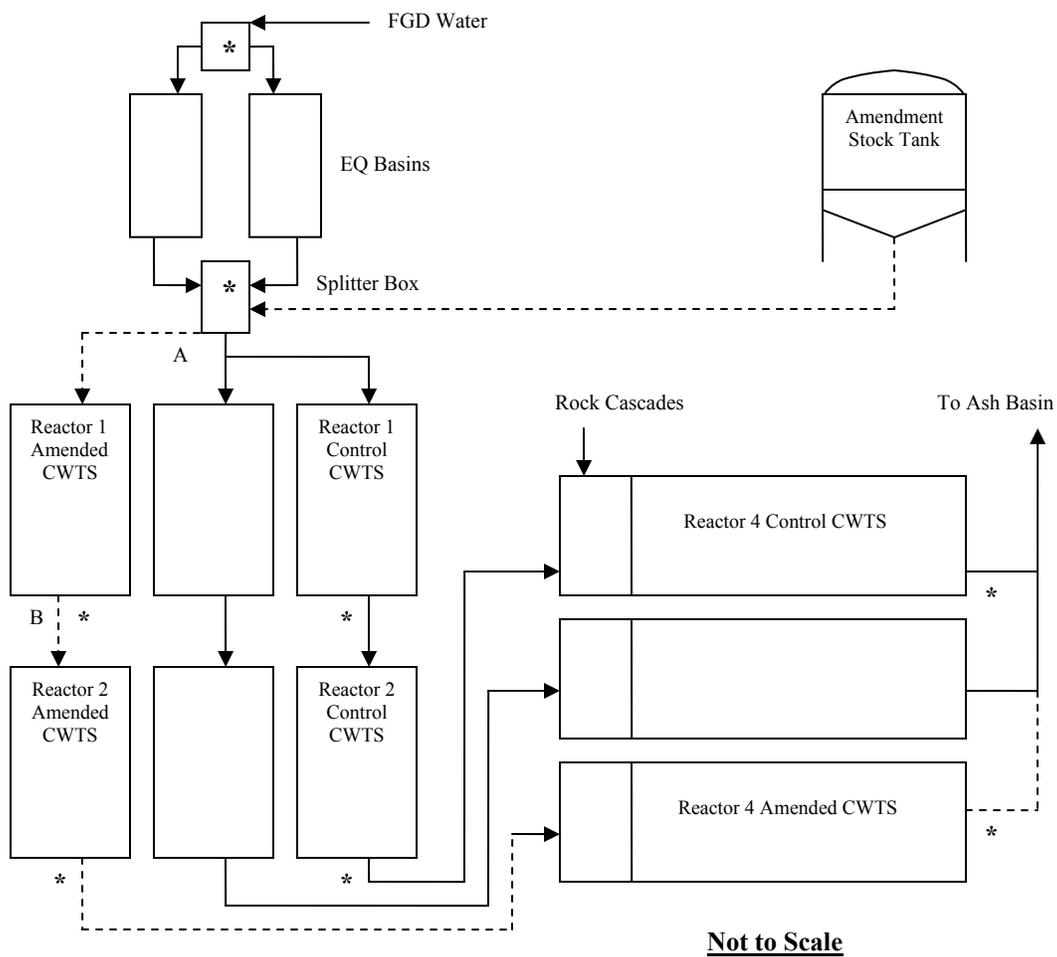


Figure 5.1 Schematic flow diagram of amended (dashed lines) and control (solid lines) CWTS series used to remove selenium from FGD water. Letters (A) and (B) indicate sites of organic carbon additions and (\*) denotes sampling locations for measurements of total selenium and water chemistry parameters. Blank boxes are reactors not monitored for this study.

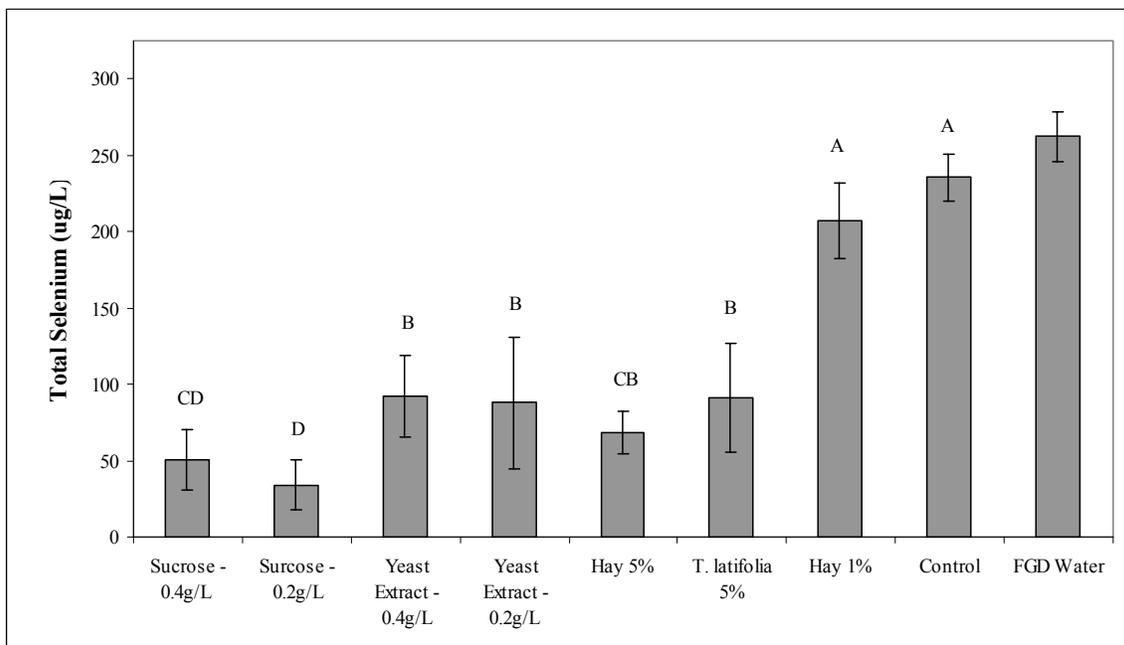


Figure 5.2 Total mean selenium concentrations in aqueous samples collected from treatments after 3, 6, and 9-d. Statistical differences indicated by letters.

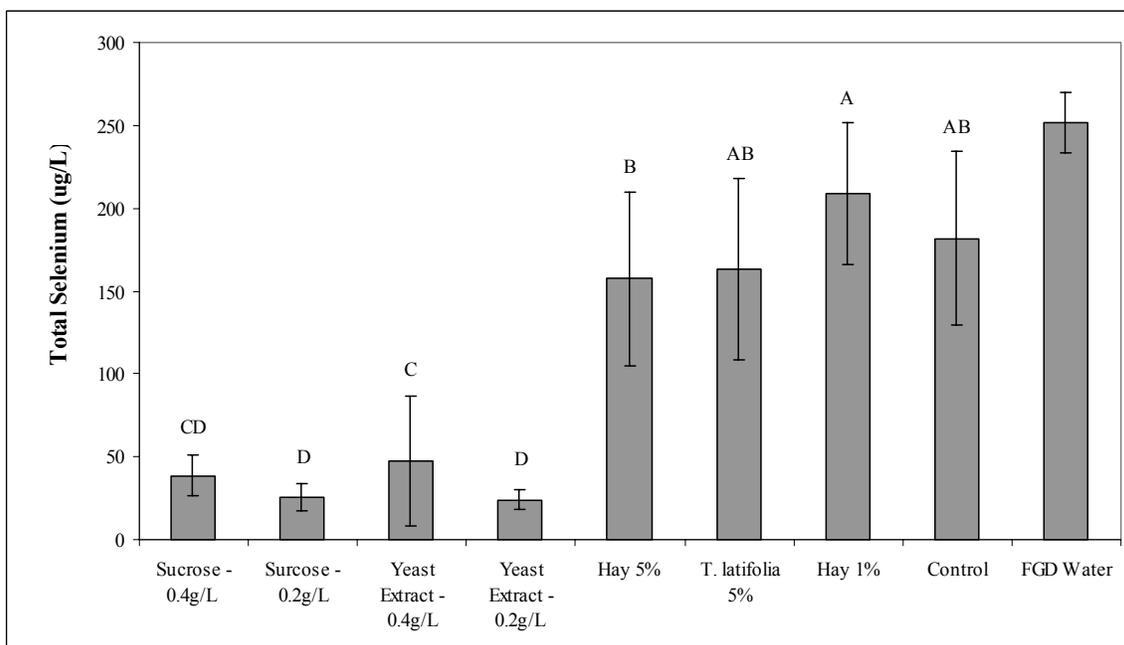


Figure 5.3 Total mean selenium concentrations in aqueous samples collected from treatments after 12, 15, and 18-d. Statistical differences indicated by letters.

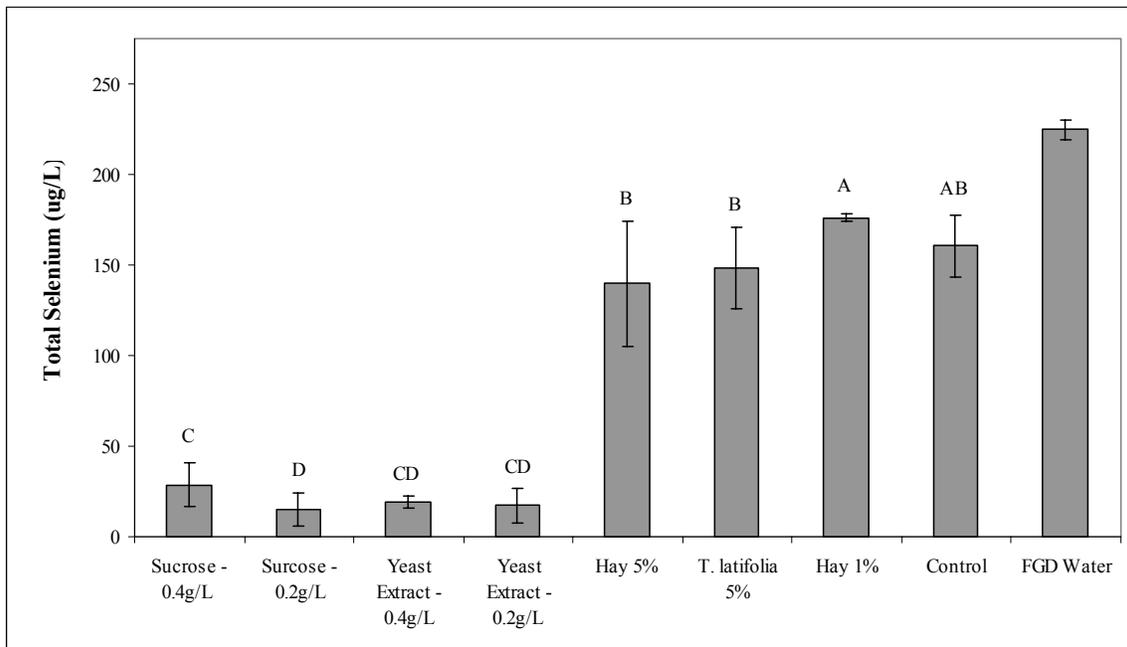


Figure 5.4 Total mean selenium concentrations in aqueous samples collected from treatments after 21, 24, and 27-d. Statistical differences indicated by letters.

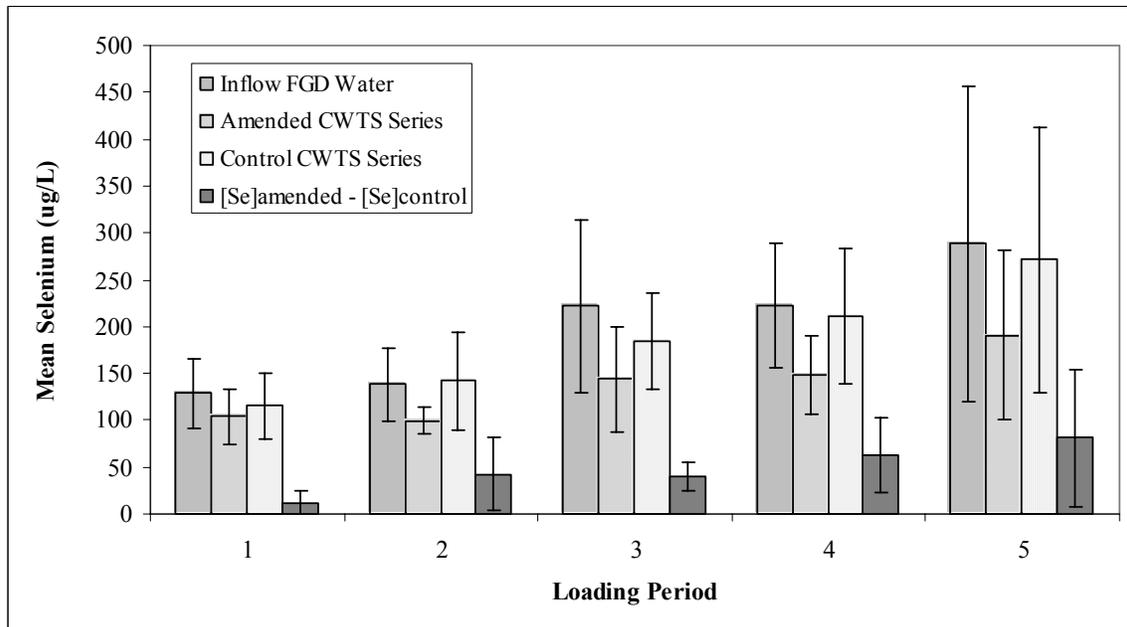


Figure 5.5 Mean selenium concentrations measured in samples from EQ basin (inflows), and outflows of reactor 1 for the amended and control CWTS and during loading periods 1 to 5. Gray bar displays the mean differences in Se concentrations between the amended and control CWTS series ( $[Se]_{\text{amended}} - [Se]_{\text{control}}$ ). Error bars represent the standard deviation of mean values.

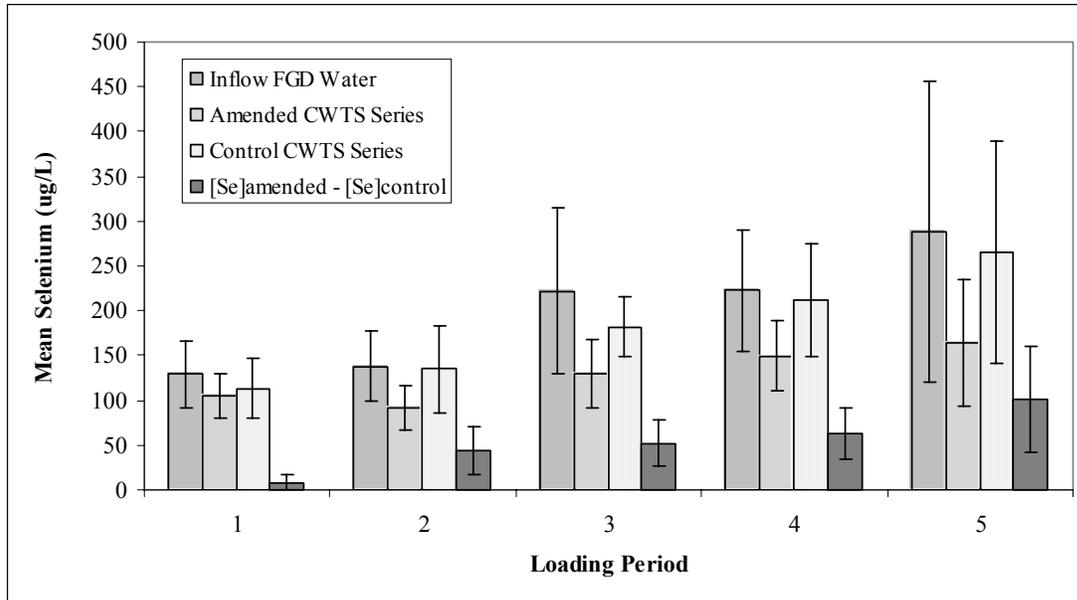


Figure 5.6 Mean selenium concentrations measured in samples from EQ basin (inflows), and outflows of reactor 2 for the amended and control CWTS and during loading periods 1 to 5. Gray bar displays the mean differences in Se concentrations between the amended and control CWTS series ( $[Se]_{\text{amended}} - [Se]_{\text{control}}$ ). Error bars represent the standard deviation of mean values.

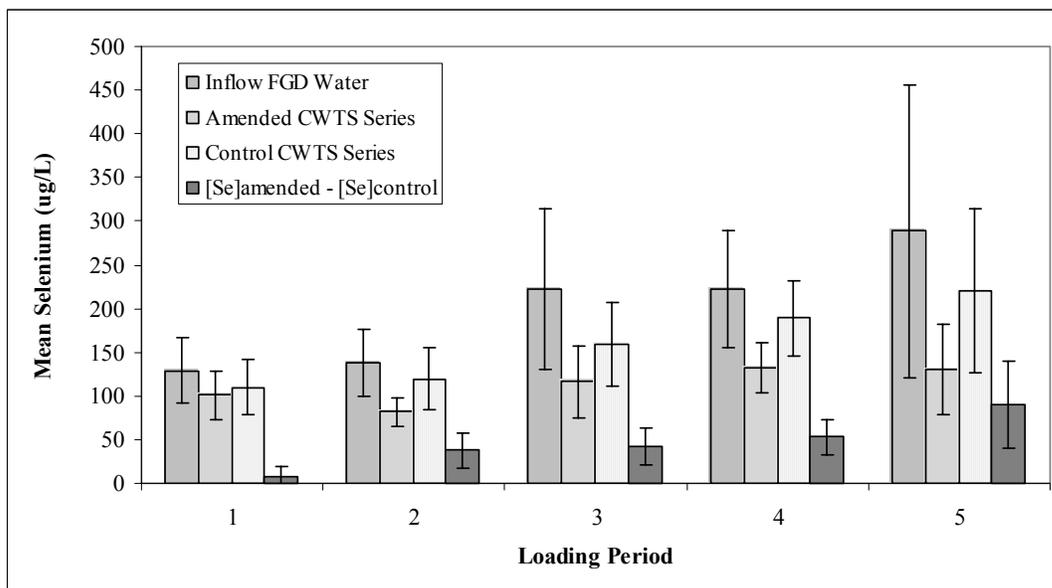


Figure 5.7 Mean selenium concentrations measured in samples from EQ basin (inflows), and outflows of reactor 4 for the amended and control CWTS and during loading periods 1 to 5. Gray bar displays the mean differences in Se concentrations between the amended and control CWTS series ( $[Se]_{\text{amended}} - [Se]_{\text{control}}$ ). Error bars represent the standard deviation of mean values.

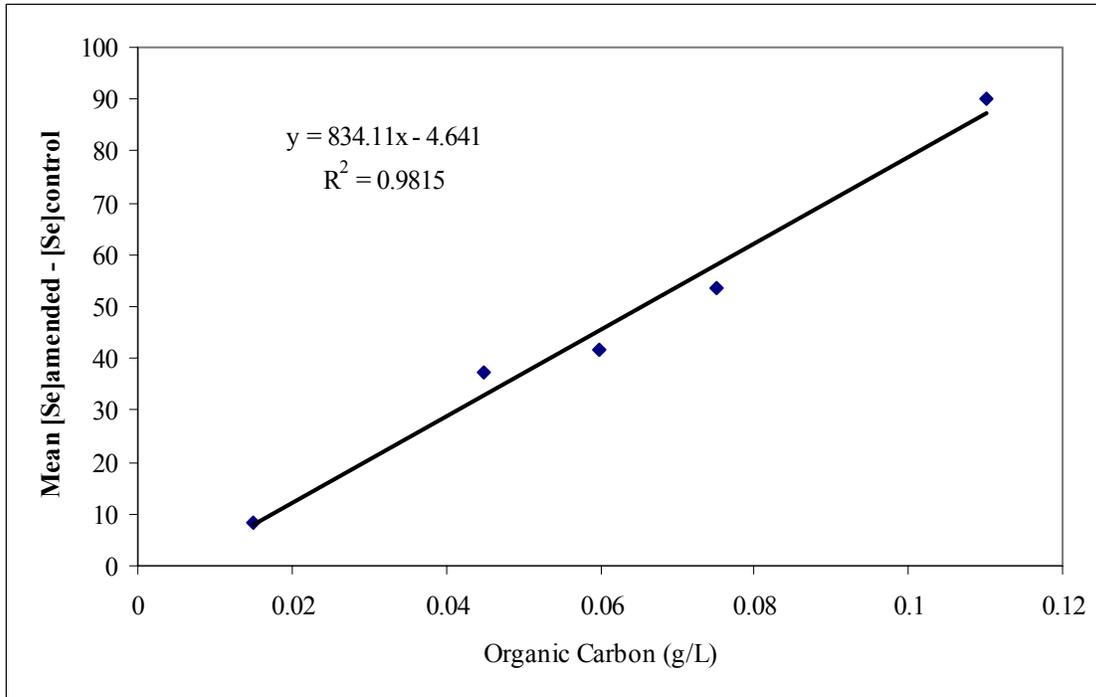


Figure 5.8 Plot of the linear relationship between mean differences in Se concentrations between the amended and control CWTS series ( $[Se]_{\text{amended}} - [Se]_{\text{control}}$ ) (x-axis) and organic carbon concentrations (y-axis) in FGD waters of the amended CWTS series during this study.

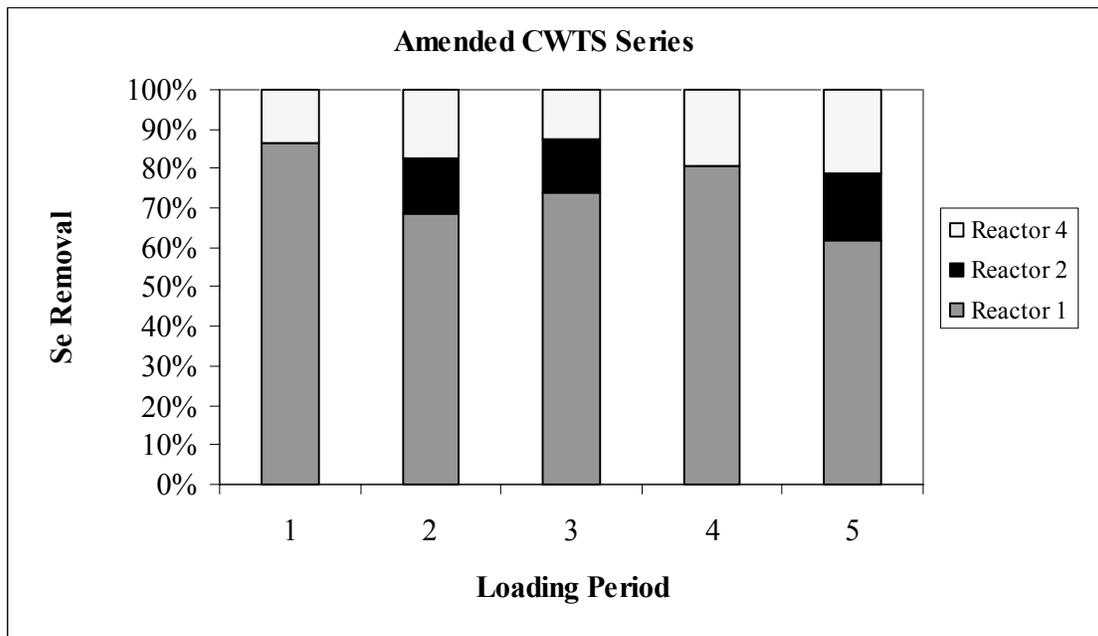


Figure 5.9 Mean percentage of total Se removed by reactors 1, 2, and 4 in the amended CWTS series for loading periods 1 to 5.

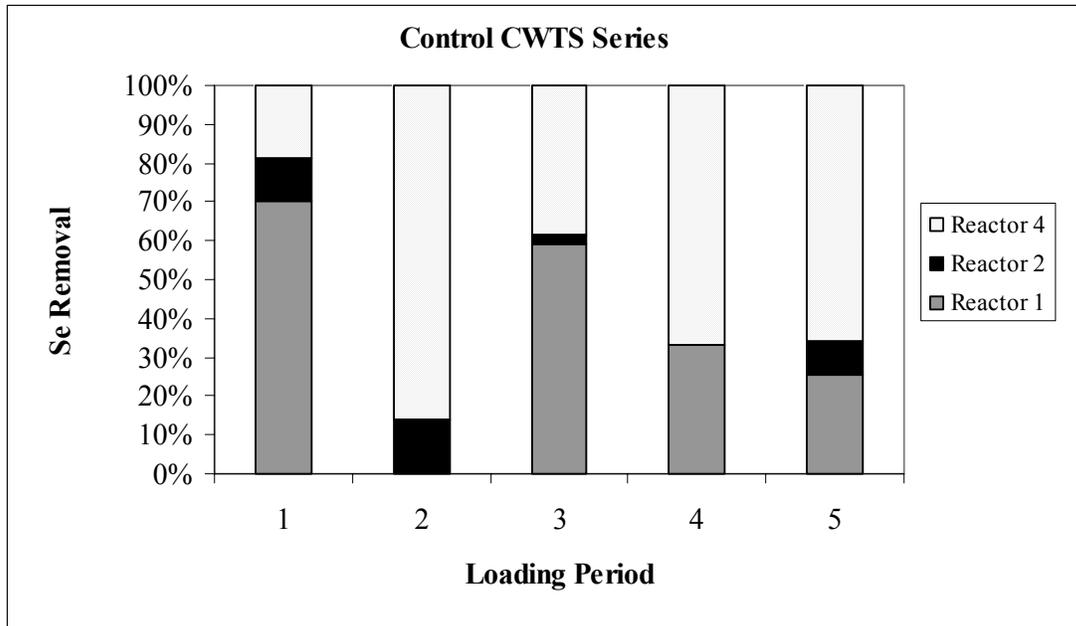


Figure 5.10 Mean percentage of total Se removed by reactors 1, 2, and 4 in the control CWTS series for loading periods 1 to 5.

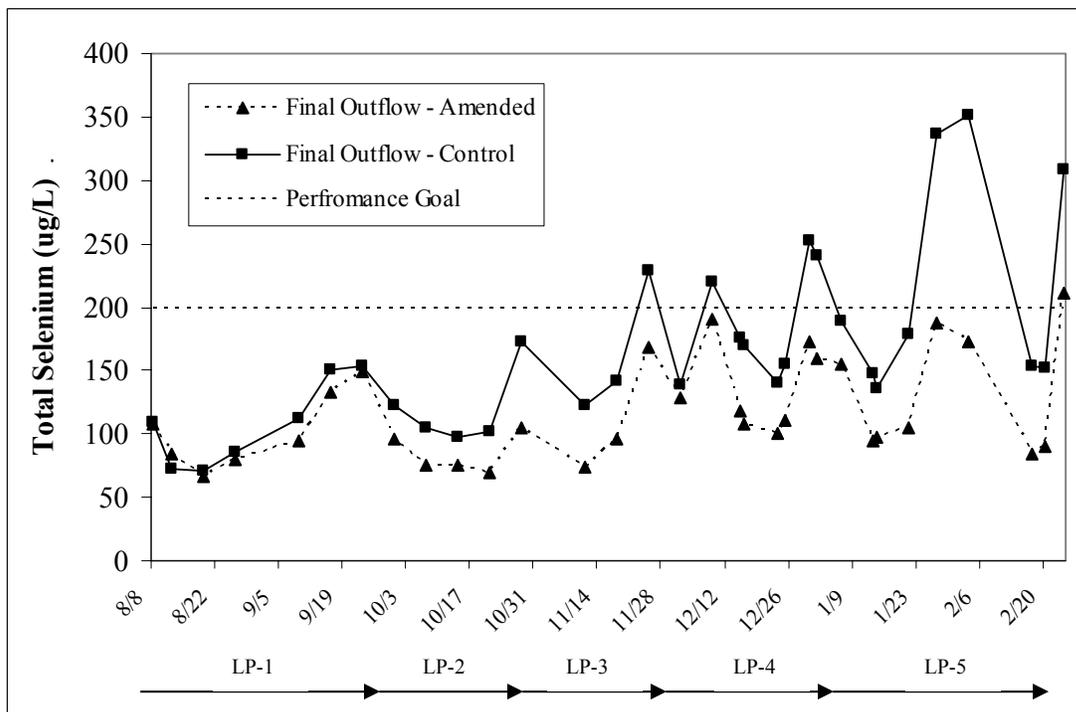


Figure 5.11 Plot of Se concentrations measured in final outflow samples (reactor four) of the amended and control CWTS series during this study. The dashed line indicates the performance goal ( $\leq 200 \mu\text{g}$  as Se/L) estimated for these experiments.

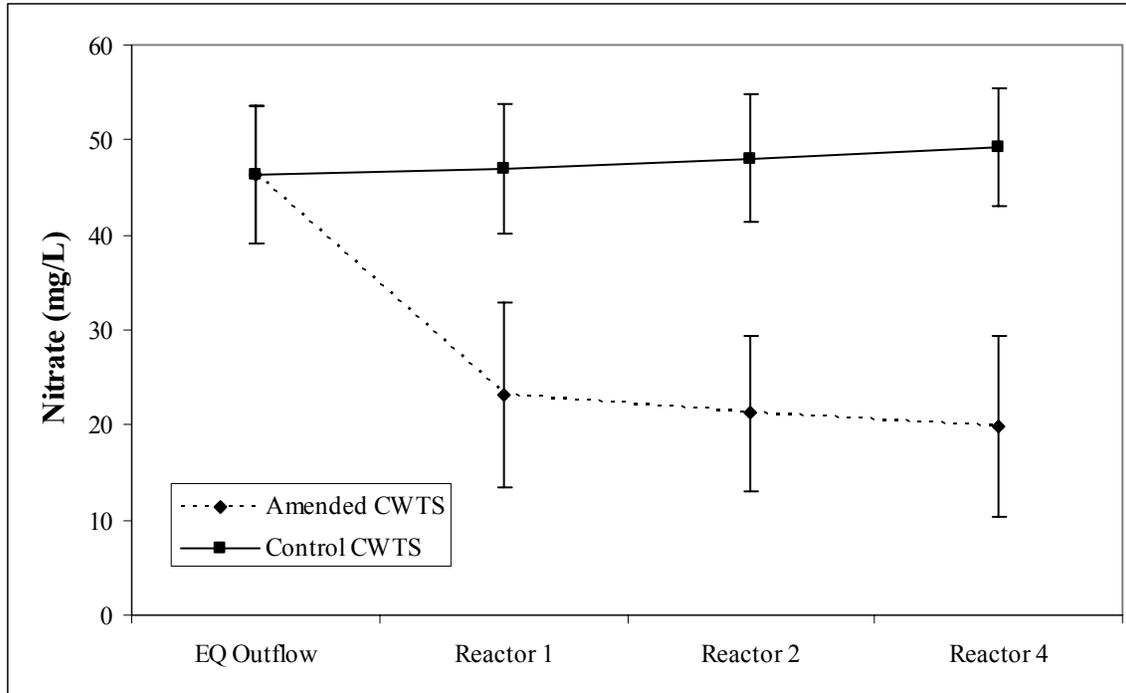


Figure 5.12 Mean nitrate concentrations measured from inflow (EQ basin) and outflow samples (reactors 1, 2, and 4) of the amended and control CWTS series during loading periods 2 to 5. Error bars represent the standard deviation of mean values.

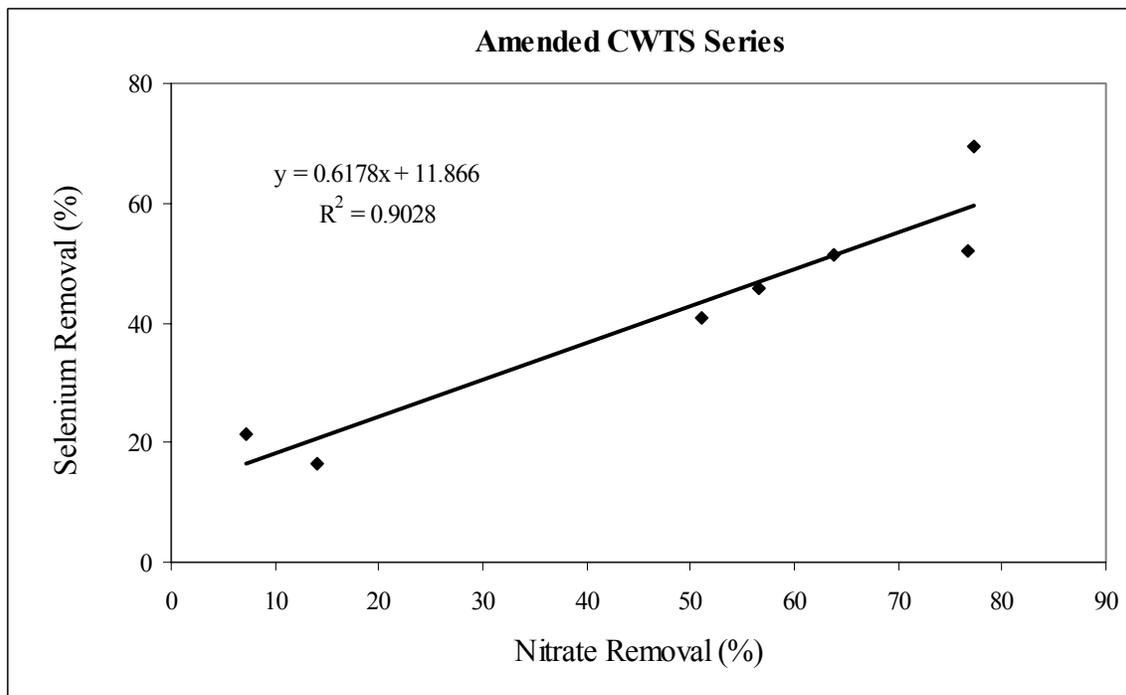


Figure 5.13 Plot of the linear relationship between monthly mean selenium removal (x-axis) and nitrate (y-axis) removal measured from samples of the amended CWTS series during this study.

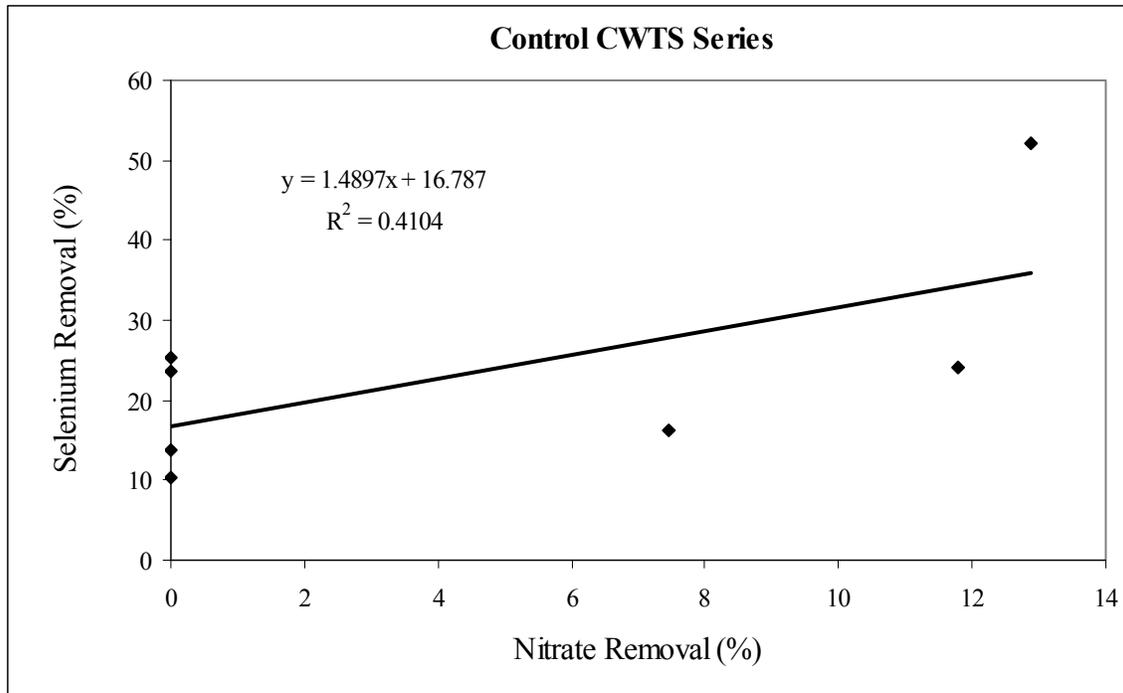


Figure 5.14 Plot of the linear relationship between monthly mean selenium (x-axis) and nitrate (y-axis) removals measured from samples of the control CWTS series during this study.

## CHAPTER SIX

### SUMMARY AND CONCLUSIONS

Implementation of air pollution control devices, such as wet flue gas desulfurization (FGD) scrubbers, has increased over the past two decades and results in transfer of some potentially toxic constituents from the gas phase (i.e. smoke stack emissions) to the scrubbing water (USDOE, 2006). These scrubber waters, referred to as FGD waters, present an industrial problem due to the large volumes produced (378,000 to 1,900,000 L/day) and regulations regarding their discharge (NPDES permits) to receiving systems (EPRI, 2006). FGD waters are specific to the site of production due differences in their chemical and physical compositions as well as constituents requiring treatment, and contain elements or compounds that are difficult and costly to treat (EPRI, 2006). In order to design treatment systems for remediation of problematic constituents in FGD waters, a thorough understanding is needed of the constituents requiring treatment. Treatment is defined here as decreasing the aqueous concentration or the toxicity of the constituent. Each constituent requiring treatment is referred to as a constituent of concern (COC). Identifying COCs requires measurements of the potentially problematic constituents in a FGD waters and comparing these concentrations to a known discharge limit or toxicity criterion. For sites with an existing NPDES permit, the discharge limits are known for quantitative (e.g. total daily maximum concentrations) and narrative (whole effluent toxicity tests) measurements. For sites without existing NPDES permits, selection of the discharge limits can be conducted by comparing the measured concentration of the constituent in a FGD water to the chronic water quality criterion

(WQC) or identified by comparing the measured concentration of the constituent in a FGD water to a reasonable potential analysis (RPA) value. By identifying the COCs and establishing their discharge limits, we can design, construct, and measure the performance of a treatment system. Designing a treatment system can be conducted by determining environments that favor the removal of COCs through biogeochemical transfers and transformations. This information can be obtained from chemical modeling programs (e.g. MINTEQ and Biochemist Workbench), published literature, and laboratory testing (e.g. bench-scale tests). Once a theoretical design is formulated and constructed, the performance can be evaluated for the treatment system to treat COCs. For the research presented in this dissertation, constructed wetland treatment systems were evaluated for their potential to treat COCs in FGD waters. These treatment systems are an economically viable alternative to concrete and steel systems and have been successful for treating COC in storm water runoff (Murray-Gulde et al., 2005), nutrient-rich water (Huett et al., 2005), acid mine drainage (Sobolewski, 1996), municipal water (Ansola et al., 2003), and agricultural runoff (Moore et al., 2000).

This dissertation provides a risk-based approach to remediate FGD waters. The steps involved in this risk-based approach include: 1) chemical and physical characterization of FGD waters, 2) identification of discharge limits, 3) determination of constituents of concern, 4) treatment system design, 5) performance evaluations of the treatment system, and 6) applications for enhancing the treatment of specific constituents in FGD waters. Using this risk-based approach to remediate FGD water will provide site specific data on the ability of the treatment system to meet acceptable discharge limits.

These approaches were used in the body chapters (Chapters 2, 3, 4, and 5) of this dissertation and the conclusions from each chapter are described in detail for the paragraphs below.

In Chapter Two, two objectives were established for this research: 1) configure a pilot-scale constructed wetland treatment system for FGD water, and 2) evaluate treatment effectiveness and performance of this system. Based on analyses of the FGD water, seven COC were identified and included boron (B), cadmium (Cd), chloride (Cl), nickel (Ni), total nitrogen ( $N_T$ ), mercury (Hg), and selenium (Se). The pilot-scale CWTS used for this research were designed based on published literature and biogeochemical models. Each system included four reducing wetland reactors (-200 to 0 mV) and two oxidizing wetland reactors (0 to +150 mV) in series. COC measured in this study included Se, Hg,  $N_T$ , and arsenic, which was added due to its ability to enhance the toxicity of these other COC. The percent removals for the measured COC ranged from 40.1% to 77.7% for As, 77.6% to 97.8% for Hg, 43.9% to 88.8% for N, and no removal to 84.6% for Se. Based on the data obtained from this research, pilot-scale CWTS decreased the measured constituents of concern in this FGD water and achieved the Hg limits ( $<0.63\mu\text{g/L}$ ) used for this study. As the pilot-scale CWTS matured, Se removal increased and this COC was sufficiently treated below its NPDES permit limit during the later sampling events. Pilot-scale CWTS were able to decrease total nitrogen concentrations, but the water quality criterion limit was not consistently achieved during this study.

In Chapter Three, three objectives were established for this research including: 1) characterize four FGD waters in terms of chemical composition and constituents of concern; 2) design constructed wetland treatment systems for remediation of constituents of concern in FGD waters; and 3) measure the performance of constructed wetland treatment systems for formulated and actual FGD waters based on available NPDES discharge limits for FGD waters. Results of this risk-based characterization indicate that Cd, chemical oxygen demand (COD), Cl, copper (Cu), Hg, Se, and zinc (Zn) are constituents of concern in these FGD waters and require treatment before discharge. Since FGD waters must meet discharge criteria established by the USEPA through NPDES permits, we designed a series of reactors, or constructed wetland treatment systems that would decrease the concentrations of the targeted constituents (except conservative elements such as Cl). This was accomplished by assessing the biogeochemical cycling of constituents of concern through literature reviews and biogeochemical models for the targeted constituents. To understand the remediation potential of CWTS for constituents of concern in FGD waters, three different FGD water types were selected for this study including formulated FGD water, two actual-amended FGD waters, and four pilot-scrubber FGD waters. Formulated FGD water was synthesized based on data from chemical analyses of actual FGD waters and was prepared through additions of high-purity salts (As, Hg, and Se), technical-grade salts (Cl and sulfates), fly ash and dibasic acid to municipal water. Actual-amended FGD waters were FGD waters collected from an operating coal-fired power plant that was co-managed with municipal water to decrease chloride concentrations to approximately 4000

to 5000 mg/L. Actual-amended FGD waters also received additions of selenium and mercury from high-purity salts in order to measure the treatment performance of the pilot-scale CWTS. Four pilot-scrubber FGD waters were produced using a pilot-scale scrubber (URS Pilot-Scale FGD Scrubber; URS Corp., Austin, TX) that treated a split-stream of flue gases produced at coal-fired power plant. These FGD waters were transported to Clemson University and were co-managed with municipal water to decrease the chloride concentrations to approximately 4000 mg/L. Based on the NPDES permit criterion of  $\leq 0.63 \mu\text{g/L}$  of total mercury in effluent samples, 85% of the post-treatment FGD waters (n=17 of 20) tested in this study were decreased less than this criterion using pilot-scale CWTS. Post-treated actual-amended FGD waters exceeded this maximum daily loading concentration for mercury ( $6.2 \mu\text{g/L}$ ; n=2), but was expected due to the high concentrations ( $136.6 \pm 5.78$  and  $163.3 \pm 5.77 \mu\text{g as Hg/L}$ ) of mercury in the pre-treated samples. These results indicate high percent removals (96.8 and 95.4%) and removal rates ( $0.864$  and  $0.770 \text{ d}^{-1}$ ) of Hg from actual-amended FGD water using pilot-scale CWTS and suggest discharge limits can be achieved with additional wetland reactors. Only one post-treated sample from the pilot-scrubber FGD waters ( $1.2 \mu\text{g/L}$ ; n=1) exceeded the mercury discharge limit of  $\leq 0.63 \mu\text{g/L}$ . Mean removal percents and rates of selenium from equalization basin samples (pre-treatment) to outflow samples (post-treatment) from pilot-scale CWTS were 84.6 % and  $0.468 \text{ d}^{-1}$  for formulated FGD waters (n=10), 80.1 % and  $0.404 \text{ d}^{-1}$  for actual amended FGD waters (n=2), and 89.7% and  $0.327 \text{ d}^{-1}$  (n=2), 63.6 % and  $0.145 \text{ d}^{-1}$  (n=2), 51.2% and  $0.103 \text{ d}^{-1}$  (n=2), and 29.5% and  $0.050 \text{ d}^{-1}$  (n=2) for the four pilot-scrubber FGD waters. The mean removal percent

and removal rate for arsenic was 64.4 % and 0.258 d<sup>-1</sup> for formulated FGD waters; however, lower arsenic removals (no removal to 61.6%) were measured for actual-amended FGD waters and pilot-scrubber FGD waters. These data suggest that arsenic forms present in actual FGD waters may differ in comparison to simulated FGD water. Another factor that may limit the removal of arsenic in actual FGD waters versus simulated FGD water is the presence of possible interfering constituents that were not added to simulate FGD water. Available NPDES permits for FGD water discharge did not contain a maximum daily concentration limit for Se or As and therefore the performance criteria for these constituents were determined using toxicity evaluations. Pre-treated FGD waters caused significant mortality and reproductive inhibition for *Ceriodaphnia dubia*. FGD waters treated using pilot-scale CWTS did not significantly affect the survival of *C. dubia* and only affected the reproduction of these organisms for one outflow sample. Reproductive toxicity was likely measured due to Se concentrations in this outflow sample ( $1.47 \pm 0.27$  mg as Se/L). Results from these studies indicated that targeted constituents of concern in FGD waters can be decreased in pilot-scale constructed wetland treatment systems, and with appropriate co-management of low-ionic strength water for chloride concentrations, toxicity is decreased to acceptable discharge limits.

In Chapter Four, three specific objectives were developed for this research that included: 1) determine performance goals for Se and Hg in FGD water through reasonable potential analysis (RPA), 2) compare and contrast removal rates and extents of removal for selenium and mercury in a FGD water using amended and un-amended

pilot-scale CWTS, and 3) determine the compliance of treated FGD waters with RPA values for Se and Hg using data from amended and un-amended pilot-scale CWTS. The calculated RPA values for Hg and Se are 630 ng/L and 263 µg/L, respectively, and these concentrations were selected as the performance criteria for this study. For post-treated samples, removal rates and extents of removal for Se were greater for amended versus un-amended pilot-scale CWTS during the months of August, September, October, and November ( $p < 0.05$ ), but no measurable differences occurred during the first month of this study. The lack of statistical differences between amended and un-amended pilot-scale CWTS was likely due to a lag-time in acclimation of these systems to additions of organic carbon. In addition to differences in post-treated samples, outflow Se concentrations from the first reactors of the amended pilot-scale CWTS were statistically lower in comparison to un-amended pilot-scale CWTS for all months after acclimation (i.e. post-July). The first reactor in each amended pilot-scale CWTS was the site of organic carbon additions and indicates that removal of Se is enhanced initially (24-h) within these systems. Of the four pilot-scale CWTS, only the sucrose-amended pilot-scale CWTS decreased Se concentrations below the RPA estimated discharge limit of 263µg/L in all post-treated samples. Yeast culture amended pilot-scale CWTS decreased selenium concentrations to  $< 263\mu\text{g/L}$  in all post-treated samples with the sole exception of the last sampling period in November (i.e. outflow [Se] = 264 µg/L). This post-treated sample did not meet the Se discharge limit, but due to the inherent analytical error in determining total Se concentration, the failure of this system to meet the discharge limit is questionable. Based on the results of this study, neither the control nor hybrid pilot-

scale CWTS decreased Se concentrations to less than the calculated RPA discharge limit of 263  $\mu\text{g/L}$ . Hybrid pilot-scale CWTS differed from control pilot-scale CWTS in that reactor hydrosols were river sand ( $> 94\%$ ) and all reactors were planted with *Typha latifolia*. Total Hg concentrations in all post-treated samples from the sucrose amended, yeast culture amended, and hybrid pilot-scale CWTS were decreased below the RPA discharge limit of 630  $\text{ng/L}$ . The control pilot-scale CWTS decreased Hg concentrations to  $<630 \text{ ng/L}$  for fourteen of the nineteen sampling periods with a mean removal extent and removal rate of  $417 \pm 231 \text{ ng/L}$  and  $-0.5552 \pm 1679 \text{ d}^{-1}$ , respectively. The highest mean percent removal and removal rate of Hg in post-treated samples were measured from the hybrid pilot-scale CWTS ( $95.9 \pm 2.3\%$  and  $0.8349 \pm 0.1324 \text{ d}^{-1}$ ), followed by the yeast culture amended pilot-scale CWTS ( $94.1 \pm 3.3\%$  and  $0.7540 \pm 0.1849 \text{ d}^{-1}$ ), and the sucrose amended pilot-scale CWTS ( $93.2 \pm 3.9\%$  and  $0.7169 \pm 0.1585 \text{ d}^{-1}$ ). Enhancing Se and Hg removal from FGD water was accomplished with amendments of sucrose and yeast culture to pilot-scale CWTS in comparison to an untreated control system. This research provides an approach to enhance Hg and Se removal rates and extents from FGD waters using CWTS and these data verify that site discharge limits may be achieved with organic carbon amendments to pilot-scale CWTS.

For Chapter Five, we developed three specific objectives for this research that included: 1) measure the change in total Se concentrations from bench-scale experiments receiving different organic carbon types and concentrations in comparison to controls; 2) measure the removal (percent and extent of removal) of total Se in FGD water from an organic carbon amended and control CWTS series; and 3) measure and compare outflow

samples from the amended and control CWTS series to estimated performance goals at this site. The performance goal of the CWTS was to decrease total Se concentration to  $\leq 200 \mu\text{g/L}$ . The performance goal was estimated based on anticipated discharge limits and co-management of treated FGD water with ash basin water. Data from the bench-scale experiments indicated that sucrose and yeast culture additions of 0.2g/L and 0.4g/L were sufficient for decreasing total Se concentrations in this FGD water in comparison to control, hay, and *T. latifolia* detritus treatments. The organic carbon sources of 1% hay and 5% hay and *T. latifolia* detritus did not increase the removal of Se in comparison to controls. Based on the results of the bench-scale experiments, amendments of organic carbon sources were tested at full-scale CWTS to evaluate Se removal between an amended and a control CWTS series. Significant differences in Se concentrations from final outflow samples were measured between the amended and control CWTS series after the first loading period to the conclusion of this study. The incremental increases of sucrose concentrations in the FGD water resulted in larger differences for Se concentrations between samples from the amended and control CWTS series. Through additions of sucrose to the amended CWTS series, Se concentrations were decreased below the performance goals for all sampling events except the last sampling event of this study whereas the control CWTS did not sufficiently decrease Se concentrations less than the performance goals for seven sampling periods. Microbial processes such as denitrification of the FGD waters likely increased with greater sucrose concentrations in FGD water. Data from this research confirm that organic carbon amendments to a CWTS

series can enhance total Se and nitrate removal and provides a solution to decreasing these constituents in FGD waters.

In summary, this dissertation provides a scientific approach for the risk mitigation of FGD waters through characterizing and identifying constituents of concern in FGD waters, developing and evaluating potential treatment pathways in CWTS, and enhancing the removal of constituents of concern (Se and Hg) within the CWTS using organic carbon additions to FGD waters. Accurate identification of the constituents of concern (COC) in FGD water is an important risk-based procedure in order to design mitigation strategies for these constituents. This research provides the understanding that selenium is consistently identified as a COC in FGD waters (e.g. all FGD waters evaluated in our research), but other elements and compounds in FGD waters such as Hg, As, Cd, Cu, COD, and Zn may require treatment before these waters are discharged into a receiving system. Previous research (Mierzejewski, 1991) documented that the chemical and physical composition of FGD waters can vary based on the coal-fired power plant and FGD system designs, but more data were needed to verify this report due to recent changes in FGD systems (e.g. design and operation of SCR, SNCR, mist eliminators, and hydrocyclones). Our results indicate that FGD waters vary in chemical and physical composition from site to site, but also temporally at sites (i.e. Chapter 4 and 5). Understanding and evaluating the performance of CWTS to changes in the composition of FGD water with time at each site provided us important information such as the robust and sustainability of these systems to treat COC during the study. Data from Chapters Three, Four, and Five indicate that removal of Se within a CWTS may be limited by the

forms of Se present in the FGD water or by other elements or compounds in the FGD water. A solution to this problem was evaluated and confirmed in Chapters 4 and 5. Additions of organic carbon have been successful for decreasing Se concentrations in low ionic strength waters under laboratory and pilot-scale experiments (Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2003, 2005), but this approach had not been tested for higher ionic strength waters such as FGD waters. Data regarding the removal of Se in a CWTS receiving organic carbon additions, such as sucrose or yeast culture, were also not available. The presented results of this research indicate that organic carbon additions can enhance the removal of Se in FGD waters and were likely due to higher microbial activity within the CWTS, based on oxidation-reduction potentials and biochemical oxygen demand measurements. Removal of nitrate concentrations were also enhanced for FGD water receiving organic carbon additions based on comparisons to control CWTS. Overall, this research study provides information on the performance of CWTS to remediate COC in multiple FGD waters and offers an approach to enhance the performance of existing CWTS.

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